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Property prediction of energetic materials with the "Research output software for energetic materials based on observational modelling" RoseBoom©

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aus

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Erklärung

Diese Dissertation wurde im Sinne von § 7 der Promotionsordnung vom 28.
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Eidesstattliche Versicherung

Diese Dissertation wurde eigenständig und ohne unerlaubte Hilfe erarbeitet.

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Sabrina Wahler

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“Of all flowers, Methinks a rose is best”

Emilia in Two Noble Kingsmen

by

William Shakespeare and John Fletcher

Blossoming Horizons: RoseBoom's Symphony of Scientific Discovery

Roses are pink, violets are blue,
With RoseBoom's aid, discoveries anew.
In this world of science, minds in sync,
No need to think if you've got no clue.

In realms of science, where dreams take flight,
RoseBoom blooms with a guiding light.
A detonation code, with a purpose clear,
Unveiling paths to the unknown frontier.

In labs of wonder and curious minds,
Seeking answers, where innovation binds,
RoseBoom's brilliance, a spark untold,
Unleashing potential, treasures to unfold.

With algorithms refined and bold,
It aids the quest for substances gold.
Novel energetic materials' grace,
Brought forth by RoseBoom's embrace.

Through simulations vast, it paves the way,
Discoveries shine like sun's first ray.
Breaking barriers, boundless heights,
Inventing wonders, powerful sights.

With each simulation's vibrant hue,
It reveals the secrets, bold and true.
Energetic materials, a treasure to find,
In RoseBoom's embrace, the future aligned.

From molecules small to compounds grand,
In RoseBoom's dance, they join the band.
Explosive energies, new to behold,
Revolutionizing, science untold.

In labs aglow, where wonders spark,
RoseBoom's power leaves a mark.
From molecules small to compounds grand,
Novel energetics at its command.

So, fear not the unknown, let curiosity drive,
With RoseBoom as a guide, we will thrive.
In the pursuit of knowledge, we link,
A symphony of brilliance, we all sync.


New green explosive
NO2
O2N–N
N–NO2
OH
O2N
ONO2
O2NO
PbN3
NH2

In memory of Otto Wahler and Alexandra Wahler.

List of Publications from this thesis (Chronologically)

I. Parisi, E., Landi, A., Fusco, S., Manfredi, C., Peluso, A., **Wahler, S.**, Klapötke, T. M., Centore, R., High-energy-density materials: an amphoteric N-rich bis (triazole) and salts of its cationic and anionic species, Inorg. Chem. 2021, 60, 16213–16222.

II. **Wahler, S.**, Klapötke, T. M., Research output software for energetic materials based on observational modelling 2.1 (RoseBoom2.1©), Mater. Adv. 2022, **3**, 7976-7986

III. **Wahler, S.**, Klapötke, T. M., Research output software for energetic materials based on observational modelling 2.2 (RoseBoom2.2©) – update to calculate the specific impulse, detonation velocity, detonation pressure and density for CHNO mixtures using the Supersloth-function, Cent. Eur. J. Energ. Mater, 2022, 19(3): 295-310

IV. **Wahler, S.**, Klapötke, T. M., RoseMortar-Equation – a universal equation to predict the strength of an explosive in a ballistic mortar test, *Int. J. Energ. Mater. Chem. Propuls.*, 21(6):47–50 (2022) ***(Top 3 Most Viewed Article March 2023)***

V. **Wahler, S.**, Klapötke, T. M., RoseTrauzl-Equation – a universal equation to predict the strength of an explosive in a Trauzl-test, 2022, J. Energ. Mater., , ***accepted Manuscript,*** https://doi.org/10.1080/07370652.2022.2150793

VI. **Wahler, S.**, Klapötke, T. M., RoseSSRT-Equation – a simple linear correlation between the dent volume in a small scale-shock reactivity test and the heat of detonation, 2023, *Int. J. Energ. Mater. Chem. Propuls.*, ***accepted Manuscript (Top 3 Most Viewed Article June 2023)***

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IX. **Wahler, S.***, Klapötke, T. M., Chung, P., Training machine learning models based on the structural formula for the enthalpy of vaporization and sublimation and a thorough analysis of Trouton's rules., 2023, J. Energ. Mater., ***accepted Manuscript***

X. **Wahler, S.***, Klapötke, T. M., Comparison of the 478 specific impulses calculated with the ISPBKW code and 2 different empirical relationships encoded into RoseBoom©, 2023, *Int. J. Energ. Mater. Chem. Propuls.*, ***accepted Manuscript, (Most Downloaded Article July 2023)***

XI. **Wahler, S.**, Klapötke, T. M., RoseBoom2.1© ("Research output software for energetic materials based on observational modelling/machine learning"), New Trends Res. Energ. Mater. (NTREM 2022) Proc., 2022, pp. 110–113.

XII. **Wahler, S.**, Proud, W.G., Klapötke, T. M. Adding Machine Learning approaches to RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning"), New Trends Res. Energ. Mater. (NTREM 2023) Proc., 2023

XIII. **Wahler, S.**, Research output software for energetic materials based on observational modelling/machine learning, in ICT Conf. Proceeding, 2023

XIV. **Wahler, S.**, Klapötke, T. M., RoseBoom2.4© (“Research output software for energetic materials based on observational modelling/machine learning"), in IPS EUROPYRO Conf. Proceeding, 2023

XV. **Wahler, S.***, Klapötke, T. M., Proud, W.G, A brief tabular mini review on the user-friendliness and sustainability of software solutions for energetic materials unrestrictedly available, 2023, **Manuscript draft**

XVI. **Wahler, S.***, Klapötke, T. M., Proud, W.G, A brief comment on the lack of experimental values for detonation parameters and future work targeted towards overcoming this issue, 2023, **Manuscript draft**

List of Oral Presentations (Chronologically)

New Trends in Research of Energetic Materials 2022 (NTREM2022), oral presentation with the title: Research output software for energetic materials based on observational modelling 2.1 (RoseBoom2.1©), Pradubice, Czech Republic, 06.04.2022-08.04.2022

Gordans Research Seminar 2022, oral presentation with the title: Research output software for energetic materials based on observational modelling 2.1 (RoseBoom2.1©), Manchester, NH, USA, 25.6.2022-26.6.2022

ArianeGroup GmBH, CRB, oral presentation with the title: Research output software for energetic materials based on observational modelling 2.2 (RoseBoom2.2©), Paris, France, 30.9.2022

Imperial College London, Event, oral presentation with the title: Research output software for energetic materials based on observational modelling (RoseBoom©), London, UK, 11.01.2023

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Next Stage to Space 2023, oral presentation with the title: RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning"), Ottobrunn, Germany, 24.05.2023

International Symposium on Special Topics in Chemical Propulsion (13-ISICP 2023), oral presentation with the title: RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning" – The RoseRocket© update), Gjøvik, Norway, 30.5.2023-02.06.2023

New Energetic Workshop (NEW 2023), oral presentation with the title: RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning" – The RoseRocket© update), Stockholm, Sweden, 07.06.2023-08.06.2023

Group on Shock Compression of Condensed Matter (SCCM2023), oral presentation with the title: RoseBoom2.4© ("Research output software for energetic materials based on observational modelling/machine learning", Chicago, USA, 18.06.2023-23.06.2023

Group on Shock Compression of Condensed Matter (SCCM2023), oral presentation with the title: RoseSTEM – A open database for energetic materials, Chicago, USA, 18.06.2023-23.06.2023

18th Workshop on Pyrotechnic Combustion Mechanisms, invited presentation with the title: RoseBoom© in the name of PEAS (**P**arametrization of **e**mpirical **a**pproximations using **s**tatistical methods), Kaiserslautern, Germany, Postponed to December

Frauenhofer ICT Conference 2023, oral presentation with the title: RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning"), Karlsruhe, Germany, 27.06.2023-30.06.2023

EUROPYRO 2023, oral presentation the title: RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning"), Saint-Mailo, France, 11.9.2023-14.9.2023

33rd International Symposium on Ballistics, oral presentation with the title: RoseBoom2.3© ("Research output software for energetic materials based on observational modelling/machine learning"), Bruges, Belgium, 16.10.2023-20.10.2023

List of Poster Presentations (Chronologically)

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Defence and Security Doctoral Symposium 2022, 3D-Art installation presentation with the title: Research output software for energetic materials based on observational modelling 2.2 (RoseBoom2.2©), Swindon, UK, 9.11.2022-10.11.2022

List of Awards (Chronologically)

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List of Scholarships/ Grants (Chronologically)

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Erasmus + Scholarship 2023

DAAD Kongressreise Stipendium Oktober 2023

LMU Exchange 2023

ESA Business Incubator Center 2023

Memberships in 2023

CapTech non-Governmental Expert (CnGE) European Defense Agency

International Pyrotechnics Society

American Physical Society

Member of the Royal Society of Chemistry

International Ballistics Society

SpaceTech Ecosystem by the European Space Agency

Committee and Board activity in 2023

Editorial Board Member – Journal of Energetic Materials

Communications Committee – International Ballistic Society

Declaration of AI-assisted technologies in the writing process

During the preparation of this work, the author used Grammarly for language editing, as well as grammar and spell checking. A GPT-3.5 Model has been utilized to assist in writing the poem “Blossoming Horizons: RoseBoom's Symphony of Scientific Discovery”. After using this tool, the author reviewed and edited the content as needed and takes full responsibility for the content of the thesis.

Summary

Since 2020, which is when the author of this thesis collected her first experiences with energetic materials 16.500 articles were published and registered by google scholar on “synthesis of new energetic materials”. This level of productivity and access to vast amounts of information was previously unheard of. In the early 1980s, home computers were just becoming possible and very few people had mobile phones. Researchers now face the challenge of sifting through a vast amount of information, with the crucial questions being about its reliability and practical use.

This thesis presents several innovations that enable researchers to access information from the literature in a selective and automated way. These innovations also allow for comparison using established models, leading to informed decisions made by experts.

The first chapter of this research serves as a comprehensive introduction to the concept of RoseBoom© and provides two examples of the application of RoseBoom© reported in literature. Chapter two delves into the development of RoseBoom©, a program that encapsulates the key discoveries of this research. The subsequent chapters consist of papers that provide detailed explanations of essential aspects of the study. Finally, the last chapter explores the wider scope of opportunities for advancing this field.

In this thesis machine learning models, empirical models, and thermo-equilibrium codes are thoroughly tested and evaluated for the prediction of energetic materials. The limits and advantages of each method are carefully evaluated and should be considered. In Chapter 1.6, the experimental situation is assessed. An overview of various measurement techniques for detonation parameters is provided, along with recent research on using modeling tests with simpler experimental setups as an alternative method. Furthermore, the deviations in experimental measurements of detonation pressures have been analyzed. Chapter 1.7 provides a comparison of various unclassified software solutions for energetic materials, including RoseBoom©. These solutions compete in eight categories and are ranked based on the points they receive.

The fundamental concept of RoseBoom© is presented in Chapter 2.3. A thorough evaluation of empirical models for energetic materials presented in the literature is given in Chapter 2.1., which was revalidated for novel energetic materials. An update for performance prediction for mixtures is given in Chapter 2.2 along with the automated input of large molecule datasets from .csv files. In Chapter 2.7 and 4.2 currently available open-source chemical structure recognition tools are investigated for implementation in RoseBoom© which further improve

the user’s experience. An update to the software for rocket propellants is given in Chapter 2.4, where the specific impulses of the ISPBKW code to two empirical models are compared. Including the application programming interface to the ISPBKW code, which allows it to be easily accessed using the RoseBoom©. In Chapter 2.5, the impact on the calculated detonation parameters was investigated by comparing the use of density and heat of formation predicted by RoseBoom2.2© to those published with corresponding molecules. A range of traditional models was tested for sensitivity to input value accuracy. This highlights the need for agreement on one software for predicting energetic material performance, starting with input values. It also increases trust in RoseBoom© predictions while raising awareness of uncertainties in published performance values. This motivated the author to conduct a study in chapter 2.6 investigating the prediction of enthalpies of sublimation and vaporization, as they are required to convert an enthalpy of formation value obtained from a gas phase calculation into a room temperature state.

The study presented in Chapter 1.5 aimed to determine whether complex machine learning models are necessary to predict material properties or if simple linear regression models can provide accurate predictions of thermochemical properties and density. The study analysed Joback's method in combination with statistical models, as well as the density predictions of Holden, Keshavarz, and Bondarchuk. Updated group increment tables for Joback's method were also included in the analysis. In the same chapter, a correlation between the plate dent test and Chapman-Jougett detonation pressure is presented, which would be an excellent candidate for lab-scale performance testing of novel energetic materials. Further studies like this are presented in Chapter 3 including the Ballistic Mortar test, the Trauzl Test, and the SSRT-Test. Chapter 4.1 is an example where some of the computational methods used in this thesis were applied to real-life problems.

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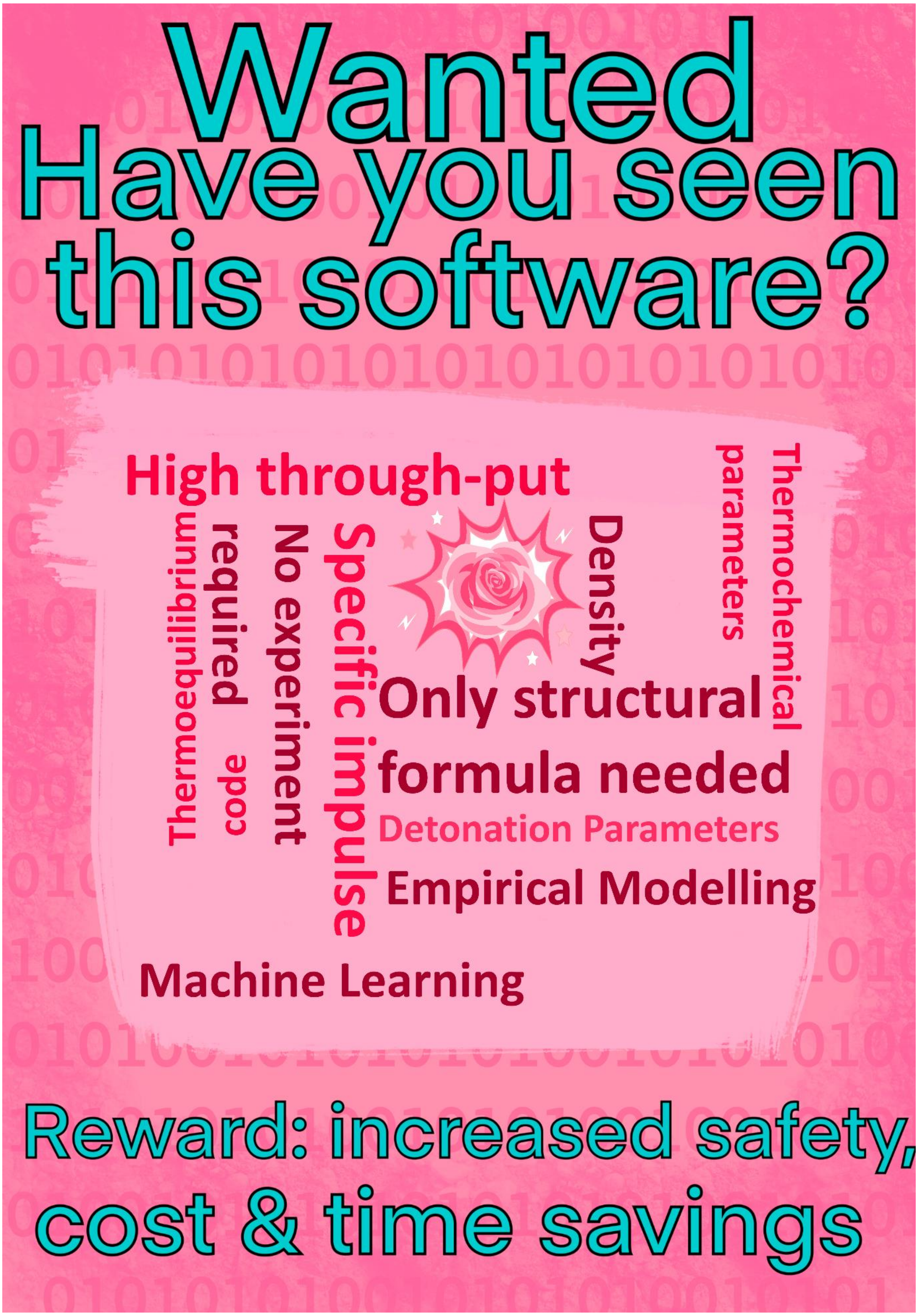
Table of content

The Supplementary information to this thesis containing databases can be downloaded from:

https://syncandshare.lrz.de/getlink/fiRGevPykHHVLQG7G9XtXV/Sabrina%20Wahler_Doktorarbeit_SI.pdf

Or by scanning this QR Code:

1 About this Work



1.1 Introduction

Motivation: Developing an environmentally friendly tool for the prevention of accidents while accelerating research drastically

In the field of chemistry, computational methods are increasingly being used to predict the properties of new materials before they are synthesized. However, the community of energetic materials lags in this area. Additionally, the synthesis of compounds, particularly energetic materials, carries significant risks.[1] It is not practical to risk people's lives in the synthesis of explosives that may not even be useful. Figure 1 Shows a pumpkin that was exploded using a store-bought canister shell firework.

Figure 1. Pumpkin blown up using a certified firework.[2] (Reproduced from https://www.youtube.com/watch?v=y8MRoEFwRSU)

These canister shells roughly contain 60 grams of energetic materials. Assuming it is mostly black powder, this would equal about 45 grams of TNT.[3] As this pumpkin got torn into pieces with a "safe" energetic material sold in supermarkets, one can imagine what can happens with uncertified research explosives, when not handled properly. Some examples of blast injuries to hands by certified Fireworks are reported Giessler *et al.*[2], these Figures are not intended for the faint of heart. Therefore, handling an energetic material should be held to a minimum and when inevitable always be done with caution. Even if the laboratory rules state, that one shall only work with small quantities of explosives, an explosion of a research explosive of 500 mg or less still could lead to finger and hearing loss. Therefore, it is essential to adapt a new working process when searching for new energetic materials. It should involve a pre-evaluation of the target compounds for their feasibility as novel propellant or explosive, unlike the current workflow described in the next paragraph.

Before RoseBoom©, to determine whether an energetic material is a viable rocket propellant or explosive, one first had to synthesize it to determine its enthalpy of formation and density, which brought many risks as illustrated above. Alternatively, one could have used composite methods, which took up to 30 days on a computer cluster and were time-consuming.[4–7] Generally, the process involves manually inputting values into thermo-equilibrium codes, which is time-consuming as well and doesn't allow high-speed throughput of compounds to obtain the performance parameters of explosives.[4–7]

Currently, there are numerous models used to predict properties of energetic materials, this means published results for novel materials are incomparable. To compare published values of energetic materials, it would make sense to establish a new international standard that allows high throughput of energetic materials.

State-of-the-Art: Current software solutions

As one examines the software options available, it becomes clear that only a few selected programs can become established global standards. Numerous thermo-equilibrium codes exist for predicting the properties of energetic materials, with EXPLO5[8] and Cheetah[9] being two well-known options. However, non-US citizens can no longer access the newer versions of Cheetah, leaving them with limited choices. Meanwhile, EMBD[10] by Keshavarz, a code based on empirical relationships, has been available for many years. Before it was restricted by export control from Iran, EMBD 1.0 was a code that provided predictions for properties of energetic materials based on molecular structural formula alone. However, a notable disadvantage of EMBD was the complicated manual input process.[10]

The ICT code[11] can provide accurate predictions, but its usage requires special permission, and it is not very user-friendly. Additionally, it cannot handle high throughput of multiple compounds. While the code is not actively updated, it still receives sufficient funding to ensure its compatibility with newer operating systems. Just like EXPLO5, the ICT code also depends on external sources to obtain heat of formation and density information.

The author of this thesis has noticed some inconvenience with the BKW code[12] when working with certain new materials. The absence of comments in the code makes troubleshooting a challenge. It may be more practical to consider rewriting the code based on Mader's published works, as done by Arno Hahma in 1998[13]. The ISPBKW[12] and BKW Code[12] are executable files that necessitate modifying a text file as input, which is both time-consuming and prone to errors. Mader's ISPBKW code, on the other hand, is more stable and can predict specific impulses without encountering crashes like the BKW code.[12] However, it may not be able to calculate specific impulses for every compound.

The codes above prove that empirical modeling and thermo-equilibrium codes are well established modeling techniques. Additionally, machine learning started emerging in property prediction of energetic materials..[14–21] Obviously the limits of current, simpler methods were soon reached and led to the innovations in this thesis.

Goal: Creating a screening platform for energetic materials

The goal of the "Research output software for energetic materials based on observational modelling" (RoseBoom©) was to directly address this problem by being a user-friendly software, that predicts the density, enthalpy of formation, sublimation and vaporization, specific impulse, detonation velocity and pressure of monopropellants and mixtures only based on the structural formula within seconds. RoseBoom©[4–7] is intended, to identify the good molecules in a large pool of compounds. Metaphorically, it can be described as a "gold pan" to separate the gold nuggets from the gravel (Figure 2).

Figure 2. RoseBoom© is supposed to act as a "gold pan" to quickly identify the "gold nuggets", hence the compounds are worth investigating fur, there and separate them from the "gravel", hence the energetic materials not worth investigating.[5]

The competition in computer software to predict the properties of energetic materials before they have been synthesized is rather low. RoseBoom© is currently the only available solution for high-throughput property prediction of energetic materials. Now, there are an endless number of models published, to predict the properties of energetic materials quickly. The thesis investigates a range of models which are: Empirical Models (like Trouton Rule[22] or Kamlet and Jacobs[23]), Thermo-equilibrium codes (like EXPLO5[8] and the ISPBKW[12]), and several machine learning models like tree-based models. One major problem, when searching for a suitable model to predict a property, is that published literature is not comparable, which means that a major part of this work was to assemble datasets and compare promising models from the literature to each other and select the most promising ones. Over 10k Datapoints were collected and used for the validation and modeling of RoseBoom©, which allowed to accomplish the goal of developing such a platform.

Application: Digging for promising energetic materials with RoseBoom©

The above-described screening platform has already found applications. For example by Lechner *et al.*[24] the density for certain picramide acid derivatives could not be obtained. Therefore, the density predictions in RoseBoom© were used to predict the density of several Picramid Acid derivatives.[24]

Table 1. RoseBoom© applied to fill the missing densities of picric amid isomers for performance. [24]

	iPAM zwitterionic exp.	iPAM neutral calc.	PAM neutral exp.	PAM neutral calc.	PAM zwitterionic cal.
$\Delta_f H^\circ$ [kJ/mol][a]	0.5	214.3	262.4	262.4	139.2
$\rho_{X\text{-}Ray}$ [g/cm 3] [b]	1.78	–	1.69	–	–
$\rho_{RoseBoom}$ [g/cm] [c]	–	1.68	–	1.68	1.67
EXPLO5 version	V6.05.04	V6.05.04	V6.05.04	V6.05.04	V6.05.04
PC-J [GPa][d]	22.5	16.6	16.3	16.0	17.5
Vdet [m/s][e]	7458	6607	6546	6513	6716

[a] calculated (CBS-4M) heat of formation; [b] X-ray density converted to 298 K; [c] calculated density according to Holden; [d] detonation pressure; [e] detonation velocity.

The density was needed to predict their performance parameters for comparison. Without RoseBoom© it would have required much more effort to obtain and predict performance parameters. As shown by this example in Table 1, synthesizing the other compounds would've been a waste of time, as they exhibit lower performance than the zwitterionic iPAM, which was obtained experimentally.

Another interesting study was published by the Frauenhofer ICT: In 2023 Omlor *et al.*[25] showed, how RoseBoom© is equally as accurate for the enthalpy of formation, sublimation and vaporization as much more complicated quantum methods that can take up to 80 days on a computer cluster.[25] The results of this study are given in Table 2.

Table 2. RoseBoom©'s Thermochemical prediction compared to CBS-QB3 calculations. [25]

	DPA		N-NO-DPA	
	CBS-QB3	RoseBoom©	CBS-QB3.	RoseBoom©
$\Delta_{f}H^{\circ}$(g) [kJ/mol]	212.5	212.78	316.8	307.8
ΔH_{vap}^{0} [kJ/mol]	67.7	79.2	72.5	80.2
ΔH_{sub}°(g) [kJ/mol]	103.9	97.6	117	115.2
$\Delta_{f}H^{\circ}$(l) [kJ/mol]	144.8	133.6	244.3	227.7
$\Delta_{f}H^{\circ}$(s) [kJ/mol]	108.6	115.2	199.8	192.6

Looking at the enthalpies predicted by the CBS-QB3 calculation and RoseBoom©, it becomes apparent that these methods show neglectable differences. Especially, when looking at the other reported quantum calculations that show a similar difference. However, RoseBoom© has the advantage, that it runs the calculations much quicker and allows high throughput, which makes its use to screen for target compounds much more feasible.

Both examples showcase how RoseBoom© has already made scientists lives easier and even showcases, that RoseBoom© can calculate the difference between different isomers. Overall, this illustrates that RoseBoom© is indeed a very promising candidate as an international standard for property prediction of energetic materials.

1.2 Theory

Methods

The first step in developing such a platform is finding which models are best at modeling the desired properties. To understand the limitations, weaknesses, and strengths of different methods, a selection of different modeling techniques was tested in this thesis. A simplified schematic representation of the methods is given in Figure 3.

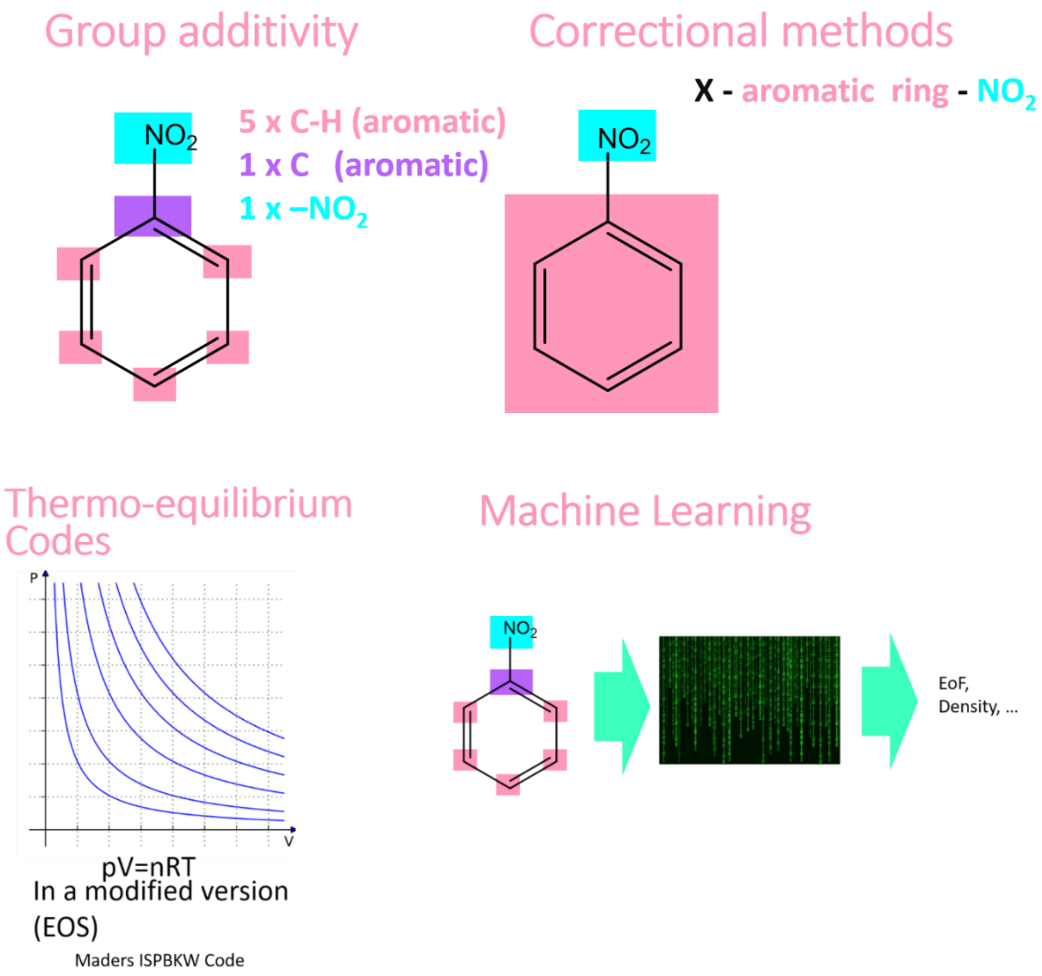


Figure 3. Simplified schematic representation of the models used in RoseBoom©. The top shows the empirical approach which can be subcategorized in group additivity methods and correctional methods. The bottom explains the less transparent methods: Thermo-equilibrium codes on the left and machine learning on the right.

In general, the empirical models can be separated into two categories: The group additivity methods and the correctional methods. In group additivity methods each molecular fragment is assigned a value, which is then summed up depending on the occurrences in the molecule. For correctional methods, a value is corrected depending on the molecular moieties in the molecule.

Thermo-equilibrium codes will calculate the detonation products in thermal equilibrium from which the detonation parameters can be derived.[26] More information is given in Chapters 2.2.

Machine learning is often seen as a black box. But this is not the case, the simplest form of machine learning is linear regression. So, a linear regression machine learning model can for example be trained in sci-kit learn[27], later on, the individual parameters assigned to the features can be extracted along with the intercept of the equation, providing an empirical group contribution that can be obtained using machine learning. When building any model, the parameters according to which it should be based and modeled must be chosen. These features for an empirical model and a machine learning model can be the same, but depending on the models chosen, more complicated statistical models will model the different parameters. In the next paragraph a detailed explanation of which models were employed and how they were employed is given.

Machine learning models and validation methods used in this thesis

1) Models

A variety of statistical models were tested in this thesis to model the properties of energetic materials. Below, the models tested in this thesis are explained.

Linear regression model

Many people are surprised that linear regression is considered as machine learning, given that it is commonly used in everyday programs like Excel or Origin. In fact, using the linear regression tools in these programs is essentially the same as using scikit-learn's linear regression machine learning model. However, using Python with the scikit-learn library offers a more comfortable way of adjusting these models. With scikit-learn, adjusting the featurization and performing cross validations is easy and does not require manually splitting the data into train and test sets. [27]

In this thesis, both Scikit-learn and Origin were utilized to obtain correlations. Origin was employed for simpler correlations with fewer features such as the RoseTrauzl, RoseDent, RoseMortar, or RoseSSRT correlations. On the other hand, scikit-learn was used for more complex models like the re-parametrization of Joback.

Tree-based Regression Models

A decision tree regressor is a type of decision tree that uses selected features to learn simple decision rules in a non-parametric supervised manner. These trees are like piecewise approximations, with the final decisions known as leaves. There are two types of models: classification and regression. Classification models are used when data needs to be sorted into different categories, while regression models are used to predict continuous values such as heat of formation and density. Therefore, this thesis only utilizes regression models. [27]

For reasons of descriptiveness, the author has chosen to utilize the wine quality dataset from scikit-learn to train the tree-based models. The aim is to showcase the rules these models follow in a visible and human-readable format using Graphviz.[28] This will help readers understand how these models work. Also, it has been successfully demonstrated that tree-based classification can model the quality of wines, which makes it an attractive model.[29]

A) Decision Tree Regressor

As explained above, a decision tree regressor is one singular decision tree, that will model the dataset based on rules. What such a tree-based model can look like the one shown in Figure 5 on the example of wine quality. [27]

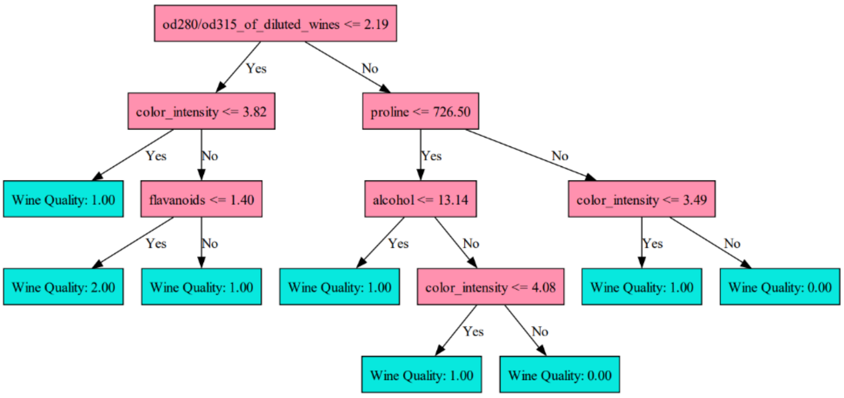


Figure 5. Decision Tree Regressor model to predict the Wine Quality based on the Wine Dataset in Sci-kit learn. The model has a R^2=0.71 on the test set.

These rules are then followed by the model when provided with unknown data. So, it will go down the nodes (pink) until it reaches a leaf (turquoise).

B) Random Forest Regressor

A Random Forest Regressor builds multiple decision trees simultaneously. Each of these trees models a value used to predict the result. The final prediction is the average of the results from all the decision trees. Figure 6 illustrates a Random Forest model with three trees used to model the quality of wine. [27]

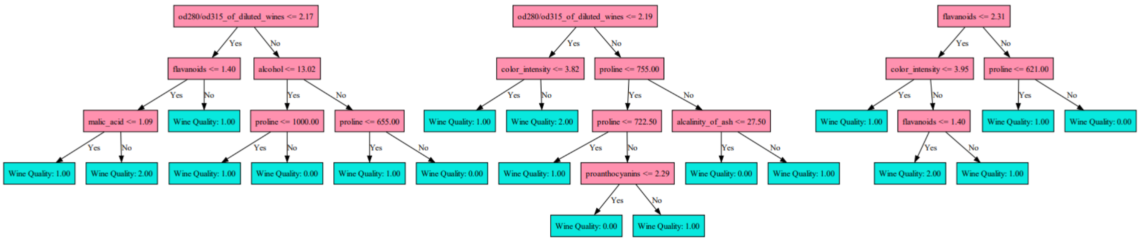


Figure 6. Random forest regressor model (R^2=0.85 on the test set) using three trees to predict the Wine Quality based on the Wine Dataset in Sci-kit learn.

As seen on the example of the quality of wine, this approach is usually more accurate (R^2=0.85) then a singular tree (R^2=0.71).

C) Gradient Boosted Regressor

In a gradient boosted regressor multiple decision trees are built in a subsequent manner, where each tree corrects the error form previous trees. Figure 7 shows a gradient boosted regressor with 3 trees modeling the quality of wine, where the prediction of every tree would be summed up.[27]

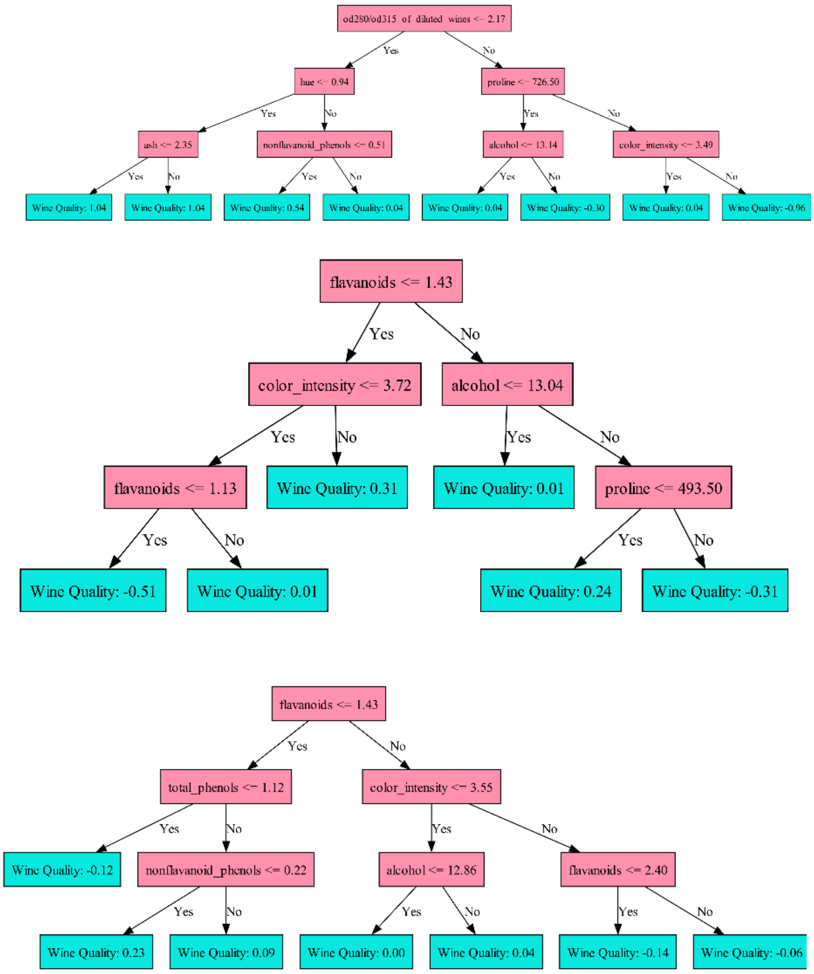


Figure 7. Gradient boosted regressor model (R^2=0.82 on the test set) using three trees to predict the Wine Quality based on the Wine Dataset in Sci-kit learn.

This model is very sensitive toward overfitting, which is probably, why it performed slightly poorer than the random forest model (R^2=0.82). However, if fitted correctly on a suitable dataset, it will give more accurate results as shown in Chapter 1.5.

Gaussian Process Regressor

One effective method for modeling complex and non-linear relationships between variables is using Gaussian Process Regressors (GPR). This Bayesian non-linear regression method is based on the concept of Gaussian processes, which refers to a group of random variables that exhibit a joint Gaussian distribution when taken in finite numbers. GPR is especially beneficial in scenarios where data may be affected by uncertainty or noise.[30] Which made it especially attractive to model experimental enthalpies of sublimation and vaporization in this thesis, as they can show high experimental uncertainties.[31] Also, even though no detailed report is given in this thesis but RoseBoom2.4© also contains models for the enthalpy of formation and density using GPR.

2) Cross Validation

To judge the model's ability to predict unknown data, it is important to validate on data the model was not trained on. An analogy to this would be, that in school/ university students are learning a new concept on a few examples, which in the exam they must apply to new examples, that they ideally have never seen before. This is used to test the student's ability to solve new problems. The same is done for machine learning models, but there are various cross validation methods to do this, just as there are different types of exams.

The models presented in this thesis all have some underlying linear correlation between the features, therefore it was of interest to use a technique which has the least bias when testing the model. Below, two methods applied are discussed and their pro's and con's.[32]

A) Monte Carlo Cross-validation

In a Monte Carlo Cross-validation, the dataset is randomly split into different training and test sets as shown in Figure 8.

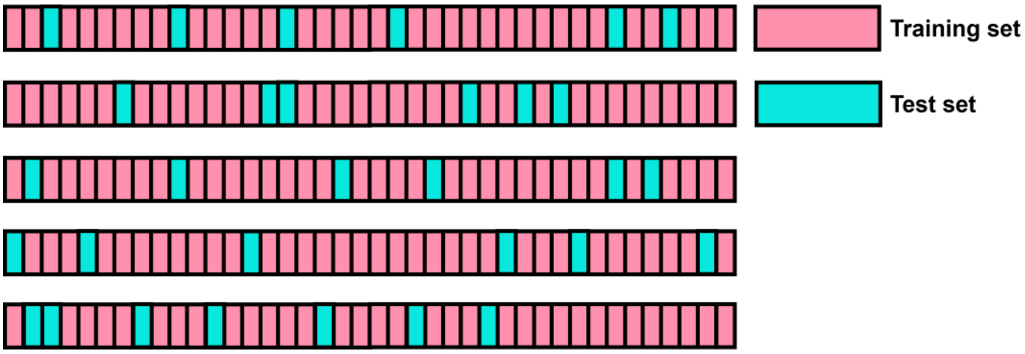


Figure 8. Graphical visualization of a Monte Carlo Validation.

According to Shao, for linear correlations a Monte-Carlo-Cross-Validation[33] will provide the lowest variance. The issue with the use of a Monte-Carlo-Cross-Validation in chapter 1.5 is, that the model relies on functional groups. This could mean that some of the features are never present in the test set with the Monte-Carlo-Cross-Validation, introducing a bias into the data, as some data points never make it into the test set. Additionally, it can be very expensive as it requires many cycles. A Monte Carlo "light" cross-validation was performed in Chapter 2.6, as the Gaussian Process Regression model used for this study was rather computationally expensive, so 5 random shuffle splits were selected over a full Monte Carlo or K-Fold Cross Validation. The next problem was that K for the K-Fold validation would have needed to be rather high, because the datasets are small due to limited experimental data available.

B) K-Fold Validation

In a K-Fold validation the dataset is split into K Parts. Then the model is always trained with K-1 parts of this dataset and tested on 1 part. This is done until all K part were used as a test set as shown in Figure 9. To ensure there is no bias the dataset should be split into at least 10 parts.[32]

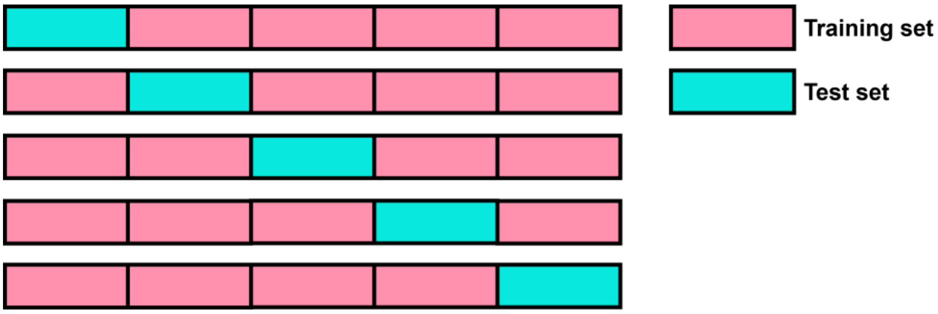


Figure 9. Graphical visualization of K-Fold validation.

As mentioned before, with a Monte Carlo validation some features may never be present in the test set, which is not good when developing a group contribution method. Therefore, the author has decided to perform a 10K-Fold validation for the group contribution models presented in Chapter 1.5, which will leave every molecule out of the training set once.

1.3 Conclusion

A) Reviewing problems with current experimental techniques

A major issue the author encountered is the limited experimental data available in literature. In chapter 1.6 a review of the complicated experimental techniques is given, from which it becomes evident that there is a need for simpler tests to determine certain values that have already been extensively performed in laboratories and are readily available. Therefore, it is important to investigate which physical values these tests may correlate to and evaluate their feasibility for characterizing new materials in terms of required sample size, accuracy, and reproducibility. It is crucial that these values can be measured easily without the need for any specialized equipment. Even though some of these tests are mainly used to evaluate the safety of energetic materials or TNT equivalents, they also correspond to some of the desired thermodynamic values. Among these tests, the plate-dent test shows promise in assessing the Chapman-Jougett Detonation pressure. However, the Trauzl-test and Ballistic Mortar seem too imprecise to draw a concrete conclusion as suggested by the RoseTrauzl and RoseMortar equation, and the SSRT-Test linearly correlates with the heat of detonation as presented in the RoseSSRT Equation. Going forward, there is a need to explore additional tests to discover one that requires minimal sample size, is highly reproducible, and doesn't necessitate specialized equipment. This would make it feasible to conduct the test in any laboratory. While the precision may not be as exact as more complex measurement techniques, it can still offer an estimate of performance that may be more accurate than calculating performance using thermo-equilibrium codes.

B) Reviewing current software solutions

To evaluate RoseBoom© a comparison of different computer software for energetic materials has been made in Chapter 1.6. They competed in 8 carefully selected categories against each other and were ranked accordingly. Unfortunately, the EMDB1.0 code is no longer available as it is restricted by export control. The ICT code is precise, but it can be challenging to use for those who are not familiar with heat of formation and density values. The BKW code may be unreliable as it occasionally crashes and lacks comments, making it time-consuming to operate. Alternatively, Mader's ISPBKW code is efficient in predicting specific impulse and is straightforward to use. However, it may not work effectively for all compounds. The software RoseBoom© achieved the highest score by obtaining a point in every category. It has been designed efficiently, allowing for a simple sketch of a compound as an input. With the use of empirical methods and machine learning, it provides predictions for density and heat of formation, which are then used in performance prediction for energetic materials. The software combines various modelling approaches, incorporating numerous revalidated empirical models, machine learning models, and coupling it to the

ISPBKW code. This makes it the ideal software as it is a collection of all different methods. It is user-friendly and efficient, being the only vastly available software for energetic materials that can extract all necessary information from a sketch of the compound or run numerous molecules in a row automatically. Additionally, it is the first and only software for energetic materials that combines all modelling approaches into one computer program. So, Chapter 1.6 nicely illustrates how RoseBoom© is addressing the problems scientists currently have.

C) The history of RoseBoom© - Progress made in this work

In 2021 RoseBoom2.0© was deployed. It had density predictions by Keshavarz and Holden embedded. The enthalpy of formation prediction was only suitable for nitrogen-rich compounds. The detonation parameter models gave good prediction. The first precursor of the software today was built using the methods given in the light pink boxes in Figure 9. Further information is given in Chapter 2.3 which summarized the concept of RoseBoom©, a very crude version, more a theoretic approach than an application was defined in the authors master thesis. Many new features had to be added to make it functional. The new models and approaches developed and evaluated are given in the dark pink boxes in Figure 10. An additional lineup of the updates and changes made is giving in Table 3.

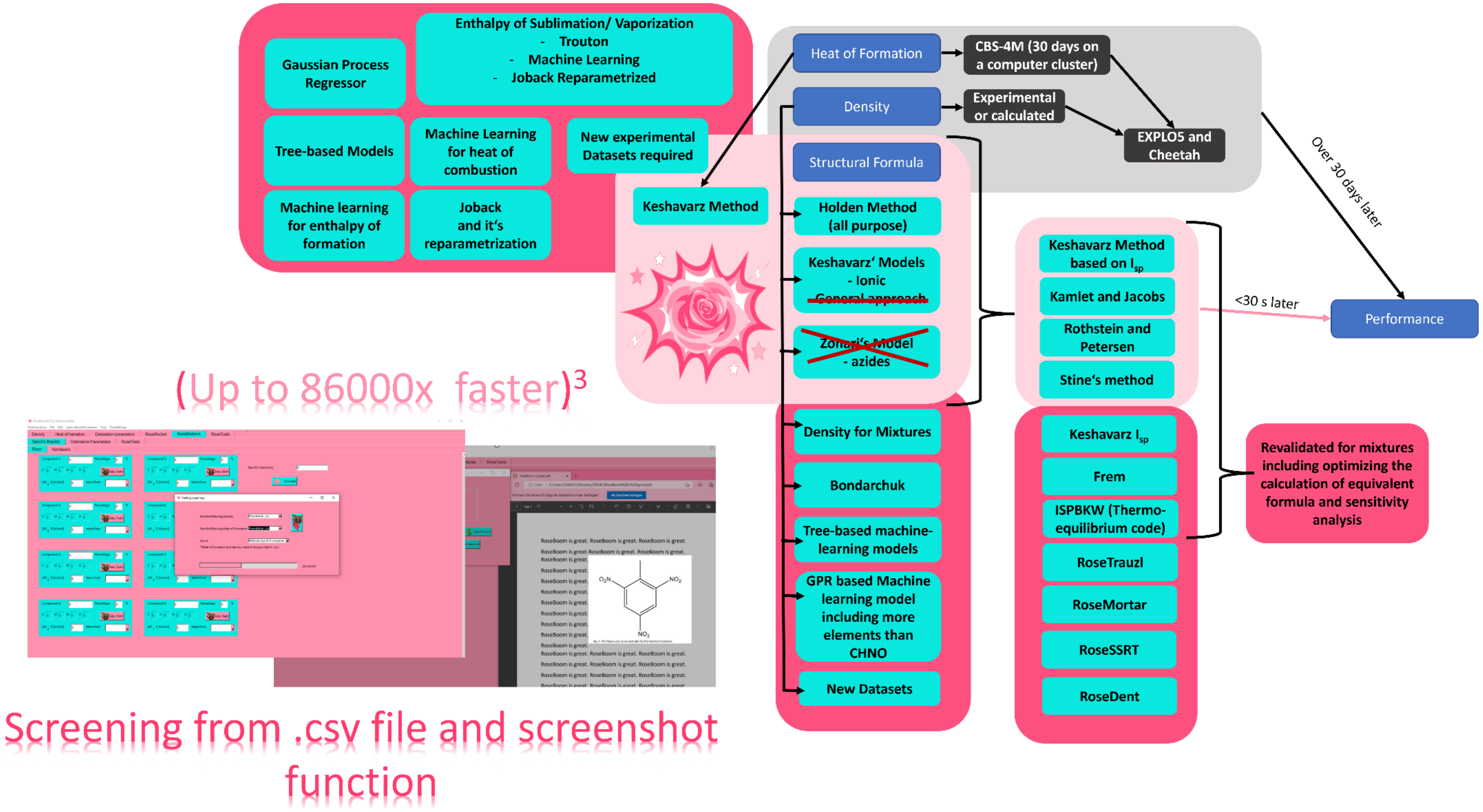


Figure 10. Updates of RoseBoom2.4 since RoseBoom2.0. The updated are in dark pink boxes, the baby pink boxes were included in RoseBoom2.0. Screenshots of new user-friendly feature as are also given.

Table 3. Additional Summary of the updates done to RoseBoom© in this thesis.

Property/ Function	**Models investigated for RoseBoom2.0© in 2021**	**Models investigated for RoseBoom2.4©**
Density	Holden Keshavarz Ionic Zohari Azide Keshavarz Azide	Gradient Boosted Tree Random Forrest Tree Regressor Gaussian Process Regressor RoseDensity for Mixtures Bondarchuk
Enthalpy of Formation	Keshavarz	Joback and Reid Reparametrized Joback Gradient Boosted Tree Random Forrest Tree Regressor Gaussian Process Regressor
Enthalpy of Sublimation	-	Trouton's Rule Reparametrized Joback Gradient Boosted Tree Random Forrest Tree Regressor Gaussian Process Regressor
Enthalpy of Vaporization	-	Trouton's Rule Reparametrized Joback Gradient Boosted Tree Random Forrest Tree Regressor Gaussian Process Regressor

Property/ Function	Models investigated for RoseBoom2.0© in 2021	Models investigated for RoseBoom2.4©
Mixture performance	-	Kamlet and Jacobs (Detonation pressure and velocity) Stine (Detonation Velocity) Keshavarz (Detonation pressure and velocity) Frem (Specific Impulse) ISPBKW (Specific Impulse) Keshavarz (Specific Impulse)
Pure Compound Performance	Kamlet and Jacobs (Detonation pressure and velocity) Stine (Detonation Velocity) Keshavarz (Detonation pressure and velocity) Rothstein and Peterson (Detonation pressure and velocity)	RoseTrauzl RoseMortar RoseDent RoseSSRT Frem (Specific Impulse) ISPBKW (Specific Impulse) Keshavarz (Specific Impulse) Evaluation of the sensitivity toward input parameters
Datapoints	Less than 500	Over 10k

Property/ Function	Models investigated for RoseBoom2.0© in 2021	Models investigated for RoseBoom2.4©
User-friendliness	Sloth-function: SMILES could be pasted into RoseBoom©, Results needed to be retrieved individually and put into a Table for comparison.	Supersloth©: .csv file with thousands of SMILES can be loaded into the software Molecule can be screenshotted and converted into SMILES using OCSR.

D) Exciting discoveries, the updates made to RoseBoom© and models investigated for RoseBoom2.4©

1. Density

After the first publication of RoseBoom© presented in Chapter 2.1, the difficult descion was made to remove Zohari's Azide model[34] and Keshavarz General Method[35], as they did not give as accurate prediction as the ionic method[36] and holden method[37]. A side effect of this was that the RoseHybrid© value was refined and improved, as it only consists of the average of the models embedded into RoseBoom©. Additionally the new model by Bondarchuk[38] was tested in Chapter 1.5. In the same chapter the Holden method is translated into a feature vector for tree-based models and tested with a Gradient Boosted Tree, Random Forest, and Tree regression model. It is not reported in this work, but RoseBoom2.4© also contains a density model prediction, which was uses similar approach as describedin Chapter 2.6. Overall, the later models investigated in this work, showed differences of <3%. When looking at the different packing densities explosives will have in their end application (as presented in Chapter 1.6 for TNT) (see Figure 11), it becomes apparent that these differences in the prediction of the theoretical maximum density in RoseBoom© are not significant.

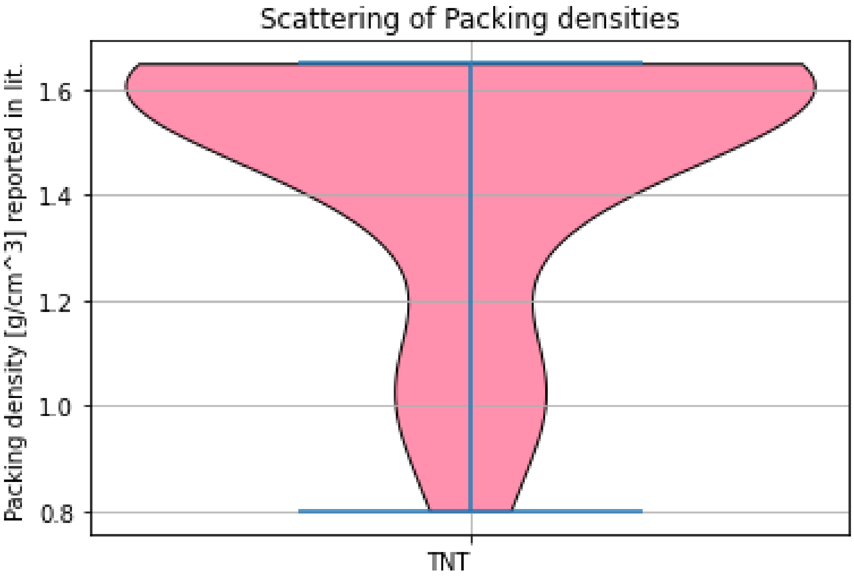


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Figure 11. Packing densities of the detonation pressure measurements for TNT reported in literature.[39]

As shown in Figure 11 the packing density of TNT can range within 0.8 - 1.6 g/cm^3. In this thesis the author paid attention to use room temperature densities, so some low temperature X-Ray values had to be converted to room temperature. The reason for using X-Ray measurements for density determination is that pycnometer measurements require much larger sample sizes, which may not be obtained in early stages of synthesizing a compound, as this can be very dangerous for compounds with unknown sensitivities. Therefore, for energetic materials, the X-Ray densities are commonly used to predict their performances while pycnometer values for novel materials are rare. However, due to Thompson Scattering, these are mostly measured at low temperatures, which results in much higher densities. These are sometimes converted to room-temperature, for example using equation 1.

$$\rho_{298K} = \frac{\rho_T}{1 + \alpha\,(298 - T_0)} \text{ with } \alpha = 1.5\ \times 10^{-4}\, K^{-1} \qquad 1$$

This equation was obtained from a study from Xue et al.[40] where they measured the thermal expansion of HMX. From this study the linear expansion coefficient α has been derived. Which is worth mentioning is different for every material. It is normally measured as an average derived from the lattice spacing change over a temperature interval ΔT = T2 – T1. (Equation 2)[41]

$$\alpha = \frac{(l_2 - l_1)/l_t}{(T_2 - T_1)} = \frac{1}{l_t}\frac{\Delta L}{\Delta T} \qquad 2$$

Alternatively values of α can be obtained by differentiating an algebraic fit to several readings lattice spacing at various temperatures. In each case the temperature interval ΔT should be roughly 10% of the measuring temperature except if α is sensibly constant over a wide range, which is unlikely at low temperatures. For an X-Ray measurement at 173 K, the temperature interval would be 153% to convert it to room temperature. These findings indicate that the formula used amongst many energetic scientists to convert the densities to room temperature, may not give the most accurate results.[41] Not only is a equation used where the linear expansion coefficient is limited to a tiny dataset, but also goes 15 times over the suggested measurement interval. So, the densities used in performance calculations may not even be accurate when measured experimentally. Also, some of the densities used in this thesis were converted from low temperatures to room temperature using equation 1, so the error in the dataset in the thesis is likely to be higher than the 3% differences between different models. Given the experimental situation, the models presented in this thesis are as accurate as they can be with the experimental uncertainty in the dataset.

2. The RoseThermo Package

I. Enthalpy of Formation

After expanding the software by implementing the Joback and Reid[42] group contribution to predict the enthalpy of formation, the assumption was, that available empirical models may not give much better predictions than what RoseBoom2.1© could do. Even though, Benson's group[43] additivity is slightly more accurate, the problem is that it is incapable of describing some novel energetic materials, as some functional groups cannot be described, so the author decided not to pursue this method further. After having added a somewhat acceptable prediction of enthalpies of formation, it was important to quantify the impact of the different input parameters (e.g., density and heat of formation) when using them to assess detonation performance. This is very relevant, as the mission of this work was to create a screening platform which does not require external input. So, it must be investigated how well RoseBoom© performs without external input. Therefore, a study was conducted, where the predictions by RoseBoom2.1© using literature values for density and heat of formation were compared to the values obtained when using RoseBoom©'s values for heat of formation and density, using RoseHybrid's values. It was shown that the detonation pressure can be influenced by over 9% depending on what model is being used.[5] Therefore, it was apparent that this value had to be refined before even thinking about refining the detonation equations. Another issue with the embedded group additivity theory was that Joback and Reid predicts an enthalpy of formation in the gas phase.[42] Therefore, not only a gaussian process regression model for the enthalpy of formation is now embedded into RoseBoom© but a thorough investigation of Joback's groups additivity theory has been performed in Chapter 1.5. The groups presented in this method were translated into a feature vector for machine learning models. It was discovered, it is not statistically significant if one uses a more complicated machine learning algorithm or a simple linear regression model as they deviate by roughly 12 kJ/mol. This is not significant when considering that experimental measurements will deviate by much more. For example, for TNT one can find values ranging from -80.5 kJ/mol to -50 kJ/mol. So, refining a model for 12 kJ/mol would a waste of time until better experimental values are obtained.

II. Enthalpy of Sublimation and Vaporization

As mentioned before, the original Joback group contribution method predicts enthalpies of formation in the gas phase, just like many DFT Methods.[44] So, depending on the aggregate state the enthalpy of vaporization or sublimation has to be subtracted from these gas phase values, to convert to room temperature, if it is a liquid or solid. Calculating these values may take up to 80 days using DFT Methods.[44] A simple method is the Trouton Rule, which is used to convert a gas phase heat of formation from the gas phase to room temperature has been shown to give poor predictions for the enthalpy of sublimation and vaporization as shown in Chapter 2.6. This is a rather shocking discovery, because this means that the enthalpies of formation from Chapter 2.1, are very unreliable, as many of those were converted using Trouton's rule. However, this left the exciting opportunity to come up with new and improved prediction models for the enthalpy of vaporization and sublimation which were introduced in this thesis in Chapter 2.6 and 1.5. Aside from giving more accurate predictions, they don't require a melting or boiling point to predict the enthalpies of sublimation and vaporization unlike Trouton's rule. Hence, prior experiments, that were required to measure the phase transition temperatures, are eliminated for their determination. This is especially great for energetic materials, as many of them don't have a melting point and just decompose, likely to make the prediction using Trouton's rule more imprecise.

3. RoseMixtures – Mixture Performance

In this thesis, empirical equations were found to be effective for the performance prediction of energetic mixtures, and the impact of various equivalent formulas was thoroughly analyzed for CHNO mixtures predicting their detonation parameters and specific impulse. More detail is given in Chapter 2.2. Specifically, 518 mixtures previously calculated with EXPLO5 were re-evaluated using empirical models. However, an issue arose when calculating the equivalent formula of the mixture. For example, in the case of a mixture containing 65% ammonium dinitramide (AND, $H_4N_4O_4$) and 35% glycidyl azide polymer (GAP, $C_3H_5N_3O$), different methods produced different equivalent formulas ($C_{1.05}H_{4.35}N_{3.35}O_{2.95,}$ $C_{1.061}H_{3.863}N_{3.156}O_{2.449}$, and $C_{1.208}H_{4.403}N_{3.597}O_{2.792}$). These discrepancies are due to the different methods used to calculate the equivalent formula (Frem's method using a fixed molar weight of 100 g/mol, and Sućeska's EXPLO5 using mole fractions). To investigate the impact of these different formulas on performance prediction, calculations were run using all sum formulas, [45,46] because the author of this thesis couldn't find any other publication/ scientific work investigating this issue as thoroughly, she took the matter in to her own hands.

4. Compound performance

a) TNT-Equivalents

Studying tests like the Trauzl test, ballistic mortar, SSRT, plate-den test, and their correlation with thermodynamic values can help understand the conversion of chemically stored energy into mechanical movement. The plate-dent test is promising for evaluating Chapman-Jougett detonation pressure, while Trauzl and Ballistic Mortar tests may not be precise. The SSRT test correlates with heat of detonation, hence it is interchangeable with a bomb calorimetric determination. Future tests should require minimal sample size and be highly reproducible. These discoveries were made by the RoseDent, RoseSSRT, RoseMortar and RoseTrauzl equation.

b) Specific impulse predictions

Aside from expanding the thermochemical predictions in RoseBoom© in this thesis, specific impulse predictions where added, which is one of the key performance parameters for rocket propellants. For this RoseBoom© has now several empirical models and the ISPBKW thermo-equilibrium code was embedded using an API. The results suggest that the density of a compound may not be as relevant to its specific impulse, as the model by Frem gave good predictions only requiring a heat of formation.[47] Also embedding them in to the software developed in this thesis makes all of the models accessible with all user-friendliness RoseBoom© has to offer.

5. Data Collection

Even though, experimental measurements should be preferred when modelling, it is not always possible to obtain experimental values in large quantities or it would take a tremendous amount of time to review literature and conduct experiments. This leaves computational chemists with a few options when having an idea for a new project: a) to not do the project, b) to invest this time or c) to rely on calculated data for an initial validation of the hypothesis made. As most scientist would never choose option a) if they are convinced of their idea, they may want to resort to relying on calculated data for an initial validation, rather than to directly invest the time into gathering experimental data, if they are unsure if the hypothesis is correct. Also, sometimes experimental data will have so high uncertainty, that it can be difficult to decide, which of the experimental values to use as the scattering can be rather high. This may also mean, a scientist may decide to rely on computed values, if the experiments give to poor values.

In this thesis experimental values were used where possible (especially for the thermo-chemical parameters and densities). However, as already mentioned before, there is a tremendous lack of published performance values, and if these are published, they may exhibit high variance (as shown in Chapter 1.6 on the detonation pressure measurements for TNT). Nevertheless, over 10 000 Datapoints were additionally collected and calculated for the work in this thesis.

6. User-friendliness

By significantly improving the user-friendliness and data input into RoseBoom© through adding the Supersloth© function, which allows to run .csv files with SMILES fully automated, the speed at which the compound properties are obtained was significantly improved. Also, for singular molecules the input was improved by adding a screenshot function, converting the picture into a SMILES. The accuracy of this tool has also been carefully tested and evaluated in the last chapter. When designing new software, it is crucial to make the models available in a user-friendly format that maximizes efficiency, but first and foremost the quality of the models should be thoroughly assessed. Both of which has been accomplished in this work.

Value Added by this work

In summary, each of the other programs for energetic materials available on the market for energetic materials has its own advantages and disadvantages. The development of each of these programs has contributed to the scientific knowledge we have today and can be considered an important milestone in the history of performance prediction. However, it is important to remember that developing new models and improving existing ones should not be overlooked. Validating each model embedded in a program is a crucial step in the process. Additionally, any reparameterization or improvement of traditional models used in predicting performance, enthalpy of formation, and density should only be done, if it significantly improves the predictions and doesn't fall within the error of experimental uncertainty. Overall, this thesis has led to a very deployable and functional computer program to predict the performance of an energetic material only based on the structural formula. RoseBoom© is the only available screening platform for energetic materials, that is user-friendly and easy to use.

1.4 Outlook – The RoseFuture

The biggest obstacle in this work was the data collection, which was the most time consuming and took up the most resources. Therefore, it is of interest to create an online platform where energetic scientists can enter their experimentally or theoretically obtained material properties and make them accessible in a machine-readable format for computational scientists. This would benefit both sides: Even if a material exhibited undesirable properties, it can be used to train machine learning models which will benefit from having negative examples at hand. Also, having an internationally standardized database accessible to everyone would accelerate the discovery of energetic materials. Which is why one of the projects that is being tackled now is programing an online database for energetic materials where scientists can enter their experimentally determined properties and make them easily accessible for data scientists. A win-win situation as this would not only mean, that even if a compound doesn’t exhibit promising properties it would get published somewhere and forgotten, but also it would mean that these examples can be used to train and improve models to hopefully find a better solution faster if entered the databases by the users which again the entering scientists will profit from.

Another important parameter for explosives is all the gurney parameters, which are used to describe kinetics of an explosive. Therefore, one should add models to predict values like the gurney energy to RoseBoom© as this is the amount of kinetic energy an explosive release and which is important to know. For this, one could start by revalidating the equations proposed by Mathieu in 2005 on novel explosives.[48] This study assumes that the gurney parameters correlate with the detonation products of a compound. One could test various simple models to obtain the detonation products like the Springall-Roberts-Rules[22] and use the obtained detonation products as a featurization vector for different machine learning models and see how they perform. Additionally, it should be investigated if it correlates to molecular structure. For example, the machine learning models presented in the next chapter could be investigated for modelling the gurney energy of a molecule.

In the past it was debated if it would be reasonable to invest resources into adding a molecule sketcher into RoseBoom©, this however, does not really give a real benefit to the user, as most users of RoseBoom© have access to ChemDraw, which is a standalone application, where much time and resources were invested into developing it. This on the other hand means, that the editor that could be embedded into RoseBoom© would not be as good as ChemDraw. However, considering that the optical structure recognition is not as accurate as expected, this may become relevant again in the future.

Overall, the number of properties RoseBoom© can be expanded for is overwhelming: predictions for melting points, decomposition and flash points, impact, friction, and spark sensitivity, toxicity, and other safety parameters. The options are infinite, meaning RoseBoom© will probably only reach its final form, if it ever stops being developed. Overall, one can describe future workflow with RoseBoom© like solving a Rubik's Cube with over 43 quintillion combinations: There is a giant number of combinations of features, models etc. however, only very few "permutations" will lead to a good prediction of a certain property. (Figure 12.)

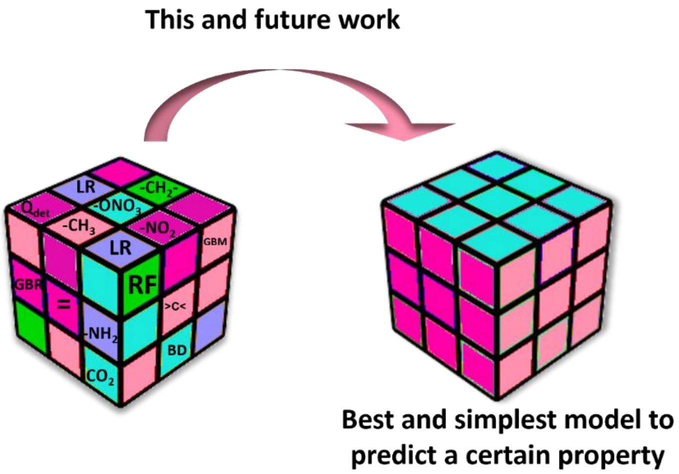


Figure 12. A metaphorical representation of the modelling of material properties. The process of finding a good model can be compared to a Rubic's Cube, several combinations must be tried to solve it, just like with finding the best and simplest model. By intelligently choosing the combinations, by applying chemical intuition, this process can be speeded up.

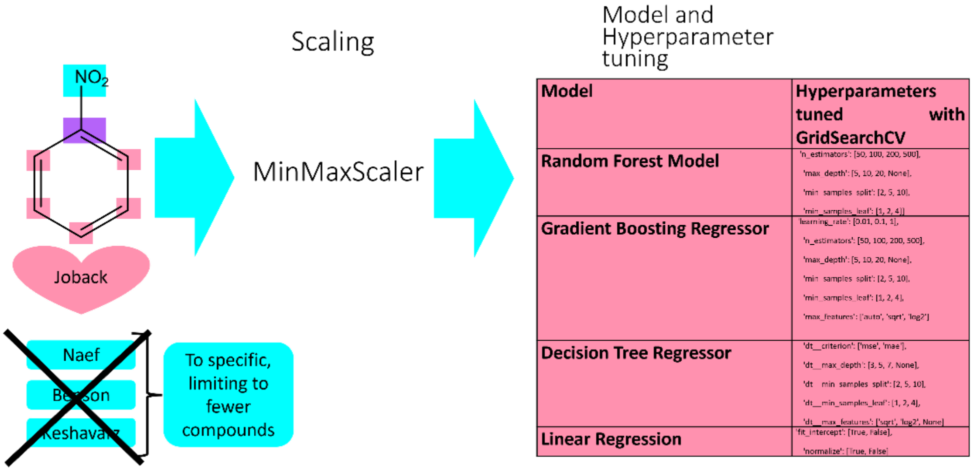
When developing such models, it is incredibly important to choose the parameter and features with chemical intuition. Additionally, it should be paid attention to the experimental uncertainty of the selected data, it does not make sense to continue refining the models once the predictions made are within the uncertainty of experimental data.

1.5 Two new models that bring the solution.

Joback group additivity theory is a widely used method for predicting the thermophysical properties of organic compounds. It was introduced in the late 1980s by Joback and Reid[42] as a means of estimating properties such as boiling point and heat capacity based on the constituent functional groups of a molecule. The theory is based on the concept of group additivity, where molecular moieties are assigned values and their occurrences in a molecule are summed.[42] In a recent study, it tested on a dataset of energetic materials.[4] In the following, the features presented in Joback's group additivity were selected for machine learning algorithms.

In recent study by Li *et al.*[49], Quantitative Structure-Property Relationships were used in a combination with a Random Forest Ensemble for density predictions of energetic materials was used. In this study well tested empirical models were used for featurization and an ensemble of Tree-based models were tested: Decision trees, random forest, and gradient boosted tree.[27]

Firstly, the Joback and Reid[42] fragments were translated into a feature vector to use for training the machine learning models for the thermochemical properties as it performed well on energetic materials[4]. For the density,[37] the Holden Method was used for featurization as this perare formed well for densities.[4] After that three different statistical models were trained with the features. A Random Forest Regression, Gradient Boosting Regressor, Decision Tree Regression, and linear regression[27] machine learning models were tested to evaluate in this study. The hyperparameter tuning was performed using an exhaustive search over the defined parameter space. The data was scaled between 0 and 1. Also, the workflow and decision process for featurization, and the model assembly is given in Figure 13.



Model	Hyperparameters tuned with GridSearchCV
Random Forest Model	'n_estimators': [50, 100, 200, 500], 'max_depth': [5, 10, 20, None], 'min_samples_split': [2, 5, 10], 'min_samples_leaf': [1, 2, 4]}
Gradient Boosting Regressor	'learning_rate': [0.01, 0.1, 1], 'n_estimators': [50, 100, 200, 500], 'max_depth': [5, 10, 20, None], 'min_samples_split': [2, 5, 10], 'min_samples_leaf': [1, 2, 4], 'max_features': ['auto', 'sqrt', 'log2']
Decision Tree Regressor	'dt__criterion': ['mse', 'mae'], 'dt__max_depth': [3, 5, 7, None], 'dt__min_samples_split': [2, 5, 10], 'dt__min_samples_leaf': [1, 2, 4], 'dt__max_features': ['sqrt', 'log2', None]
Linear Regression	'fit_intercept': [True, False], 'normalize': [True, False]

Figure 13. Assembly of the machine learning models.

The experimental thermochemical data selected consist of 5031 CHNOClFBrIS compounds with enthalpies of formation, 2180 molecules with the same composition for the enthalpy of sublimation and 3932 enthalpies of vaporization.[31,50–53] The experimental density data selected consists of 975 CHNO energetic compounds (See Literature Section B) with densities at Room temperature that were selected as the training set. For the density, the Holden method[37] was translated into a feature vector to use for training the machine learning model.

Firstly, the accuracy of the current enthalpy of formation increments in the Joback[42], model was investigated. Figure 14 shows the reevaluation of Joback's model on a large set of experimental enthalpies of formations of 5031 CHNOFClBrIS compounds.

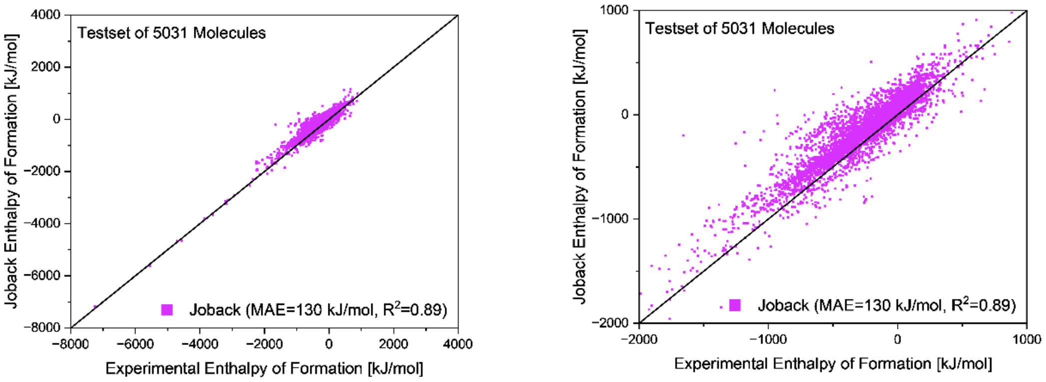
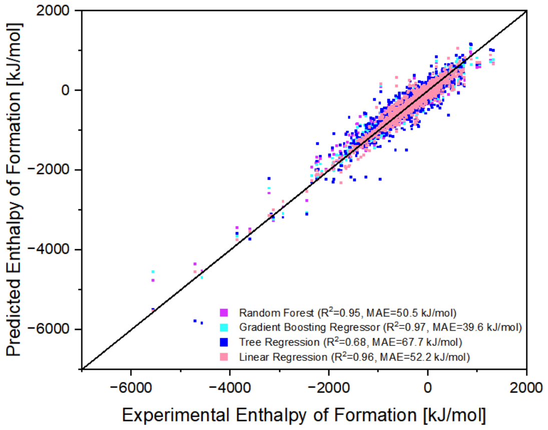
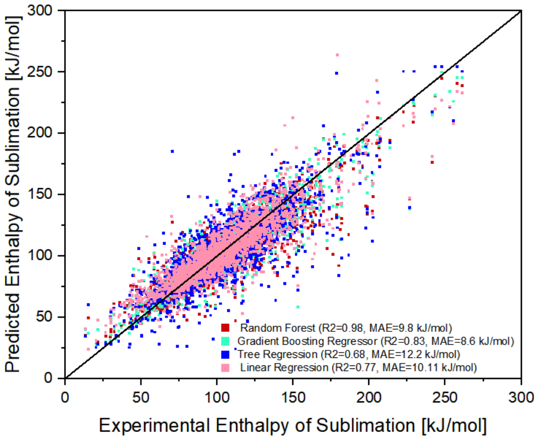


Figure 14. Scattering plots of the experimental enthalpies of formation plotted against the predicted enthalpies of formation using Joback. The graphs are shown at different scales on the left and right.

The correlation coefficient and the mean absolute error (MAE) remained within the results of the previous evaluation.[4] However, one can clearly tell, that the scattering of the predicted values is high. One reason that many values are too high, might be, that Joback predicts the enthalpy of formation values in the gas phase[42], like many quantum methods, which is a major downside when predicting new compounds that have not been synthesized before, because their aggregate at room temperature state is not known yet known. However, there is clearly a correlation between the increments that were selected for Joback's group additivity theory and the enthalpy of formation. Therefore, it may be worth reparametrizing it.

So, a linear regression, random forest, and gradient boosting regressor and tree regressor were selected for modeling of the enthalpy of formation, sublimation, and vaporizations. All these models deal well with linear correlations[54] but the last two can also account for slightly non-linear correlations between the selected feature vectors. As features the Joback group increments were selected, with the only difference that for the ring increments it was differentiated between aromatic and non-aromatic atoms. The result for the thermo-chemical parameters is shown in Figure 15.





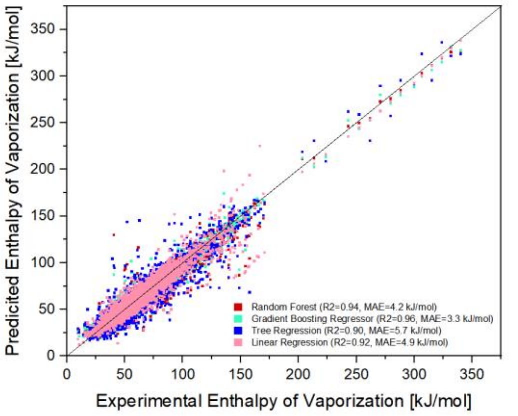


Figure 15. Scattering plots of the experimental enthalpies of formation, vaporization and sublimation plotted against the predicted leave-out test sets of the 10 K-Fold validations using the models described in methods with the features from the Joback-method.

Overall, one can say, that all the models performed somewhat similar, because experimental measurements can show rather high deviations[25,55,56] Tree regression model performed the poorest in all cases, which may be an indicator that it doesn't account as well for linear correlations. The Gradient Process Regressor modelled the dataset the best and the linear regression model work just as good as the random forest model. However, the goal of this thesis was to predict properties of molecules only based on the structural formula, ideally without the need of a special model and beginner programing skills. Therefore, the Joback method was reparametrized for the Enthalpy of formation at room temperature and the enthalpy of sublimation and vaporization.

For the density, the features presented in the Holden Method was selected for featurization on a dataset of 975 energetic materials with known aggregate states were tested. The results are displayed in Figure 16.

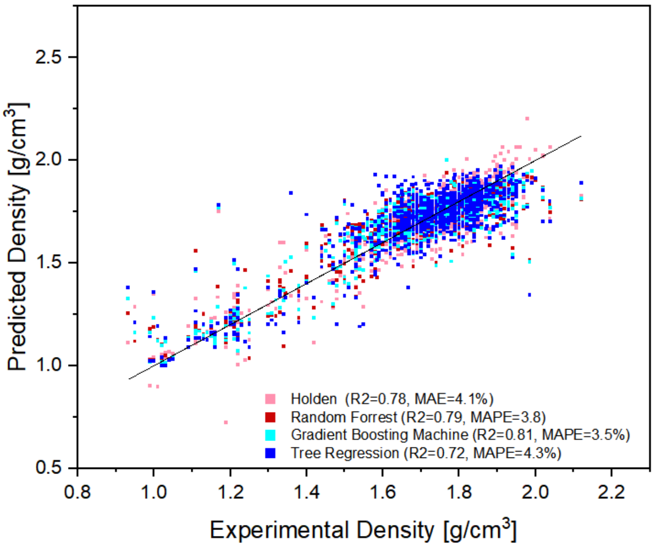


Figure 16. Scattering plots of the experimental densities plotted against the predicted densities of the leave-out test sets of the 10 K-Fold validations the models described in methods with the features from the Holden-method.

The Gradient Boosting Regressor showed the lowest error again while the Tree Regressor showed the highest error, which matched the observation with the thermo-chemical parameter. The Holden method exhibited so low of an error, that this was not improved by linear regression in sci-kit-learn, which is why the original model was used for comparison. Random forest models are ensemble learning algorithm that creates multiple decision trees and combines them to produce a more accurate prediction while, gradient boosted trees build decision trees in a sequential manner, where each tree is built to correct the errors of the previous trees, improving the accuracy of the model.[54] This may explain the neglectable difference between the models.

However, it is safe to say, that it doesn't make much sense to refine a model by 0.6% when the uncertainty of the experiment is higher than that. Therefore, one can say, that the empirical equation, which is much simpler and more transparent to use is of higher practical relevance.

As a conclusion, one can say, that in some cases for material property prediction converting a linear regression model, into a group additivity model may just work as well as more complex algorithm. Even though a machine learning model may make a difference of 0.5-1%, in some scenarios, this is not significant as experimental data will usually exhibit higher uncertainty. This work can by no means cover every possible combination of parameter tuning, and modeling, but it may be an indication that in some cases, scientists can rely on much easier and more transparent methods to use. This also may suggest, the selected features are more important than the model itself.

This work provides the energetic community with a reparametrized version of the Joback method, which can be used alternatively to a time-consuming quantum calculation, or a machine learning model, which may not be reproducible if different scientists use different databases. Due to the small fragments described in the Joback method, looking mostly at individual atoms with the bonding almost every novel material can be described. Also, it shows that simple empirical approaches will work just as well as more complex machine learning algorithms, leading to the conclusion that machine learning scientists should maybe check more often if they can model their dataset with the corresponding choice of features using a simple linear regression.

The following part is partially reproduced from this year ICT Conference Proceeding by the author.[57] *Also, a DAAD Scholarship has been obtained to present the correlation at the 33rd International Ballistic Symposium.*

It would also be useful to have a model to correlate the detonation performance to simple small-scale tests, for example like the plate dent test. It doesn't make sense to refine detonation models until high-quality experimental datasets are available. Also, it is required for many software packages to enter TNT equivalents of new energetic materials, to compute their properties. The problem is that there are numerous tests out there which are used to assess the TNT equivalents experimentally. But if one is to compare these test it becomes clear, that they don't give homogenous results.[58] Recent studies however show, that they all measure different abilities of an explosive and each property like the heat of detonation or the volume of detonation gases influences the tests used for classifying the strength of an explosive differently.[3,59–61] Studies have been conducted to use the plate dent test as a measure for the TNT equivalents and deduce the detonation pressure from it.[62] Evidence of its usefulness to assess the detonation pressure is, that it correlates to the same parameters as the detonation pressure.[63] When looking at other measurement techniques for the detonation pressure, they deviate by 6% from each other.[64] Therefore it is of interest to use a technique that is easily reproduceable on a lab scale, doesn't require expensive equipment and can also be performed on smaller samples. The experimental setup is shown in Figure 17.

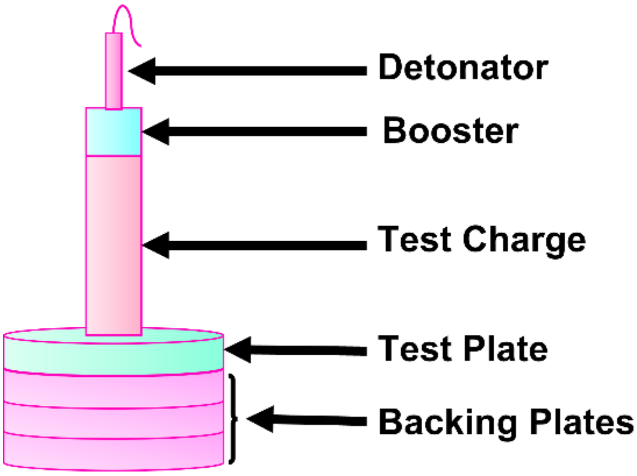


Figure 17. Experimental setup of the plate dent test.

For the test and backing plates various materials can be used to dent like Steel, Lead or even Beryllium.[62] This study will focus on the Steel data, as the other metals pose a greater health hazard, which makes them less attractive to integrate into a standardized characterization of energetic materials.

All calculations were performed using the thermochemical equilibrium code EXPLO5 (version 6.05.04).[8] As initial density the packing density from the plate dent experiments was chosen[62] and the enthalpies of formation from the EXPLO5 database were used.

Two correlations were obtained: one to predict the Chapman-Jouguet detonation pressure from the TNT-equivalents in a plate dent (**1**) and the other one to predict the TNT-equivalents in a plate dent test from the Chapman-Jouguet detonation pressure (**2**). To obtain the TNT-equivalents, one must divide the dent resulting from the compound of interest by the dent resulting from TNT.

p_{c-j} [kbar] = (-14.723) + (2.14488) * TNT eq. [%] **1**

TNT eq. [%] = (13.691) + (0.437923) * pc-j [kbar] **2**

A model with a Pearson coefficient of 0.97 and a R^2 of 0.94 was obtained. The data these equations were derived from are given in Table 4. which is graphically displayed in Figure 18.

Table 4. The packing density, dent depth[62], TNT equivalents and Chapman-Jouguet detonation pressure calculated in EXPLO5.

	Density	**Dent [in]**	**High-quality**	**p_{cj} [kbar] EXPLO5**
Nitromethan	1.133	0.163	62	131
TNT	1.633	0.265	100	180
Composition A (91/9-RDX/Wax)	1.631	0.322	122	266
29.7/649/5.4 HMX/NQ/Estane	1.712	0.291	110	253
90/10 - HMX/Estane	1.767	0.37	140	288
93.4/6.6 - HMX/Estane	1.8	0.384	149	324
Tetryl	1.681	0.319	121	235
Cyclotol (77/23 RDX/TNT)	1.754	0.369	140	292
Cyclotol (75.2/24.8 RDX/TNT)	1.2	0.121	80	142
60.8/39.2 - TNT/DNT	1.579	0.228	86	167
Composition B (64/36-RDX/Wax)	1.714	0.339	128	253
Tritonal (80.9/19.1 - TNT/Al)	1.73	0.241	91	175
Octol - 76.3/23.7 HMX/TNT	1.809	0.396	150	309
PETN	1.67	0.386	146	271
86.4/13.6 -HMX/Estane	1.738	0.345	131	267
85.6/9.2/5.2 - HMX/DATB/Estane	1.798	0.404	153	306

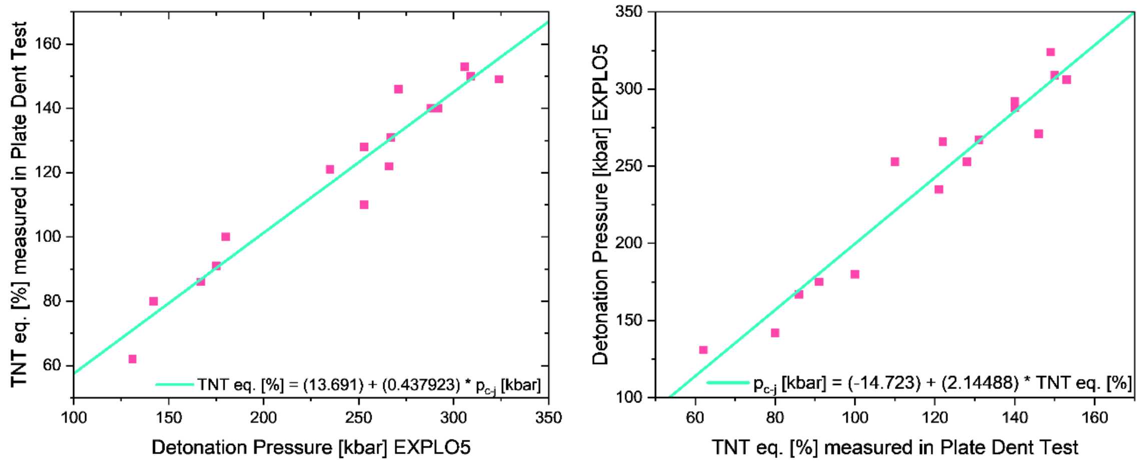


Figure 18. The TNT equivalents plotted against the Detonation pressure (left) and the detonation pressure plotted against the TNT equivalents (right).

It is apparent as proven already by Smith[62] that there is clearly a linear relationship between the plate dent test and the detonation pressure. However, not all energetic compositions agreed with this correlation as already proven by Smith and now also is shown in Table 5.

Table 5. Some outliers which are predicted to be much higher using the RoseDent-Equation than the thermo-equilibrium code EXPLO5.

	Density	**Dent [in]**	**TNT eq. [%]**	**p_{cj} [kbar] EXPLO5**	**p_{cj} [kbar] RoseDent**
23.3/73.0/3.7 - RDX/Pb/Exon	4.606	0.405	153	194	313
Baratol (76/24 - Barium Nitrat/TNT)	2.61	0.127	48	211	88

Both outliers contained metals in their composition, that lead to a non-ideal detonation. The BKW EOS is fit to ideal explosives, which is likely to be the reason why the predictions of the Chapman-Jouguet pressures show high errors for these mixtures.

Unlike with the other tests to asses TNT-equivalents[3,59,60] it becomes apparent that the packing density ultimately influences the result of the test, as it correlated to the power of two to the detonation pressure[4]. To achieve better reproducibility in such performance tests one should measure the densities the tests are performed at, as its significance is demonstrated in the experiments by Smith.[62] The results indeed show, that it would make sense to fit predictive models for the detonation pressure to plate dent test data. This becomes especially evident, when looking at currently employed detonation pressure predictions, that show high deviations from each other.[4,65] The results of this study are also an indicator, that the BKW EOS equations may not be the most powerful tool to predict non-ideal explosives, however they are a good indicator for ideal explosives.

The plate dent test could be established as a standardized test for characterizing new energetic materials, as it doesn’t require too large quantities of sample and is a great indicator for the performance of energetic materials that could even be performed in laboratories that are only equipped to handle energetic materials in smaller quantities. This is especially interesting for novel materials that introduce new molecular moieties into the world of energetic materials, as they usually are unstudied, scientist simply assume, that the models we validated and trained on a very different training set can be applied to these novel material classes.

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1.6 A brief comment on the lack of experimental values for detonation parameters and future work targeted towards overcoming this issue – *manuscript draft*

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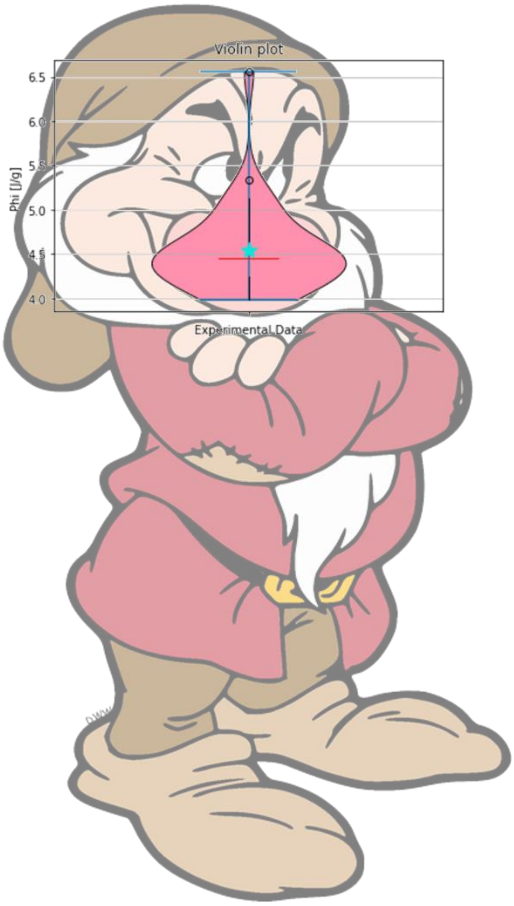
Sabrina Wahler: Data collection, Project Planning, Manuscript Preparation, acquisition of funding

William G. Proud: Supervision, Manuscript Revision

Thomas M. Klapötke: Project Supervision

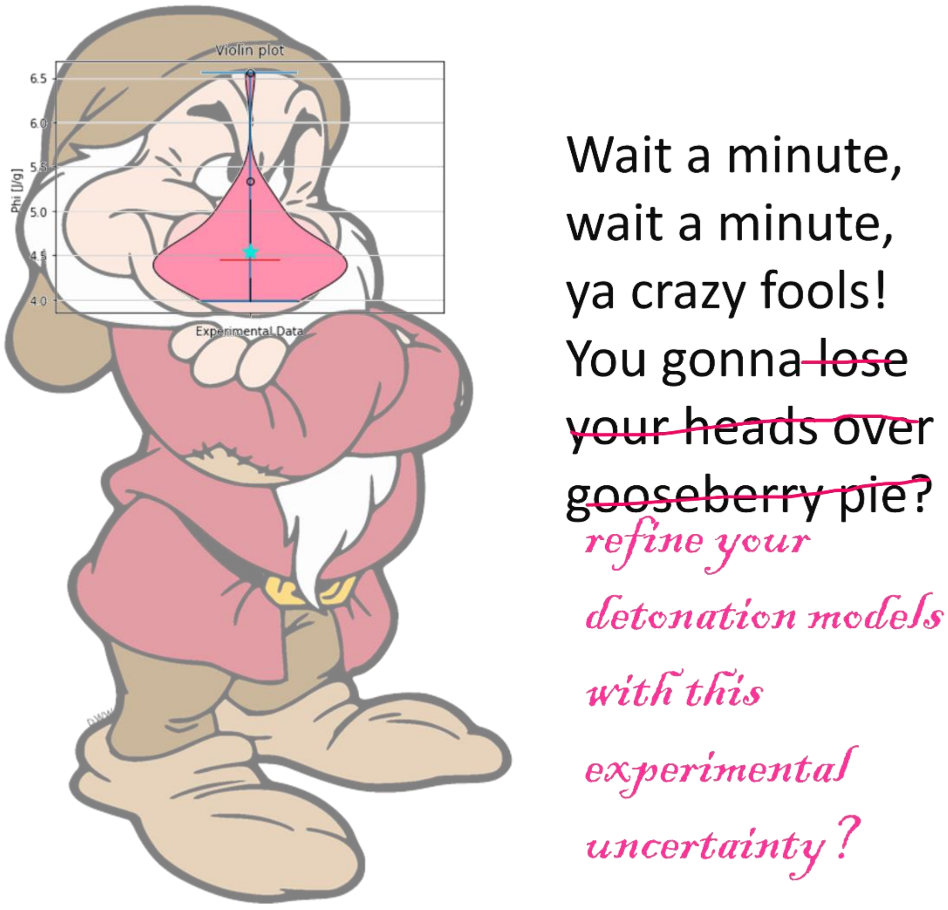


Wait a minute,
wait a minute,
ya crazy fools!
You gonna ~~lose your heads over gooseberry pie~~?
refine your detonation models with this experimental uncertainty?

Abstract

This mini-review provides a quick overview of different measurement techniques for detonation parameters and summarizes recent works in finding alternative methods by modelling tests with the simpler experimental setup. Additionally, the deviations of experimental measurements of detonation pressures have been analyzed.

Graphical Abstract



Review

When searching for performance values for energetic materials often there is a significant gap in the data reported from experimental measurement.[1,2] Such measurement is often technically complex, time-consuming and require large amounts of materials. The filling of experimental samples may require incremental pressing to avoid a wide density variation within the charge, some materials shrink after casting or can segregate.[3]

For showing the wide range of data reported in the literature, the in 1967 proposed equation by Kamlet and Jacobs, from which the C-J Point can be derived is used. It corresponds to the detonation pressure - can be calculated from the density of the explosive ρ_0 [g/cm^3], the numbers of moles of gas released (N), the mass of gas in grams released by the reaction (M) and the heat of explosion (Q) (Equations 1 and 2).[3,4]

$$p_{C\text{-}J}\ [\text{kbar}] = K\rho_0^2\Phi \tag{1}$$

$$K = 15.88$$

$$\Phi\ [\text{J/g}] = N(M)^{0.5}(Q)^{0.5} \tag{2}$$

For evaluation and comparison, we have derived the parameter Φ [J/g] from the detonation pressures reported at the density they were measured at. The data is given in Table 1 and graphically displayed in Figure 1.

Table 1. Experimental TNT detonation pressures [kbar] and the corresponding Φ [J/g].

TNT detonation pressures [kbar] and Density measured at	**Lit.**	**Φ [J/g]**
190 (@ 1.64 g/cm^3)	[5,6]	4.448519
187 (@ 1.61 g/cm^3)	[5]	4.542965
202 (@ 1.59 g/cm^3)	[6]	5.031606
190 (@ 1.63 g/cm^3)	[6]	4.503269
222 (@ 1.65 g/cm^3)	[6]	5.134931
189.1 ± 1 (@ 1.637 g/cm^3)	[7]	4.443689
202 (@ 1.59 g/cm^3, pressed)	[8]	5.031606
190 (@ 1.640 g/cm^3, pressed)	[8]	4.448519
189 × 103 atm. (@ 1.64 g/cm^3)	[8]	4.425105
178 (@ 1.64 g/cm^3)	[8]	4.167559
182 (@ 1.64 g/cm^3, @ 93 °C, liq.)	[8]	4.261213
62.2 (@ 0.95 g/cm^3)	[9]	4.340029
76.3 (@ 1.0 g/cm^3)	[9]	4.804786
179.0 (@ 1.59 g/cm^3)	[9]	4.4587
94 (@ 1.14 g/cm^3)	[9]	4.554783
123 (@ 1.30 g/cm^3)	[9]	4.58319
162 (@ 1.45 g/cm^3)	[9]	4.852086
177 (@ 1.63 g/cm^3)	[9]	4.195151
210 (@ 1.62 g/cm^3)	[9]	5.038935
225 (@ 1.63 g/cm^3)	[9]	5.332819
115 (@ 1.051 g/cm^3)	[9]	6.556045
40.5 (@ 0.8 g/cm^3)	[10]	3.984965
63.4 (@ 1.0 g/cm^3)	[10]	3.992443
71.8 (@ 1.061 g/cm^3)	[10]	4.016458
124.7 (@ 1.36 g/cm^3)	[10]	4.245591
144.6 (@ 1.45 g/cm^3)	[10]	4.330936
182.4 (@ 1.59 g/cm^3)	[10]	4.543391
197.1 (@ 1.64 g/cm^3)	[10]	4.614753
192 (@ 1.69 g/cm^3, cast TNT)	[8]	4.233283

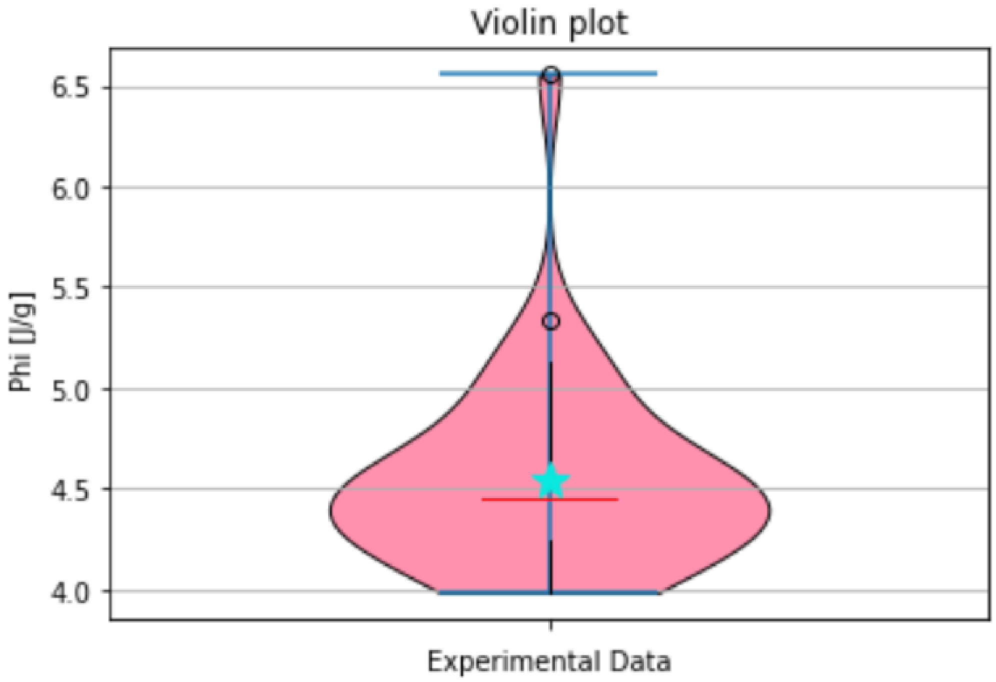


Figure 1. Violine Boxplot of the Φ [J/g] derived from the experimental detonation pressures. The Mercury Red line shows the median value and the copper turquoise star shows the mean value.

When looking at Figure 1, one can tell that there is high variance in the measurements for TNT, which is not desirable, as the results obtained for different explosives should be comparable. While a number of different techniques exist, based around conductivity, light intensity, interferometry[3,11] in this paper a number of optical techniques are discussed.

When dealing with novel materials, these are often produced in small quantities, a few grams. As such this sample size is often used for sensitivity studies and determining go/ no-go thresholds in for example, drop-weights.[3,12–14]

Performance parameters such as detonation velocity are generally reserved for materials available in larger quantity. Sometimes these can be adapted to involve only a few grams. e.g. the small scale gap test, which exists in several versions, has been used to assess detonation velocity.[15]

The measurement of detonation velocities is complicated, time-consuming and require large amounts of materials. The optical fiber technique can be used to determine the detonation velocity. The light signal emitted by the detonation front can then be recorded either by using a high-speed streak camera (as shown in Figure 4) or by converting it into an electric signal through photodiodes (as depicted in Figure 5). [3,13]

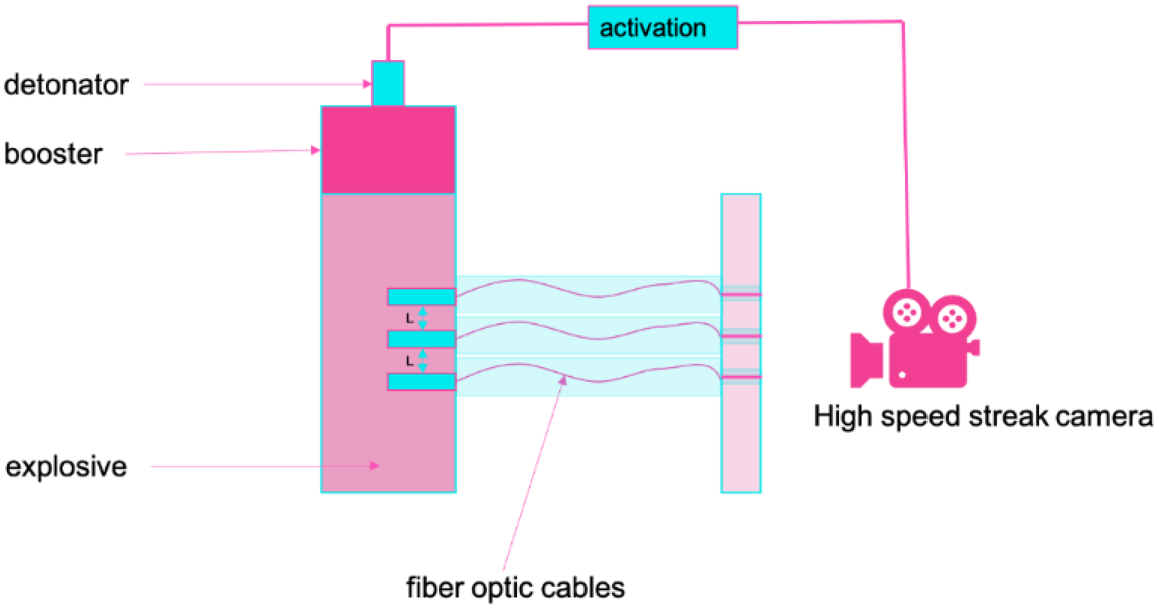


Figure 2. Setup of the measurement of the detonation velocity using a high-speed streak camera. [3,13]

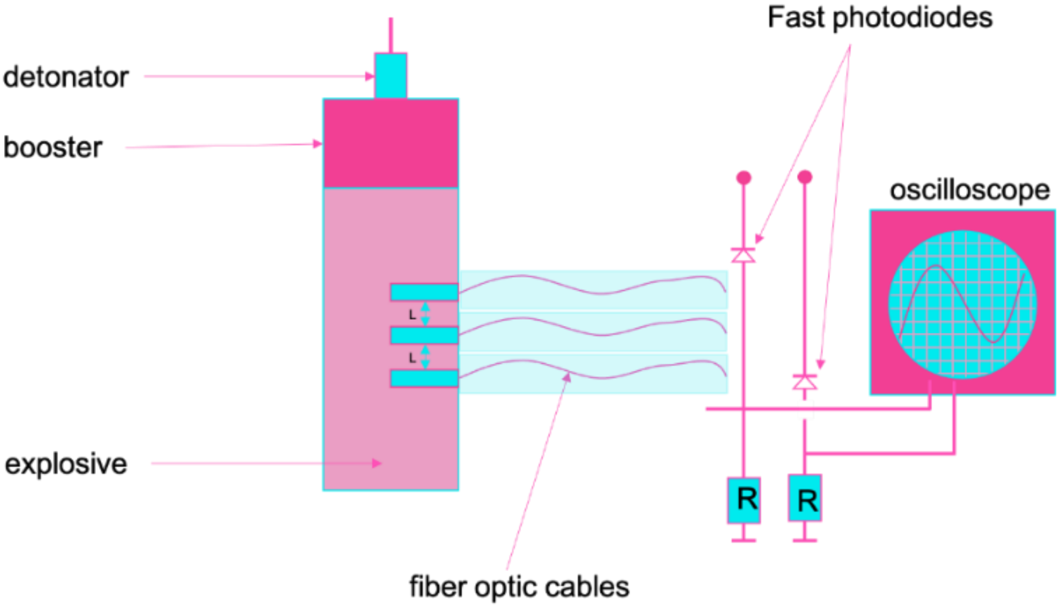


Figure 3. Setup of the measurement of the detonation velocity using an oscilloscope. [3,13]

The optic fibers are positioned apart at a fixed length L. From the time it takes the detonation front to travel between the electric fiber the velocity can be calculated. The measurement of the detonation velocity is a lot less complicated than the measurement of the detonation pressure due to which it is used more frequently. [3]

As already mentioned before, the measurement of the detonation pressure is a lot more complicated than the measurement of the detonation velocity.[1] Generally three methods employing photonic doppler velocimetry can be applied: The flyer plate method, the impedance window method and the detonation electric effect method (see **Fehler! Verweisquelle konnte nicht gefunden werden.**).[1]

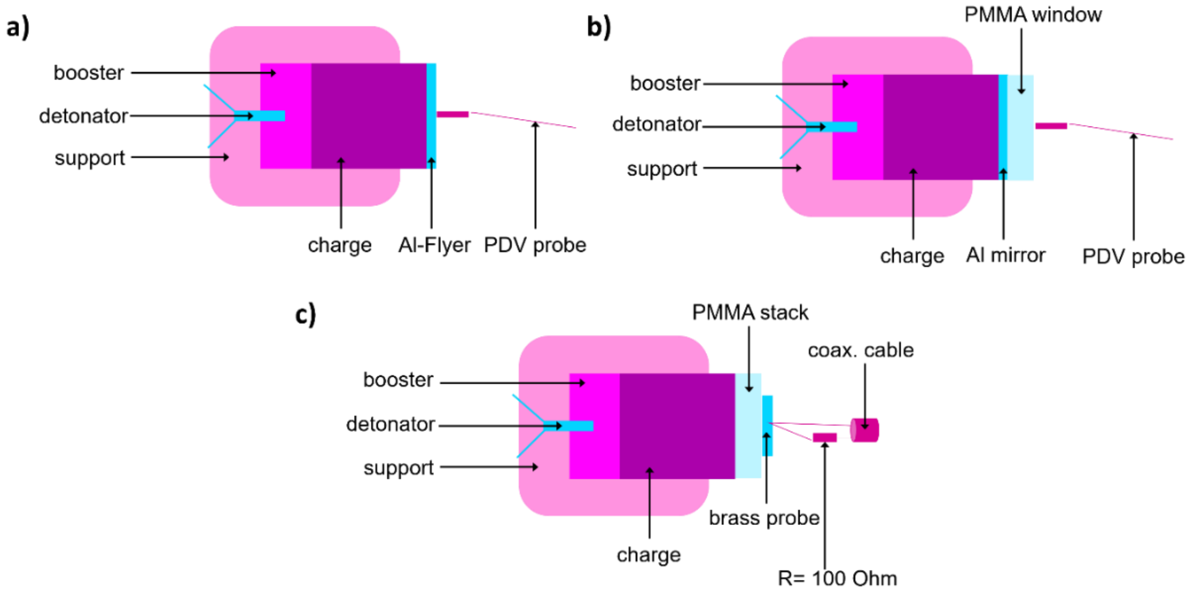


Figure 4. Schematic representation of the different measuring apparatus used for measuring the detonation pressure: a) The flyer plate method (FPM), b) the impedance window method (IWM) and c) the detonation electric effect method (DEM).[1,13]

The experimental setups of FPM (**Fehler! Verweisquelle konnte nicht gefunden werden.**a) and IMW (**Fehler! Verweisquelle konnte nicht gefunden werden.**b) are closely related. They consist of a detonator attached to a booster connected to a charge, which is held together by a support. In the FPM setup an aluminum flyer plate is placed in front of the charge, which gets burst into small pieces after the explosive is ignited.[1] The velocity of the aluminum plate is measured with a photonic doppler velocimetry probe (PDV probe).[1] For the IMW measurement a thin aluminum foil is glued on the charge with a PMMA window in-between the foil and the PDV probe. [1] The experimental setup of DEM (**Fehler! Verweisquelle konnte nicht gefunden werden.**c) is partially the same as the two other methods – part of it consists of a detonator attached to a booster connected to a charge.[1] But this part is then followed by a PMMA stack and a brass probe, which is connected to a resistance of 100 Ohm and a coax. cable.[1] FPM and IWM are supposed to give measurements within a 1% - range within the corresponding values calculated using a thermodynamic code, while DEM is almost 7% lower than the other two methods.[1] This however, cannot be generalized, because every calculation models will have outliers.

The test above requires large amounts of explosives, which often cannot be handled, if the material is too sensitive. Additionally, only very few novel compounds are upscaled to the needed quantity, as they don’t exhibit the desired properties. To overcome this issue, Gottfried developed a very promising method called LASEM (‘Laser-induced air shock from energetic materials“)[16] . The experimental is shown in Figure 3.[16]

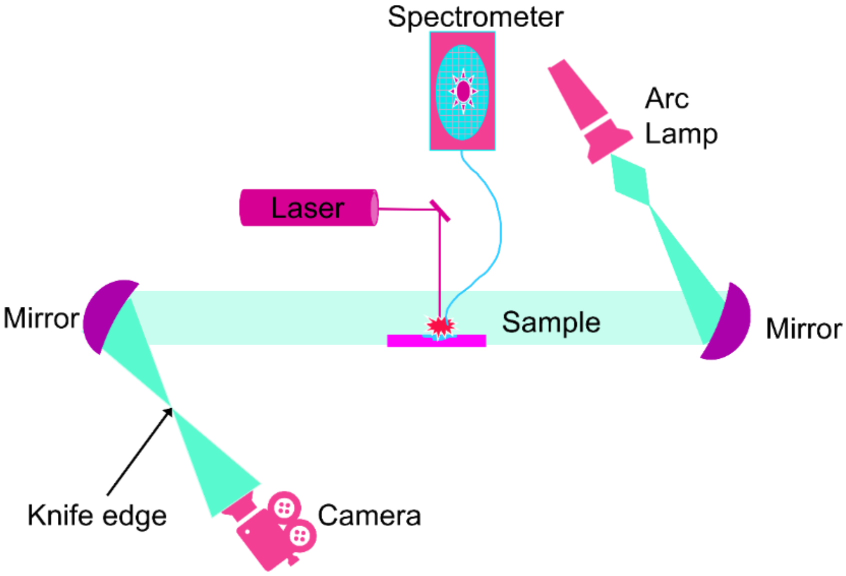


Figure 5. The setup of a LASEM experiment to measure detonation velocities on a lab scale. It consists of the sample, which is ignited by a laser. The shock-front propagation is then measured with a z-type schlieren setup.[16]

LASEM allows to determine the detonation velocities using small samples 10 - 20 mg on a lab scale.[2,17] These sample sizes, are most of the time safe to handle with appropriate protective clothing. This makes it a promising future technology to be used in every lab as a pre-screening tool before upscaling to the other velocity measurements.[16] Past work has been performed to compare the measured velocities using LASEM to calculated values.[18] Further comparison to the other methods described is given in Table 2.

Table 2. The advantages and disadvantages of each other of all the detonation velocity measurements explained before.

	High-speed camera	Optic Fibers	LASEM
Pro	Provides visual evidence: High-speed cameras capture a several of images of the detonation, giving visual proof of the events taking place. This supports the understanding of the process of the explosion. Non-contact measurement: High-speed cameras do not require to be in contact with the material to measure the detonation front, which makes it safer for researchers to perform measurements. High accuracy: High-speed cameras capture images at extremely high frame rates, which provides accurate measurements of the detonation.	Large field of view: Optic fibers can measure detonation velocity over a large distance and area, providing comprehensive data and increasing safety. Lower cost: Optic fibers are relatively inexpensive. Portable equipment: Optic fibers are relatively small, handy and portable, making them extremely convenient. Also, they are not as fragile as a camera.	No-contact needed: LASEM does not require any contact with the detonation material, after taping it down, because a LASEM is used to ignite the explosive, which makes it safe for researchers to perform measurements. Also, the sample sizes are very small, posing a lower threat to the experimenter.
Con	Limited camera angle: High-speed cameras have a limited angle, which may not capture all of the detonation. Expensive equipment: High-speed cameras are very expensive.	Lower accuracy: Optic fibers are less accurate than high-speed cameras when measuring detonation velocity. Contact measurement: Optic fibers need to be in contact with the detonation material, which pose a safety risk for researchers when inserting the fibers, especially if the substance is sensitive towards friction.	Requires specialized equipment: LASEM requires specialized equipment and expertise to operate. Expensive: LASEM is expensive compared to some other measurement methods.

Some other small scale testing methods include the the gap test[3,15] which is initiating the explosive by shock and its variations like the card gap test. Figure 1 illustrates the Pantex Modified NOL (Navy Ordnance Laboratory) card gap test.[19]

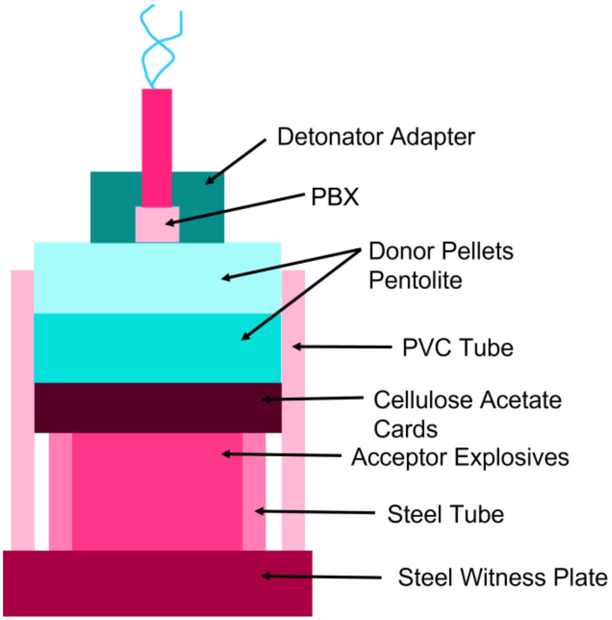


Figure 6. The experimental setup card gap test. [19]

Using the gap test, you can compare other explosives and see how far they are from a threshold, as well as compare the margin to other explosives. It cannot be used to predict the response of an explosive to shock in a different configuration since the data only pertain to the configuration of the test. In each configuration, the shock is not one-dimensional, it is not sustained, and it determines a threshold. Moreover, Explosive D was arbitrarily designated as the standard in the IHE gap test requirement.[19]

A very interesting variation of the gap test was developed by Plaksin for small-scall testing involving optical fiber measurements. The method used to observe the propagation of detonation waves (DW) in PBX mini and p-samples involved a polymeric ribbon with 64 optic fibers, each with a diameter of 250±lpm, connected to a fast electronic streak camera for detecting light. Several variations of multi-fiber optical probes (MFOP) were developed to detect light from shock or detonation fronts. Furthermore, a micro gap test called the p-gap test was created to study the ignition phase of DW formation in coarse energetic crystals surrounded by a binder, as a function of crystal size and binder. The experiment used four PBX p-samples, each containing pairs of coarse crystals ranging in size from 540 to 740 pm, surrounded by 52.3% fine HMX crystals with either inert HTPB or energetic GAP binder. The experiment tested four different PBX samples based on HMX with either energetic (GAP) or inert (HTPB) binder.[20,21]

Many other small-scale testing option are available. Such as exploding foil detonators,[22] and laser driven flyer plates, consisting of impactor with laser drive producing short duration shock [23,24].

It is clear that there is a need for simpler tests to determine these values, ones that have already been extensively performed in laboratories and are readily available. It is important to investigate which physical values these tests may correlate to and evaluate their feasibility for characterizing new materials in terms of required sample size, accuracy, and reproducibility. Hence, it is essential to explore the correlation between tests like the the Könen-test[25], Trauzl-test[26–29], ballistic mortar test[13], SSRT-Test[14], plate-dent test[32–34] and thermodynamic values that result in mechanical deformation or movement. It is important that these values can be measured easily without the need for any specialized equipment. Although some of these tests are primarily used to evaluate the safety of energetic materials or TNT equivalents, they also correspond to some of the desired thermodynamic values..[28,35] Out of these tests the plate-dent test seems promising for assessing the Chapman-Jougett Detonation pressure. The Trauzl-test and Ballistic Mortar seem to be to imprecise to draw a concrete conclusion[26,30] and the SSRT-Test linearly correlates with the heat of detonation.[31] Moving forward, the authors seek to explore additional tests to discover one that requires minimal sample size, is highly reproducible, and doesn't necessitate specialized equipment. This would make it feasible to conduct the test in any laboratory. While the precision may not be as exact as more complex measurement techniques, it can still offer an estimate of performance that may be more accurate than calculating performance using thermo-equilibrium codes. This is exemplified by the outliers in Smith's plate-dent test series.[33]

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Conflict of interest

The authors have no conflicts to declare.

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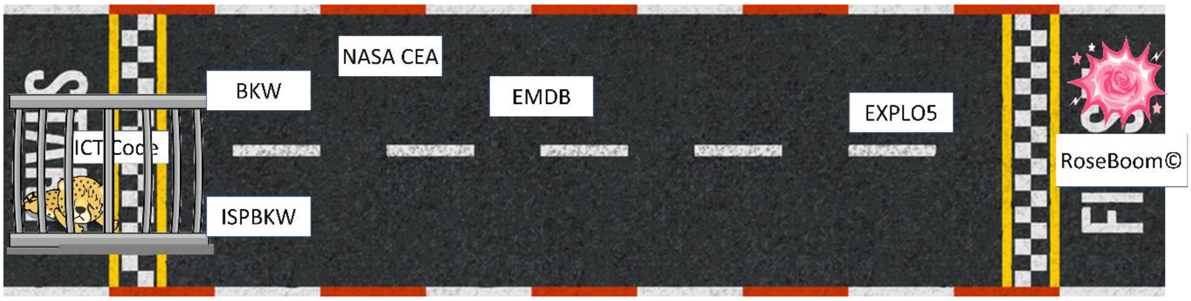
1.7 A brief tabular mini-review on the user-friendliness and sustainability of software solutions for energetic materials unrestrictedly available – *manuscript draft*

Author contributions

Sabrina Wahler: Data collection, Project Planning, Manuscript Preparation, acquisition of funding

William G. Proud: Supervision, Manuscript Revision

Thomas M. Klapötke: Project Supervision



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Abstract

In this paper, different software solutions for energetic materials, which are unclassified are competing in 8 categories against each other and ranked according to the points they received.

Introduction

When developing new energetic materials, it is of interest to predict their performance before synthesis, so that only compounds with the potential of replacing current benchmark molecules are synthesized. By pre-screening the profusion of chemicals and waste production is reduced and no time is wasted when synthesizing compound which don't exhibit the desired properties. Also it is of interest to agree on one software as an international standard for performance prediction including the enthalpy of formation of energetic materials for publishing novel compounds, because different models and programs give different results.[1,2] Aside from that the energetic community should agree on a standardized or normed performance prediction including the enthalpy of formation, because different models and programs give different results, which often makes it impossible to compare the published values for novel energetic materials.[1,2] Another thing to keep in mind when agreeing on a new standard in the community, is the sustainability of the product. Aside from that, scientific software should not be limited to the "old-school" programming, it should use modern cheminformatics to its fullest. Generally, the method that are most applied to predict the performance of energetic Materials are Thermo-equilibrium codes,[3] Empirical Modelling[4–6] and Machine Learning.[7] It is important to note that the later one has gained popularity in property prediction of energetic materials in recent years.[8,9] All of these methods have their up and downsides. Some of them are listed in Table 1:

Table 1 Tabular overview of the problems associated with different modelling approaches.

	Empirical Models	Machine Learning	Thermo-equilibrium codes
Pros	- It is possible to fit these on very small datasets (10-20 Datapoints[10–13]) - Transparent	- Precise predictions possible, requiring less computational power than a composite method	- Can give accurate predictions
Cons	- May be less accurate depending on the model and property.[2]	- Large Datasets are needed (if limited data is available, this will mean the quality of the data will suffer under this.) - Require a density and heat of formation. - In transparent - Statistical Modelling, which means each time training the model a slightly different result will be received	- In transparent solving of the chapman-jougett conditions. - Big library of detonation products needed.

Empirical Models are great to use, as they only require a pen and a paper to be applied. Embedded into a computer program which allows automation, they become a even more powerful tool to screen a large number of molecules using minimal computational power.[1,2,14] The accuracy may be lower in some case, however they are great for pre-screening a large number of compounds. Machine learning methods will give very accurate predictions but may take a slight bit more computation time to give a result. There is another big downside to this, when it comes to data collection for machine learning models: they require large datasets. This is not always available for energetic materials, as many tests require large quantities of explosives.[15], which often cannot be handled. Also, there are other values where only a limited amount of data is available. This means on the other hand side, that to one must find a balance between the quality of the data and the lack of data available, so that it does not impact the quality of the model to drastically.

There are several comparisons between different detonation codes and different models available in the literature[3,14] All of these focus on their accuracy, which from a scientific point of view is the most important. However, to some extend all these published and used model and works have been validated, therefore will ask a different question in this work: How easy is it to use and how long-lived is the software in terms of maintenance? The different computer programs will be compared by competing in 8 different categories.

Scoring categories

To objectively rate the selected computer programs, 8 categories were carefully selected. The first one is, if complicated and time-consuming manual input is required as this hinders screening of large amounts of compounds. The next issue faced with many computer programs to predict the performance of energetic materials, is that they will require external information as the enthalpy of formation or density. Depending on the source of these values, the accuracy of the predicted performance can be affected. The next category is the question if the software is accessible to all nations that are at least member in the NATO. When predicting values, it is of interest to predict any unknown value using multiple methods, because if all the predictions stay withing the same range, it is safer to assume that the values are close to them. The next category is the number of updates released each year. Every software should be regularly updated and adjusted to novel compound classes. It is also important to adjust everything to current cutting-edge modelling techniques. To deploy regular updates of the software and constantly improve it, active funding is required. The last category the number of modelling techniques the software uses are compared to each other. Only the winning program was given a point, which contains the most modelling approaches. The result of the comparison is shown in Table 2.

Table 2. Software solutions to predict the performance of energetic materials.

	EXPLO5[16]	**EMDB**[17]	**BKW by Mader**[18]	**ICT Code**	**NASA CEA**	**ISPBKW by Mader**[18]	**RoseBoom©**
Complicated manual input required	Yes	Yes	Yes	Yes	Yes	Yes (But not anymore with the RoseAPI coupling it to RoseBoom©)	No
External information required (experiment or composite method)	Yes	No	Yes	Yes	Yes	Yes	No
Available to all NATO Nations	Yes	No	Yes	No	Only after application process	Yes	Yes
Code still Maintained	Yes	Yes	No	Yes	Yes(?)	No	Yes
Multiple models used for one parameter	Multiple BKW codes	Yes, but for different materials	No	No	No	No	Yes
Multiple updates per year released	No (~1 update per year)	No	No	No	No	No	Yes (3 major in 2022)
Actively funded by an agency in 2023	Supported by OZM	(?)	No	Enough to maintain	(?)	No	Yes
Scientific basis	Thermo-equilibrium	Empirical models	Thermo-equilibrium	Thermo-equilibrium	Thermo-equilibrium	Thermo-equilibrium	Empirical Models, Machine Learning and Thermo-equilibrium (ISPBKW by Mader)
Scoring	5/8	2,5/8	0/8	2/8	2/8	0/8	**8/8**

Starting with the only code which is only based on empirical models: EMDB1.0. It is unfortunately not available anymore due to export control from Iran. It contained a wide variety of empirical equations developed by Keshavarz[4], allowing to predict the properties of energetic materials only based on the structural formula of a molecule, which made it a very interesting software to use. However, one downside, was that there was a lot of complicated manual input required.

To use the ICT code a special permission must be obtained, which makes it rather difficult to require. While it will provide accurate predictions,[19] it is not very user-friendly and doesn't allow high throughput of many compounds. It is not further improved now, but enough funding is put into it to keep it running under newer operating systems. Also, it requires a heat of formation and density, that need to be obtained from other sources.

When using the BKW code, it happens for some novel materials classes as used in the validation set of RoseBoom©[2], that the code crashes and won't stop writing to the output file. This is a massive inconvenience because it requires the user to stop the code using task-manager. The lack of comments to the code don't allow easy debugging. Therefore, it might be easier to simply rewrite the code based on Mader's publications. Both the ISPBKW and BKW Code are executable files, which require to change the information in a text-file as input. This is very time consuming and prone to mistakes.

Mader's ISPBKW code, which is a thermo-equilibrium code to predict the specific impulse, does not crash like the BKW Code, but isn't able to give a specific impulse for ever compound. This scored 0 points in all categories, however it is known to give accurate predictions[20], which made it a promising code to couple to RoseBoom©, providing the maximum user-friendliness.

RoseBoom© scored the highest, achieving a point in every category. It is efficiently designed so that only the sketch of a compound is enough as an input. The software includes density and heat of formation predictions using empirical methods and machine learning, which then allows to feed these into the performance prediction for energetic materials. It combines all three modelling approaches, by embedding numerous empirical models which were extensively revalidated,[2,21] machine learning models and additionally coupling it to the ISPBKW code. This makes it the ideal software because it is a collection of all different methods. In terms of user-friendliness and efficiency it is also clearly the best – it is the only commercially available software for energetic materials extracting all necessary information from a sketch of the compound or allowing to run numerous molecules in a row automatically. Also, it is the first and only commercially available software for energetic materials combining all modelling approaches into one computer program.

Conclusion

As a conclusion, one can say that all the presented programs have their up and downsides. The development of each individual program, contributed to the scientific knowledge, we have today and could be considered as miles stones in the history of performance prediction, along with many others which did not make it into the scope of this review.[3, 5,22] It is important to not forget, that developing new models and improving current ones should not be neglected. Also, the validation of each model embedded into a program is a crucial step in the process. Another thing to keep in mind, is, that reparameterization or improvement of traditional models used in predicting performance, enthalpy of formation and density only makes sense, if it is significantly improved, so that the correction applied does not move within the error of experimental uncertainty. When designing new software, it is important, to make the models available in a format, that gives the user a pleasant experience and is designed for maximum efficiency, but first and foremost, the quality of the models should be thoroughly assessed. Overall, RoseBoom© seems like a promising program to be established as an international standard, it offers a wide variety of methods which were thoroughly tested. It is well maintained and constantly expanding the parameters it can predict.

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Conflict of interest

Sabrina Wahler has a financial interest in RoseBoom©.

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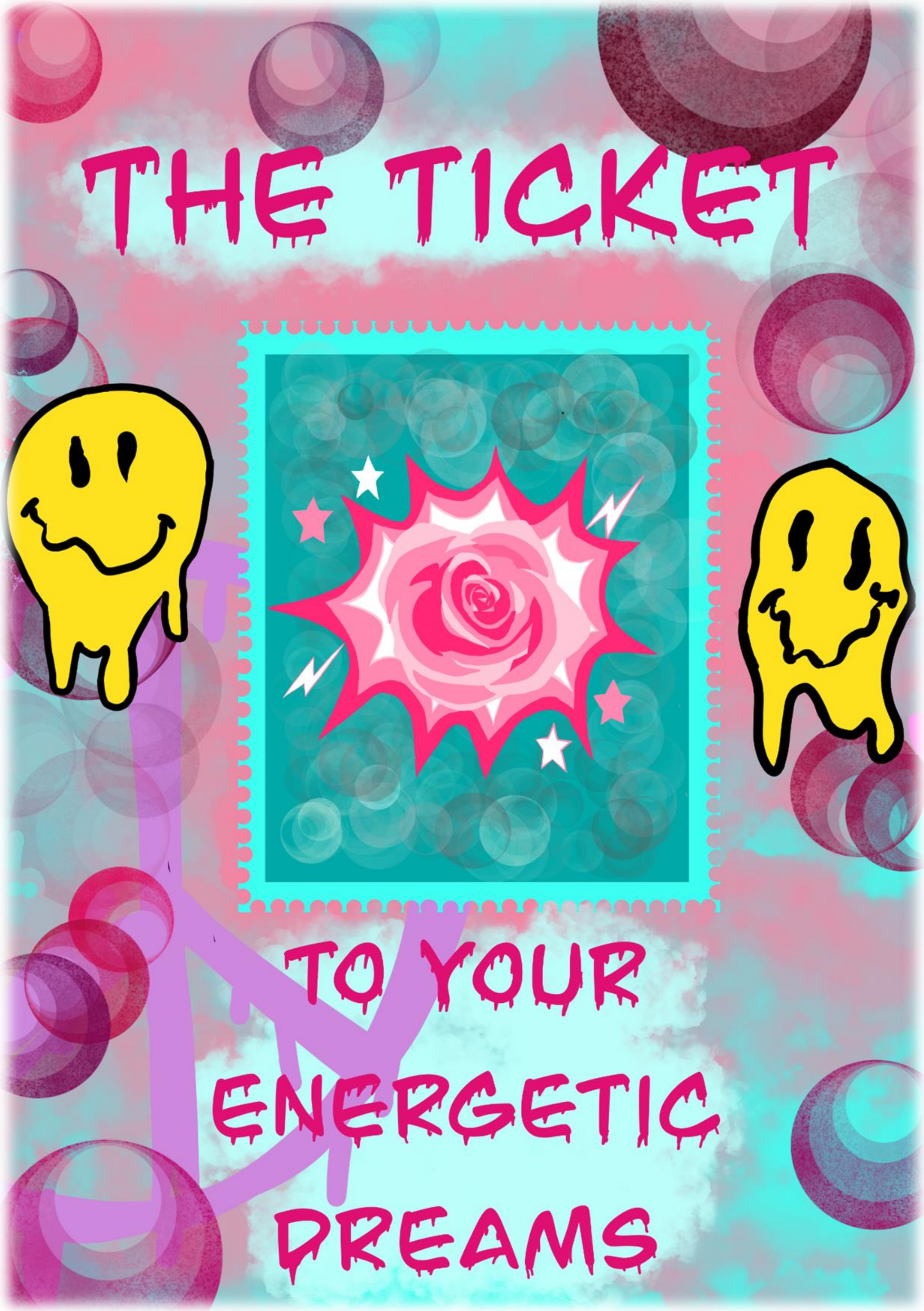
2 RoseBoom©

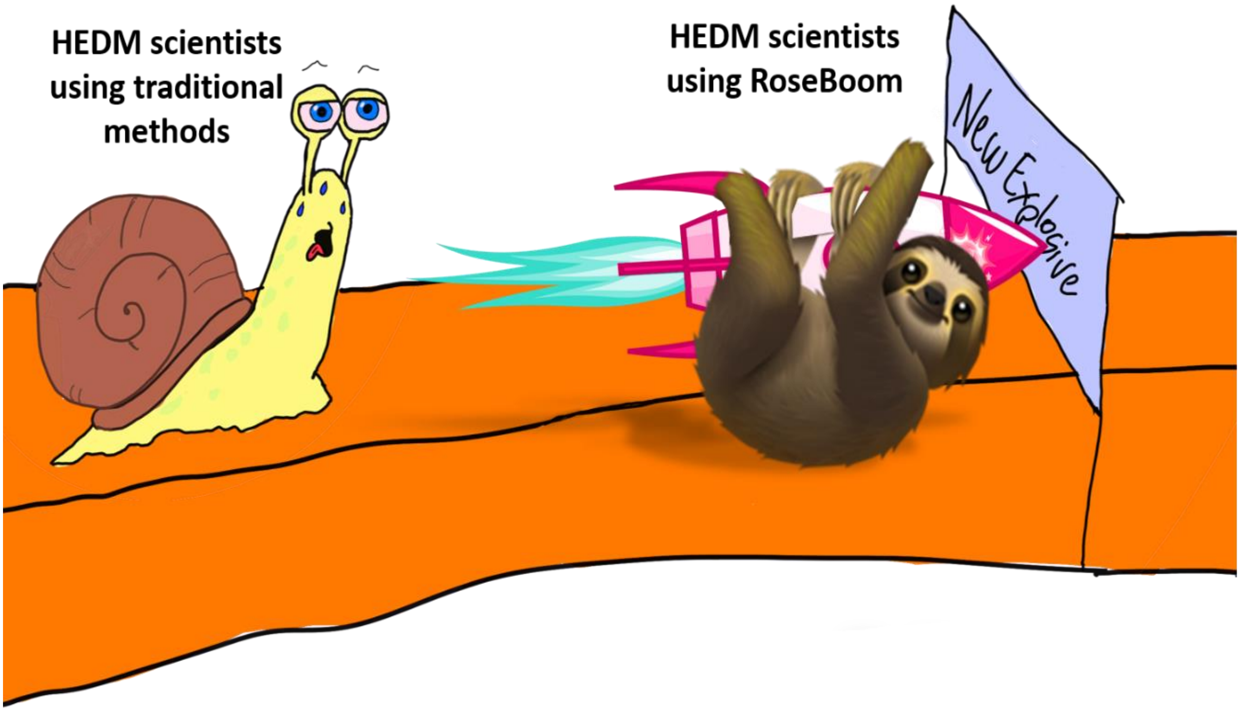


2.1 Research output software for energetic materials based on observational modelling 2.1 (RoseBoom2.1©) - published

Author contributions

Sabrina Wahler: Development of RoseBoom©, Data collection, Manuscript Preparation

Thomas M. Klapötke: Project Supervision



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Research output software for energetic materials based on observational modelling 2.1 (RoseBoom2.1©)†

Sabrina Wahler[ab] and Thomas M. Klapötke*[a]

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There is huge scope for the implementation of sustainable methods in the research of new energetic materials and there are a number of ways this can be achieved. With the development of the program "Research output software for energetic materials based on observational modelling"(RoseBoom©), it is hoped that the development of new modern energetic materials will be advanced, since it aims to provide access to quick and easy prediction methods which will indicate performance parameters (*e.g.* the detonation velocity and pressure, the key indicator for the power of an explosive) – before they have been synthesized.

Introduction

Modern green chemistry should not only focus on aspects like atom economy,[1] but also to eliminate failed synthesis attempts. Not only would it decrease the waste production and the profusion of chemicals, but it would also save a lot of time, meaning that the progress humanity makes in a certain research field is speeded up. The synthesis of energetic materials is associated with considerable risks – especially when synthesizing a new explosive with unknown sensitivity and strength. Therefore, decreasing the amount of practical work in this field would also increase the safety. To achieve this, a computer program would be employed. There are many computer codes already available such as EXPLO5[2] or Cheetah 9.0,[3] however, they both require an accurate density and heat of formation for the explosive as the input in order to calculate the detonation velocity and detonation pressure. Or they need the user to supply a lot of information about the molecule manually like Energy[4] and EMDB.[5] Therefore, it is of great interest to find other methods for calculating the detonation velocity, detonation pressure and other related values which are more time-efficient and don't require knowledge of the density or necessitate calculation of the heat of formation for an unknown compound, which can be time-consuming to calculate, or needs to be determined experimentally. Another problem that occurs when determining many properties using experimental methods is that many of the tests require larger amounts of the explosive, which are often not available.[6] For this reason, theoretical calculations of explosives provide not only safer working conditions for the research scientists, but can also provide information about a compound that has not or cannot be obtained experimentally.[6]

The computer program developed in this thesis, has the advantage of requiring only information that can be obtained from drawing the structure of the compound on a piece of paper and doesn't require for some of the methods included the density or heat of formation that both the EXPLO5 and Cheetah programs require (Table 1).

Developing a computer program that would provide accurate predictions about the performance of an energetic materials, based only on the structural formula would already add a new aspect to the research on energetic materials. Such a predictive tool could function as an intersection between machine learning, artificial intelligence, data science tools, and synthetic work. As a proof of concept, first big steps towards this future goal have already been made in this work namely, testing the selected empirical relationships in combinations with cheminformatic tools, as well as linking the program to an optical structure recognition software.[7] However, before these high-tech routes can be used to optimum capability, a foundation needs to be built, which can process the generated information from currently available informatic tools. A visual representation of the gap RoseBoom© fills and the gravel in the gearbox it removes is shown in Fig. 1.

Currently, the energetic-materials community is trying to find a replacement for commonly used explosives which exhibit high toxicities such as RDX, HMX and TNT.[6] Furthermore, to commercialize promising environmentally friendly alternatives, inexpensive starting materials must be used, which are then converted to the desired product, in high yields.[6] This is why modern research on energetic materials goes hand in hand

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† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d2ma00502f**

Table 1 Summary of the advantages and disadvantages of the different approaches for calculation of the detonation velocity and detonation pressure of secondary explosives

Method	EXPLO5	Cheetah 9.0	RoseBoom2.1©
Pros	Accurate results Results known for a large number of compounds for comparison	Accurate results Results known for a large number of compounds for comparison	Fast Requires only a sketch of the structure of the compound
Cons	Heat of formation must be calculated using composite methods which requires computer cluster or determined experimentally	Only available in the US Heat of formation must be calculated using composite methods or determined experimentally	Results may be less accurate

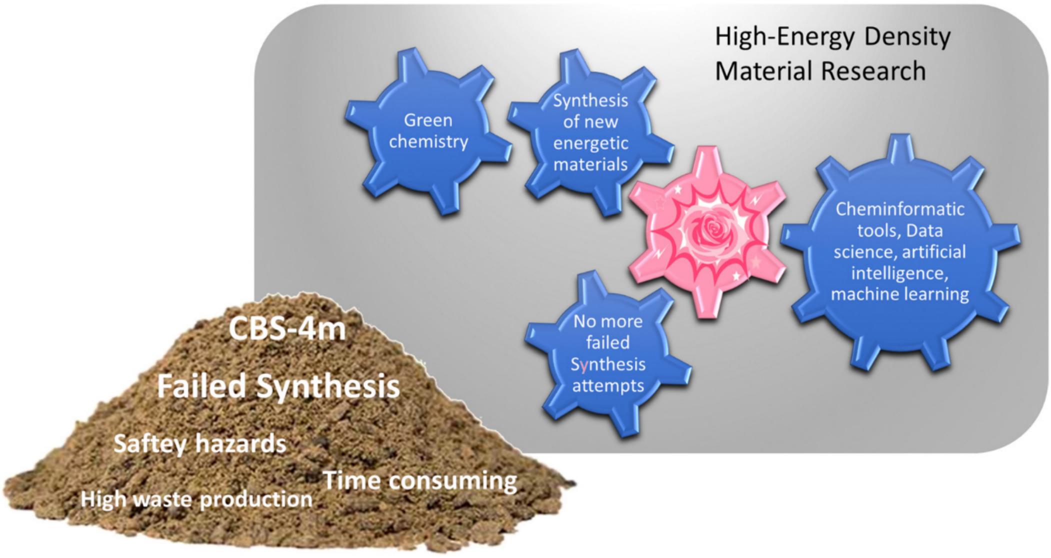


Fig. 1 The position RoseBoom© is supposed to take in the future is represented by the cogs on the left. RoseBoom© should connect the synthesis of new energetic materials, green chemistry, the different computer science disciplines and the elimination of failed synthesis attempts. By this, many problems, shown by the pile of gravel on the left will be solved. By adding RoseBoom© to the high-energy density materials research field, shown as the gigantic machine, it will run smoothly without needing to twist every cog separately.

with green chemistry (Fig. 1). However, so far it has not been possible to combine these goals with the one dream every synthetic chemist has, that is to obtain a compound with the desired properties in every synthesis that is attempted. The most promising method to reducing waste and emission in research in the future, is to incorporate theoretical methods like cheminformatic methods, artificial intelligence, data science and machine learning. Currently, there is a gear missing in the big machine of high-energy density materials research, which is the pink cog (Fig. 1). RoseBoom© aims to connect all of these disciplines and clean out all of the gravel in the gearbox that is currently taking its place. The goal for this work is to build the first prototype of this cog, connecting the different aspects and disciplines of high-energy density materials research, allowing the machine to run smoothly.

The program

RoseBoom2.1© can be used to quickly predict the detonation parameters of CHNO compounds based on their structural formula. Currently, it is intended to be used as a tool to support the development of new energetic materials, by allowing quick scanning of a long list of compounds to evaluate which ones are worth of pursuing further. It is based on different empirical models. In order to provide a general overview of which methods are efficient and could potentially replace thermodynamic codes, a general overview of empirical methods to predict the detonation velocity, detonation pressure, heat of formation and density tested in this work is given in Fig. 2.

Generally, there are three different variables which the selected methods were based on, that were used in this work: heat of formation, density and relative composition/structural formula (or the molecular moieties present in the molecules). In order to obtain insight into how important the density and heat of formation for the prediction of the detonation velocity is, two methods based on the two values were selected, namely, the Stine as well as Kamlet and Jacobs methods. The Keshavarz model for the detonation velocity and pressure was also selected, which is based on the density and the structural formula. This was used in order to provide insight into how important the heat of formation is with respect to prediction of the detonation parameters. The Rothstein and Petersen

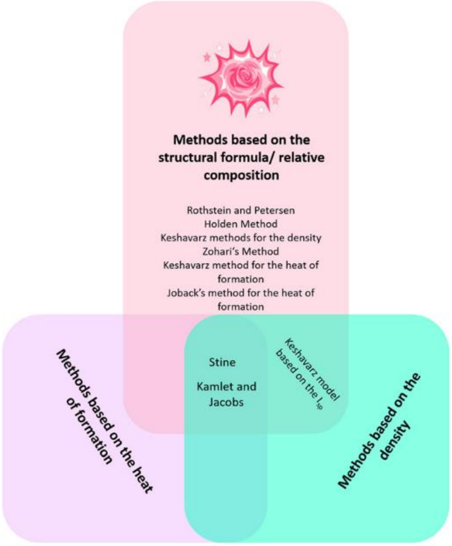


Fig. 2 A schematic overview of the empirical relationships evaluated in this thesis and their scientific basis.

method was selected to get an insight in to the accuracy of the predicted detonation parameters if the empirical relationship is solely based on the structural formula. Lastly, four different methods based on the sum formula and structural formula to predict the density were evaluated: Keshavarz model for ionic compounds, his method for molecules containing nitro groups, Zohari's model for azides and the Holden method. An approach by Keshavarz to predict the heat of formation based on the structural formula was also tested and the Joback model.

A schematic overview of the route with RoseBoom2.1©, is shown in Fig. 3.

After encoding all of the empirical relationships into the new computer program RoseBoom2.1©, the goals of this work were set even higher, and it was decided that the aim should be to be able to calculate the different parameters in 30 seconds with only the structural formula. By achieving this goal, the computational development of new energetic materials could be up to 86 000 times faster – depending on the size of the energetic molecule under consideration. For a comparison: The circumference of the earth is about 40 000 km. If one were to surround it with a constant speed of 100 km h^{-1}, it would take about 16.6 days. If it was possible to go 86 000 times faster, hence 8.6 mio km h^{-1} it would only take 16.7 seconds to be back to the starting point.

As a background color for the interface, Baker–Miller–pink was chosen. In psychology experiments it has been proven to reduce aggressive behavior,[8] which is very common in scientists' reactions to computer programs which don't work properly, mostly due to wrong installation or wrong use. Even if RoseBoom© runs very smoothly in windows, meaning it shouldn't cause any aggression, some other problems may occur when using a computer program leading to aggressive behavior, which can be reduced by a careful choice of the background color. Reduced aggression may also increase attention span and concentration, because it is easier to focus when experiencing lower stress and aggression levels. However, no effects on the concentration of Baker-Miller-Pink have been reported in experiments.[9] But, since it has been proven that pink results in less emotional responses than other colors,[10]

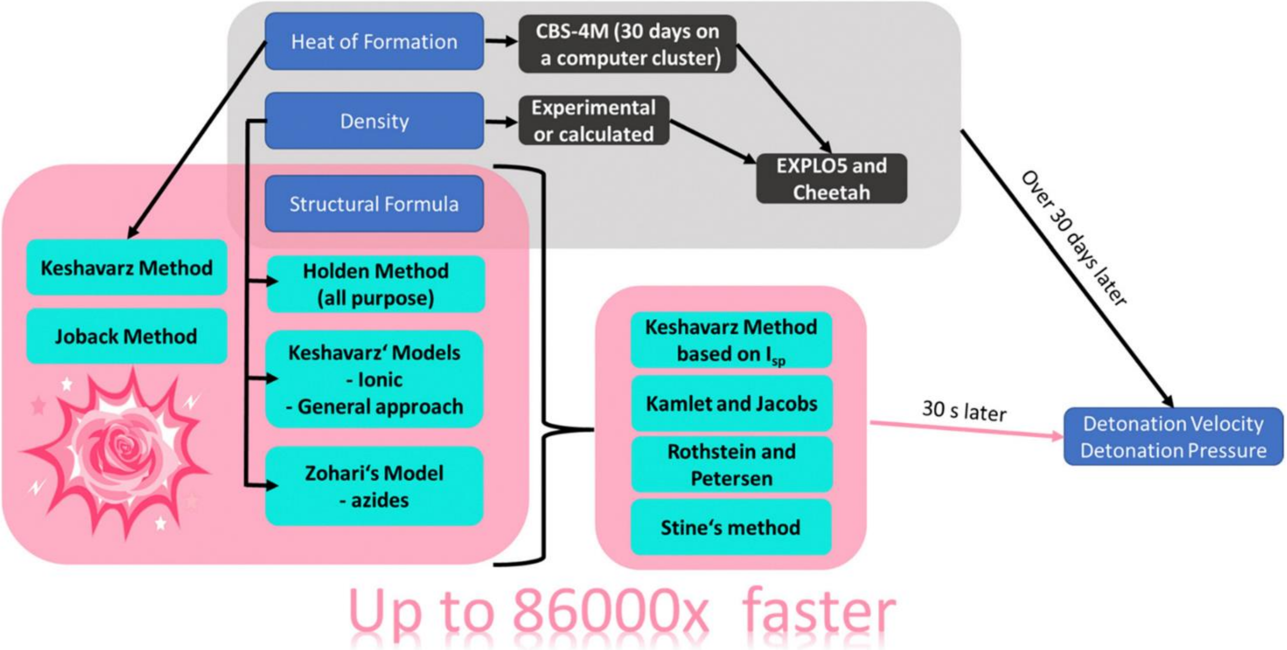


Fig. 3 Schematic overview of the methods which are currently commonly used (grey) to predict the detonation parameters, as well as the approaches take in this work (pink), along with durations required for the two different methods.

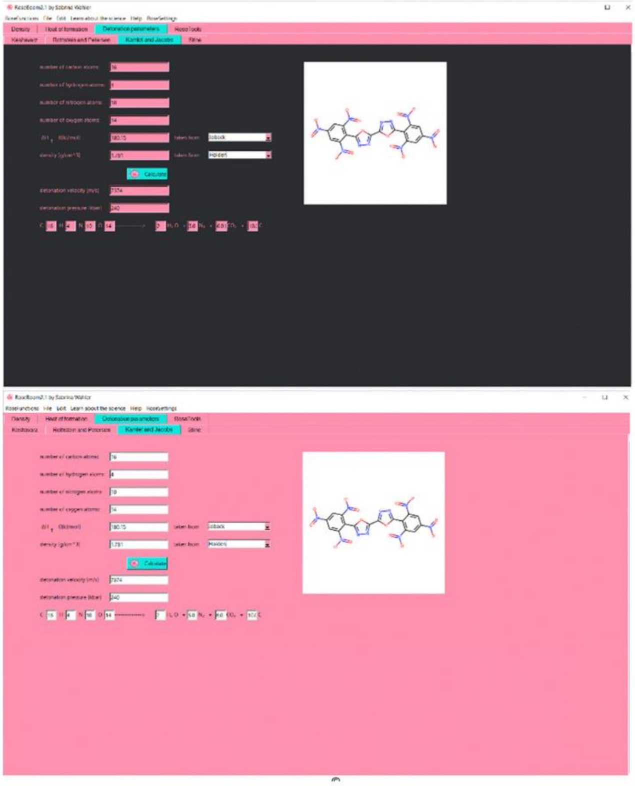


Fig. 4 User interface of RoseBoom2.1© in the TKX-61 Mode (Top) and the RoseMode© (Bottom).

pink programs in science may lead to more objective results. The interface of RoseBoom2.1© is shown in Fig. 4.

A lot of user friendliness in RoseBoom2.1© is provided by the Sloth-function, which allows the user to enter his molecule as a SMILES (Simplified Molecular Input Line Entry Specification), which will fill out all the entry boxes. This reduces man-made mistakes and saves a lot of time. It is also possible to upload a picture of a molecule into RoseBoom2.1© or take a photo with your webcam, with the RoseCam© function, which will then be converted in to SMILES. Another useful RoseFunction© is RoseDanger©, with which the user can take a picture of any chemical bottle, and the corresponding safety data is automatically opened.

Materials and methods

There are many empirical models for predicting the density, heat of formation, detonation pressure and detonation velocity published in the literature. All of them have been trained on compound sets, which naturally could only include molecules which were known at the time the model was established. Hence, the Rothstein and Petersen (published in 1978) or Holden (1970's or even earlier)[4] approaches were not trained on modern explosives such as TKX-50 or TKX-55. Modern energetic compounds utilize different functional groups and structural approaches to those used 60 years ago, and often utilize the concept of nitrogen-rich compounds which was not the case in the past (Fig. 5). Therefore, it is important to test these models on a wide variety of compounds including "modern" explosive compounds, for example LLM-105 or TEX, and not just presume that they are applicable to such modern explosives because they were suitable for long-known explosive compounds such as TNT, TATB *etc.* which typically contain a carbon backbone which acts as a fuel with and nitro groups which act as an oxidizer. A general overview of the evolution of explosives is displayed in Fig. 5 along with the chronological

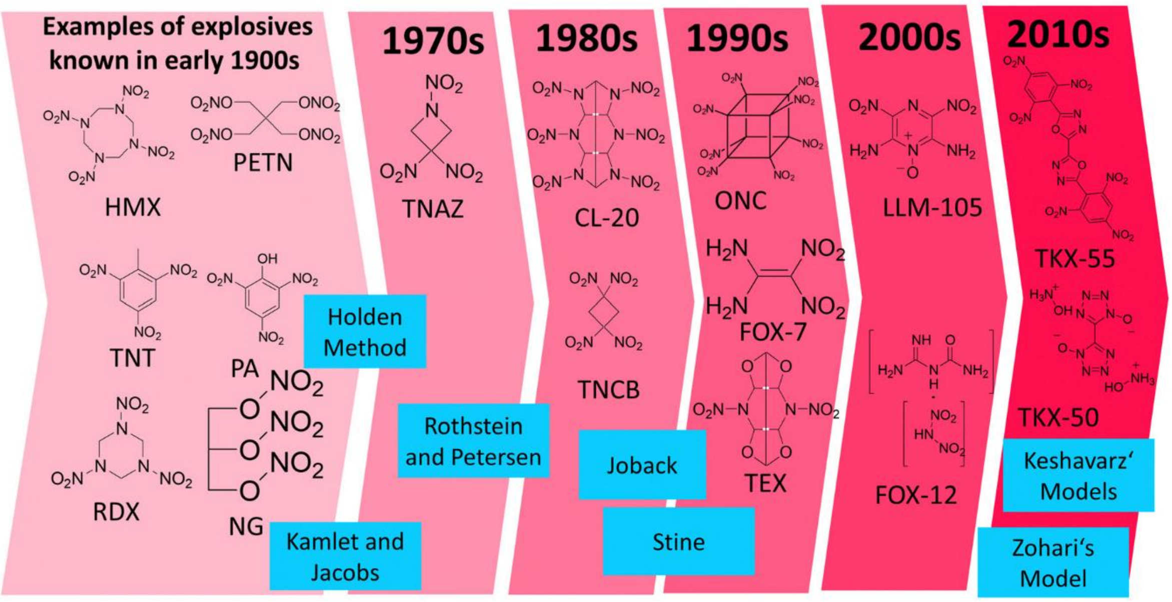
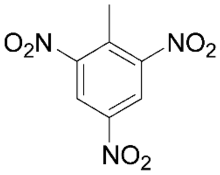
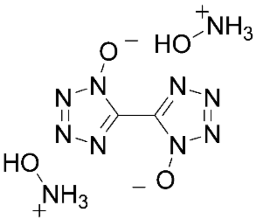


Fig. 5 The evolution of explosives in chronological order of their discovery along with the empirical models in the chronological order of their development which are employed in RoseBoom2.1©.

Table 2 A comparison of the structural formulas of a classic old explosive (TNT) with a modern explosive (TKX-50)

Classic explosive	Modern explosive
 **TNT**	 **TKX-50**
Nitrated carbon-backbone Nitro groups as oxidizer Aromatic carbocycle Poor oxygen balance	Ionic Nitrogen-rich N-oxide as oxidizer Tetrazole Non-toxic N_2 gas as main detonation product N–N bonds stabilized by formation of aromatic rings Formation of N–N triple bond N_2 in releases large amount of energy

order of the different empirical models implemented in RoseBoom2.1©, a direct comparison between old and modern explosives is given in Table 2.

The work reported in this thesis contributed to the further testing of these models, with the aim of determining whether they are only suitable for the classical nitrated-carbon-backbone type of explosive molecules, or whether they can also be applied to the new-generation explosives from the 2000s and 2010s which are commonly nitrogen-rich, contain N-oxide groups or are cages, and which have not been tested using the older models of Rothstein and Petersen,[11] Holden,[4] Stine,[12] Joback,[13] Kamlet and Jacobs.[14] Additionally, recent models by Zohari[15] and Keshavarz[16–19] were implemented into RoseBoom2.1© to investigate whether using the newer models will provide more accurate predictions. The Models are described in the ESI.†

Results

In order to find out which models are suited to predict the detonation parameter of the newer classes of compounds, 482 molecules were calculated in RoseBoom2.1© out of which most molecules were designed and published in the years 2017 or later. The molecules were sorted into 19 categories to thoroughly evaluate whether the selected models are suited for the class of compounds. The mean absolute percent deviations (MAPE) are shown in Table 3.

The goal was to predict the detonation velocity within a range of 5% of the EXPLO5 values, because the predicted values in EXPLO5 differ by up to 5% of the experimental values.[23] Taking a look at Table 3 shows, that the Stine method produced values closest to the EXPLO5 values for most compound classes. The few exceptions were: zwitterionic molecules, cyclic nitramines, peroxides and molecules containing trinitromethylgroups. However, it is

Table 3 Average deviation of the detonation velocity from the EXPLO5 values in the calculated set of molecules of Keshavarz model, Rothstein and Petersen's, Kamlet and Jacob's, Stine's models and the RoseHybrid©-values.[20–22]

Compound class	Samplesize	MAPE Keshavarz [%]	MAPE Rothstein and Petersen [%]	MAPE Kamlet and Jacobs [%]	MAPE Stine [%]	MAPE RoseHybrid© [%]
All Molecules	482	6.3	6.7	7.5	4.2	5
Neutral molecules	332	4.9	9.8	7.7	4.2	4.6
Ionic	113	11	6	8	4.2	5.9
Zwitter ionic	3	1.9	2.9	7.5	3.4	7.5
Aromatic	418	6.1	6	7.6	4.1	4.6
Non aromatic	67	8.3	9.4	5.8	4.4	0.9
Cyclic nitramines	15	3.8	7	3.6	3.6	3.5
Acyclic nitamines	113	7.3	4.3	6.1	3	3.5
Molecules with Nitro groups	377	5.9	6.1	5.8	3.6	3.7
Molecules without Nitro groups	104	7.7	15.4	13.4	6.2	9.2
Diazoles	137	4	4.5	5.8	3.2	2.9
Triazoles	115	8.9	6.6	9.6	4.7	5.9
Tetrazoles	133	5.8	6.5	9.6	4.6	5.5
Oxazole	96	6.1	5.8	6.7	3.7	3.7
Ethers and esters	34	7.5	10.3	4	2.8	4.6
Peroxides	10	4.8	37.8	9.3	10.99	15.9
Nitroxides	45	5.86	9	8.2	4.1	5.6
Molecules with $-C(NO_2)_3$ groups	28	4.9	4.97	2.7	2.9	3.3
Azides	41	4	11.68	8.2	2.5	4
Nitrate esters	25	6.4	5.3	3.4	3	3.7

important to note, that the Stine and Kamlet and Jacobs equations require both a density and a heat of formation which can be difficult to determine. Therefore, ideally a method should be used which doesn't need these two values. One such method is that of Rothstein and Petersen. This empirical relationship shows a high deviation of 10.0% from the EXPLO5 values and above for molecules without nitro groups, peroxides and for diazoles. This may be due to the way the model was formed: It was developed in 1978 for compounds which generally contained an oxidized carbon backbone, and therefore, the training set of molecules that was used to establish the relationship and was never adjusted to consider tetrazoles, triazoles, diazoles *etc.* which are a major current trend in energetic materials of the future. This model performed even worse for peroxides with a deviation of 37.8%, which may be due to the same reason. Surprisingly, the Keshavarz model predicted the detonation velocity better for peroxides, even though it was not fitted to peroxides. However, the deviation of 31.4% for the detonation pressure is predicted very poor.

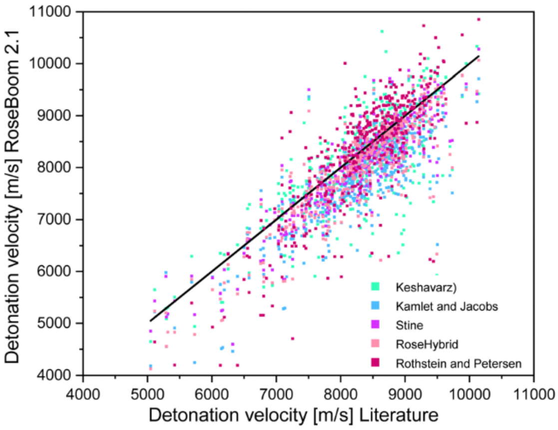


Fig. 6 Scattering plot of the detonation velocities predicted with the methods implemented in RoseBoom2.1©, plotted against the literature values.

With respect to the different categories, it appears that, even though the average deviation for the RoseHybrid© value may be higher than for the other methods, less values with extreme deviations are observed as in the case of the other models. Therefore, the average deviation may be higher, but there is a higher certainty that the predicted values are somewhere within the range of the EXPLO5 values. However, the Stine method remained the closest to the EXPLO5 Values (Fig. 6).

The detonation pressure was predicted for the same set of molecules as the detonation velocity. The molecules were sorted into the same 19 Categories to thoroughly evaluate whether the selected models are suited for the corresponding compound class. The mean absolute percent deviations (MAPE) are shown in Table 4.

Since the goal of this project is to predict detonation parameters solely based on the structural formula, the Rothstein and Petersen method may appear at first glance to be the better choice for this purpose than the Keshavarz equations based on the specific impulse, since the former doesn't require the density. But since the new version of RoseBoom© has density prediction methods implemented which can predict the density within 5% of the experimental value (Table 5) the absence of a value for the density of a compound can be somewhat combatted. Overall, the two methods which don't need a heat of formation should give satisfying results if the compound class is taken into consideration and the better equation for this class of compound is selected.

With the newly introduced "value" in this work, the RoseHybrid© value, it appears that it isn't more accurate than the other methods, but also not that much worse (Fig. 13).

Table 4 Average deviations of the detonation pressure from the EXPLO5 Values in the calculated set of molecules using the Keshavarz model, Rothstein and Petersen, Kamlet and Jacobs and RoseHybrid© value

Compound class	Sample size	MAPE Keshavarz [%]	MAPE Rothstein and Petersen [%]	MAPE Kamlet and Jacobs [%]	MAPE RoseHybrid© [%]
All molecules	476	15	39.2	8.8	11.2
Neutral molecules	327	15.5	27.3	9.2	11.7
Ionic	113	13	23.04	7.6	10
Zwitter ionic	3	12.4	16.6	9.1	8
Aromatic	416	15.8	24	8.4	8.6
Non aromatic	63	17.4	25.8	9.9	12
Cyclic nitramines	15	8.7	16.2	4.6	4.7
Acyclic nitamines	112	9.5	15.6	7.5	7.3
Molecules with nitro groups	377	12.1	37.1	7.2	8.4
Molecules without nitro groups	104	16.8	46.2	13.9	23.9
Diazoles	137	9.6	16.4	6.5	6.7
Triazoles	115	12.3	25.1	9.8	9.8
Tetrazoles	133	12.6	20.7	9	8.9
Oxazole	96	11.1	18.6	7.4	7.4
Ethers and esters	34	24.7	26	10	12.4
Peroxides	10	31.4	—	17.4	20.0
Nitroxides	**45**	**11.2**	**27.6**	**9.3**	**10.1**
Molecules with $-C(NO_2)_3$ groups	28	14.8	17.7	9.9	14
Azides	41	11.5	7.6	10.6	42
Nitrate esters	22	12.7	14.3	5.2	7.3

Table 5 Average deviations of the density in the calculated set of molecules using the Holden method, Zohari's model for azides, Keshavarz model for ionic molecules, Keshavarz model for molecules containing nitrogroups and the RoseHybrid©-values

Compound class	MAPE Keshavarz Ionic [%]	MAPE Azides [%]	MAPE Keshavarz General [%]	MAPE Holden [%]	MAPE RoseHybrid© [%]
All molecules	4.8	16.5	7.1	4.0	5.0
Neutral molecules	—	16.03	7.3	3.7	5.0
Ionic	4.8	—	—	5.1	5.1
Zwitter ionic	1.2	—	12.2	3.2	3.6
Aromatic	4.8	21.4	7.5	3.9	5.1
Non aromatic	3.4	6.3	5.1	4.8	4.4
Cyclic nitramines	—		3.7	4.22	4.2
Acyclic nitamines	5.5	14.05	7.4	4.15	5.3
Molecules with nitro groups	3.7	15.44	5.1	3.8	4.1
Molecules without nitro groups	5.6	12.4	15.74	5.1	7.6
Diazoles	3.6	18.8	7.7	3	5
Triazoles	5.6	26.5	9.1	4.4	5.7
Tetrazoles	4.8	20.9	10.3	3.5	5.7
Oxazole	4.1	—	5.4	4.1	4.4
Ethers and esters	—	6.2	8.4	4.9	4.6
Peroxides	—	—	4.4	5.6	4.7
Nitroxides	6.1	—	9.5	3.4	6.2
Molecules with $-C(NO_2)_3$ groups	3.1	8.9	4.7	4.0	4.4
Azides	2.1	16.6	17.8	5.4	9.7
Nitrate esters	3	—	5.3	3.4	3.5

As a benchmark, the range of the deviation between theory and experiment of 10% was selected, because the predicted values in EXPLO5 differ by up to 10% from the experimental values.[23] The model by Rothstein and Petersen gave the least satisfying results. Only the detonation pressures of cyclic nitramines could be predicted within a reasonable range. Peroxides, ethers and esters seem to be difficult regardless of the method used. But if a deviation of 10% of the EXPLO5 value is taken to be acceptable, the Keshavarz method based on the specific impulse becomes a lot more promising. Following this assumption almost all values are within a useful range, except for peroxides, esters and ethers. The poorly predicted detonation pressure for peroxides is very surprising because this model performs best for the detonation velocity. Since the two equations for the detonation pressure and detonation velocity were fitted using two different regression plots, they can be considered as being two different models. This, explains the different accuracy of the two values. A scattering plot of the all the predicted values is shown in Fig. 7.

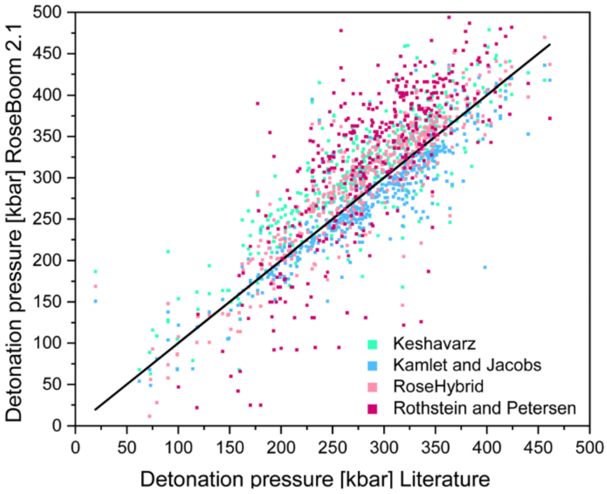


Fig. 7 Scattering plot of the detonation pressures predicted with the methods implemented in RoseBoom2.1©, plotted against the literature values.

Kamlet and Jacobs gave the most promising results, however it is important to note, that this method requires a heat of formation and a density as input, which can be difficult for some classes of compound even using the method implemented in RoseBoom2.1©.

The density was predicted for the same set of molecules as the detonation velocity. The molecules were sorted into the same 19 Categories to thoroughly evaluate whether the selected models are suited for the corresponding compound class. The mean absolute percent deviations (MAPE) are shown in Table 5.

The desired minimum accuracy for the prediction of the density is 5%, because this deviation can also be observed between values which were determined with a pycnometer and values which were calculated from a SC-XRD. Taking a look at the table it is obvious, that the volume-based Holden method gives overall the best results and except for peroxides and ionic molecules the benchmark of 5% is not exceeded. Even though, the method is old, it is still under non-disclosure by the US-Army, therefore, there is little information about its scientific basis readily available. The two compound classes: peroxides and non-aromatic molecules can be predicted within 5% of the experimental value with Keshavarz model for molecules with nitro groups. However, it is important to note that TPTP was calculated using the Holden method, since it wasn't possible to predict it's density using the Keshavarz' method because it doesn't contain nitro groups. Therefore, peroxides which don't contain nitro groups in addition still need to be predicted using Holden method. The other compound class, for

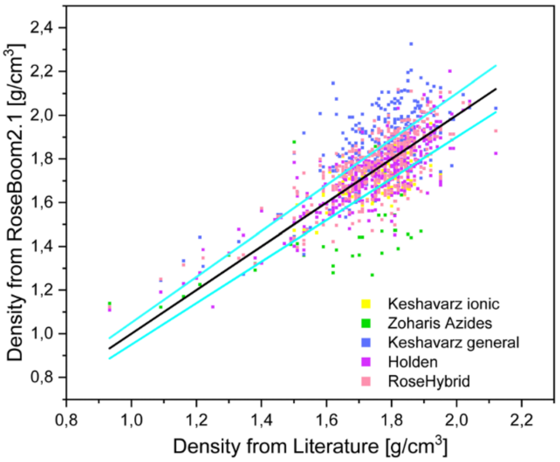


Fig. 8 Scattering plot of the densities predicted with the methods implemented in RoseBoom2.1©, plotted against the literature values and sky-blue errorbars of 5%.

which a different method should be used other than the Holden method is for ionic molecules. This category can be predicted within a range of 5% using the method for ionic molecules by Keshavarz. The only method which does not give satisfactory results is the model for azides by Zohari. This model could maybe be evaluated further with a focus on molecules with the molecular moieties which are accounted for in the method. But aside from the Keshavarz model for ionic compounds, the volume-based Holden method (where a functional group is assigned a specific volume) is found to provide better results than the correctional methods by Zohari and Keshavarz (Fig. 8). These later two methods function by correcting a value depending on the functional groups present in the molecules.

However, it is important to note, that for all of the methods implemented in RoseBoom2.1© only one method should be used as predictive tool for the evaluation of a set of compounds in order to get comparable results. As already mentioned, it is important to have a well predicted or measured densities to obtain well predicted detonation parameters. High deviations can cause major errors when predicting the detonation parameters as shown in Fig. 9.

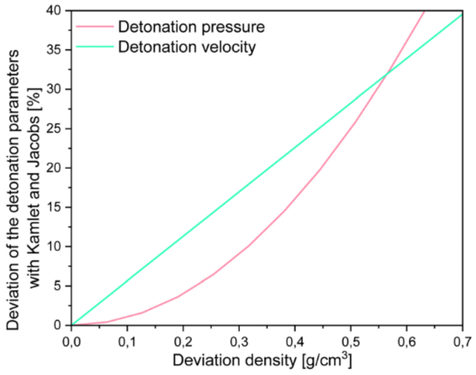


Fig. 9 Deviation of the detonation pressure (magenta) and the detonation velocity (turquoise).

It becomes very obvious when looking at Fig. 9, that for the more realistic deviations with practical relevance of ≤0.25 g cm^{-3}, the impact on the detonation velocity is bigger than on the detonation pressure. Which means the density is actually very important in predicting molecules.

When considering the deviations, the functioning of empirical models comes in very handy, when one remembers what RoseBoom© is made for: Prediction of performance parameters, to evaluate which compounds are worth to pursue in a synthesis. Usually, a scientist will have several derivatives of one compound, with slightly different groups present. Thanks to the empirical models, it is possible to determine which groups attached will increase and decrease molecular stacking, hence which compounds will have a higher or lower density. With these predictive models, one can distinguish between compounds which should have a good performance and those which have a poor performance. Therefore, one should use RoseBoom© to compare different molecules, but not to replace proper experiments. Also, one needs to consider, that it is always possible, that a different polymorph is predicted than it was compared to, which means, that RoseBoom© may predict an undiscovered polymorph which is denser or less dense than the one RoseBoom©'s value is compared to.

In order to come one step closer to eliminating the time intensive CBS-4M calculations, an empirical relationship previously published by Keshavarz to estimate the heat of formation was implemented in RoseBoom2.1© and tested on 333 neutral molecules and compared to the Joback method, which is expanded with newly calculated RoseIncrements©. To obtain the RoseIncrements© molecules with the missing fragments were calculated, as if those fragments were not present, and the obtained values were subtracted from the literature values. Then the average of the difference was taken, which are now the RoseIncrements©. A value for a nitrogen with three neighbors in a ring, an azide group and a Cuban correction was obtained like this. Also, for the heat of formation a RoseHybrid©-value was tested by taking the average of the two previously mentioned methods.[§] The heat of formation was evaluated based on the average deviation of the calculated value from the reported literature in kJ mol^{-1} (Table 6).

This is because it doesn't make much sense to describe the deviation in % from the literature value, because for example, if the model predicts −2 kJ mol^{-1} as the heat of formation, but the literature value is 1, the deviation is 300%, however this minimal difference is not significant when using the heat of formation for the calculation of the detonation parameters. It is also important to take into consideration, that the heat of formation does not influence the detonation parameters as drastically as the density. Therefore, a prediction within ±200 kJ mol^{-1} is still useful. This range is depicted in Fig. 10.

The Pearson correlation value for all methods are similar, however the average deviation for Keshavarz' method is 22.6 kJ mol^{-1} lower than for the Joback method, even though it was not taken into consideration that Keshavarz' method is only fitted for molecules with a nitrogen content of less

Table 6 Average deviation of values for the heat of formation calculated with Keshavarz model, Joback method and the average of both, the RoseHybrid©-value

Compound class	Deviation Keshavarz [kJ mol^{-1}]	Deviation Joback [kJ mol^{-1}]	Deviation RoseHybrid© [kJ mol^{-1}]
Neutral molecules	134.6	157.2	118.4
Aromatic	126.9	165.9	119.7
Non aromatic	187.2	119.5	123.7
Cyclic nitramines	167.2	123.3	140.56
Acyclic nitamines	120.3	173.8	122.2
Molecules with nitro groups	123.35	146.8	111.2
Molecules without nitro groups	180	194.8	144.3
Diazoles	105.9	131.7	91.5
Triazoles	160.8	218.2	168.7
Tetrazoles	148.7	121	103.8
Oxazole	139.3	281.7	179.0
Ethers and esters	168.0	112	104.7
Peroxides	161.0	77.4	107.6
Molecules with –C(NO2)3 groups	115.0	103.6	93.0
Azides	217.9	155.0	110.4
Nitrate esters	73.3	176.0	108.4

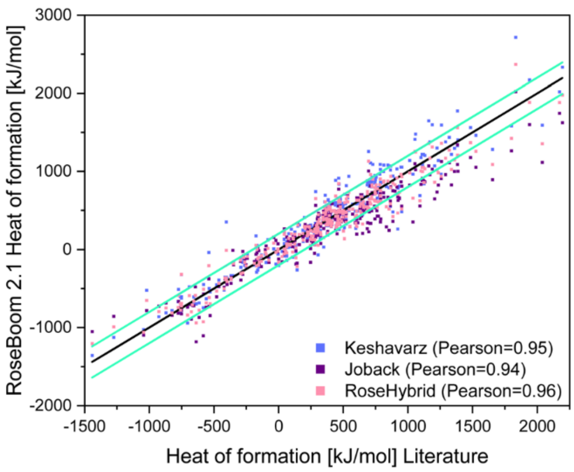


Fig. 10 Scattering plot of the heat of formations predicted with the methods implemented in RoseBoom2.1©, plotted against the literature values, with turquoise error bars marking a range of ±200 kJ mol^{-1}.

than 50%. The best predictions in RoseBoom2.1© come from combining the two models together into the RoseHybrid©-value with an average deviation of 118.4 kJ mol^{-1} (Table 6). Triazoles, oxazoles and nitrate esters are predicted better with Keshavarz' model, while non-aromatic compounds and cyclic nitramines are predicted better with the Joback-method. However, the overall performance of the RoseHybrid©-value is better – and just like with the other values predicted in RoseBoom2.1© only one method should be used as predictive tool with each value, for the evaluation of a set of compounds to get comparable results. Hence, for the heat of formation the RoseHybrid©-value is the best choice. Aside from that, when taking a look at Fig. 10, the RoseHybrid©-value has the least outlier outside of the turquoise error bars.

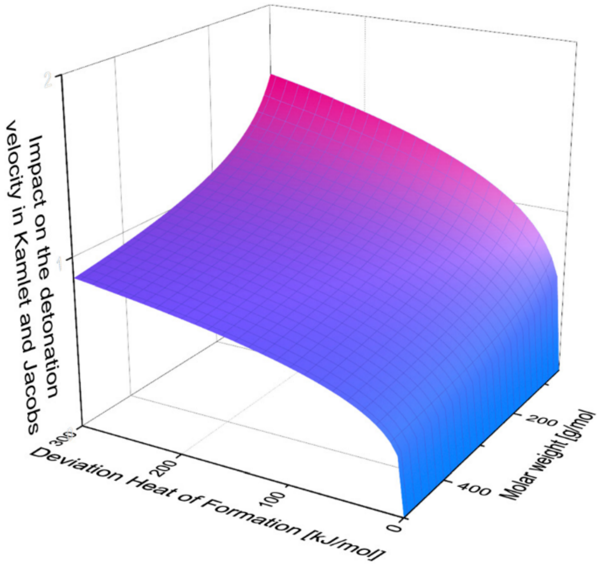


Fig. 11 The Impact of heat of formation depending on the molar weight in neglect of the detonation products.

It is also important to keep in mind, that for example in the Kamlet and Jacobs equations the heat of formation is divided by molar mass, which means, the bigger the molecule, the less significant the deviation. Moreover, it is multiplied by numerous factors and coefficient and then the forth root is taken from these factors. Unfortunately, due to the complexity of this equation it is not possible to graphically display the deviation in [%] against the deviation in [kJ mol^{-1}] as for the density. But for visualization one can neglect all the detonation products and simply plot, the forth root of the heat of formation divided by the molar weight against the impact on the detonation velocity (Fig. 11).

Looking at Fig. 11, one can tell, that the accurate heat of formation is less important for molecules of high molar mass. Also, one can tell easily, that the impact difference between an error in the heat of formation of 200 kJ mol^{-1} and 300 kJ mol^{-1} is less dramatic than between 0 kJ mol^{-1} and 100 kJ mol^{-1}. Therefore, the change of deviation for few values outside of the turquoise bars in Fig. 10, is less dramatic then the inside the error bar.

Conclusion

Since previous versions of RoseBoom© have already been employed in two research projects which lead to publications[24,25] – even before it was published, it has already been proven, that it very useful and that there is a big demand for a computer program for the quick and easy prediction of performance parameters. Even though, RoseBoom2. 1© cannot replace a proper experiment, but it will give useful predictions to evaluate which molecules should be pursued in a synthesis. It is possible to predict a density close to experimental values, just like the heat of formation, which has a much smaller impact in the detonation parameters, than the density and the

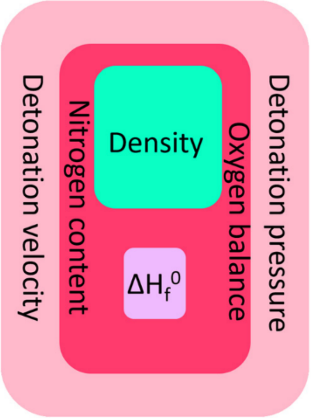


Fig. 12 A schematic overview of importance of the different values, density (turquoise), heat of formation (violet), nitrogen content and oxygenbalance (magenta) influencing the detonation parameters (Baker-Miller-Pink)

elemental composition, which are represented in Fig. 12 by the oxygen balance and the nitrogen content.

RoseBoom© should be employed before every future synthesis, to evaluate whether the molecule is worth the synthesis or one should put the time, effort, chemicals and money into another compound.

Outlook – the RoseFuture

The next step for RoseBoom©, is to test more different models to predict the different parameters and hopefully find a more precise model. For the future of RoseBoom©, it is very important to be able to predict the heat of formation precisely. Because this would mean, that composite methods would not be required. Although RoseBoom© should contribute to increasing safety, because compounds which have undesirable properties can be eliminated before synthesis, a toxicity prediction in addition for the product would be of great interest. A promising method, that could be implemented in the future is Quantitative structure-activity relationships (QSARs).[26] Implementing this into RoseBoom© would mean that researching scientists could prepare appropriately for dangers they might encounter during the synthesis. Another function that could be implemented in a future version of RoseBoom© is a synthesis planner, which would save a lot of time doing literature search.

Currently, scientists have to go through a long journey to find a new explosive. First a small-scale synthesis needs to be done, in order to collect first knowledge about the sensitivity. Once the sensitivities are determined, the synthesis can be upscaled. Only after these steps have been completed, a few kilograms can be synthesized for thorough evaluation (Fig. 13).

This exhausting synthetic journey could lead to failure at every step, if the end-compound doesn't have the desired properties. Additionally, the synthesis of energetic materials comes with many risks. Therefore, the future goal is to predict the properties of energetic materials with RoseBoom© so precisely, that only synthesis attempts are undertaken for compounds which have a future without failure.

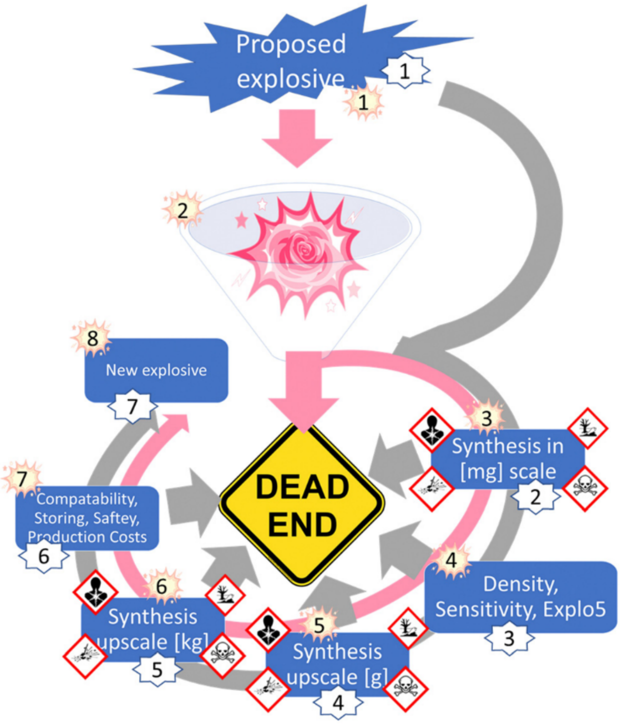


Fig. 13 The treasure hunt for new energetic materials with and without RoseBoom©.

The program RoseBoom2.1© is already superior to current programs based on empirical modeling like Energy[4] and EMDB[5] in terms of user-friendliness due to the sloth function, which also eliminates man-made mistakes when entering the variables. In addition to that it has no mistakes in the empirical formulas encoded into it unlike Energy.[4]

Author contributions

All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Notes

More information about the software can be acquired over **https://www.roseexplosive.com/**. To order it send an E-Mail to info@roseexplosive.com.

Conflicts of interest

Sabrina Wahler, Founder and CEO of RoseEnergetic UG (haftungsbeschränkt) and RoseExplosive UG (haftungsbeschränkt) has a financial interest in the software presented in this publication.

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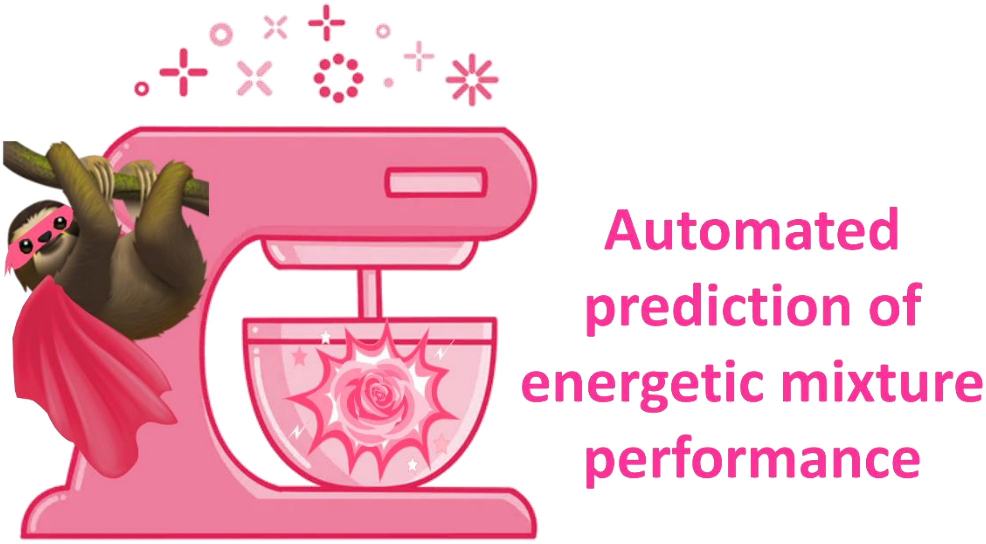
2.2 Research output software for energetic materials based on observational modelling 2.2 (RoseBoom2.2©) – Update to calculate the specific impulse, detonation velocity, detonation pressure and density for CHNO mixtures Using the Supersloth-function - published

Author contributions

Sabrina Wahler: Development of RoseBoom©, Data collection, Manuscript Preparation

Thomas M. Klapötke: Project Supervision



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Research paper

Research Output Software for Energetic Materials Based on Observational Modelling 2.2 (RoseBoom2.2©) – Update to Calculate the Specific Impulse, Detonation Velocity, Detonation Pressure and Density for CHNO Mixtures Using the Supersloth-function

In memory of Otto Wahler and Alexandra Wahler.

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Abstract: RoseBoom2.2© can calculate parameters for CHNO mixtures, automatically minimizing user-input. In the present study, RoseBoom's© results were compared to 518 EXPLO5 calculations. The new version of RoseBoom© can calculate a variety of parameters for mixtures. The detonation pressure and detonation velocity, and the specific impulse were calculated using different methods. In the present study different approaches for calculating the average sum formula have been evaluated.

Keywords: calculations, EXPLO5, detonation parameters, specific impulse, RoseBoom, mixtures

1 Introduction

Current computer programs like EMDB or EXPLO5 for energetic materials all require time-consuming manual input of the sum formula, density and heat of formation [1, 2]. The input for these programs for single molecules can be done fairly easy, even though the entry is still very prone to man-made mistakes and is time-consuming. The determination of the needed heat of formation and density require prior synthesis or time-consuming composite methods. Recent advances, directly addressing this problem and overcoming it, were made with the Software RoseBoom2.1© (Research Output Software for Energetic materials Based On Observational Modelling) licensed by RoseExplosive UG (in German: *haftungsbeschränkt*) [3]. This software combines empirical relationships for energetic materials published in different epochs of high-energy density materials (HEDMs) research. They have been revalidated for modern compounds on a dataset of over 480 compounds and merged in the user-friendly tool RoseBoom©, which allows quick and easy access to the performance parameters of HEDMs within experimental uncertainties [4, 5].

Often energetic materials will not exhibit the desired properties (*e.g.* oxygen balance, stability, mechanical properties) in a pure form, which is the reason why they are used in mixtures, to achieve a balance, with optimum performance (Figure 1).

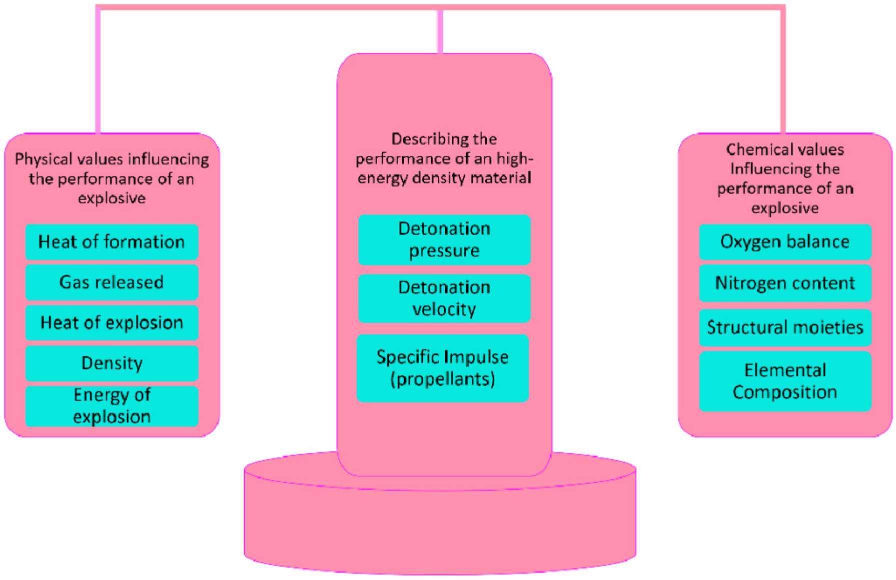


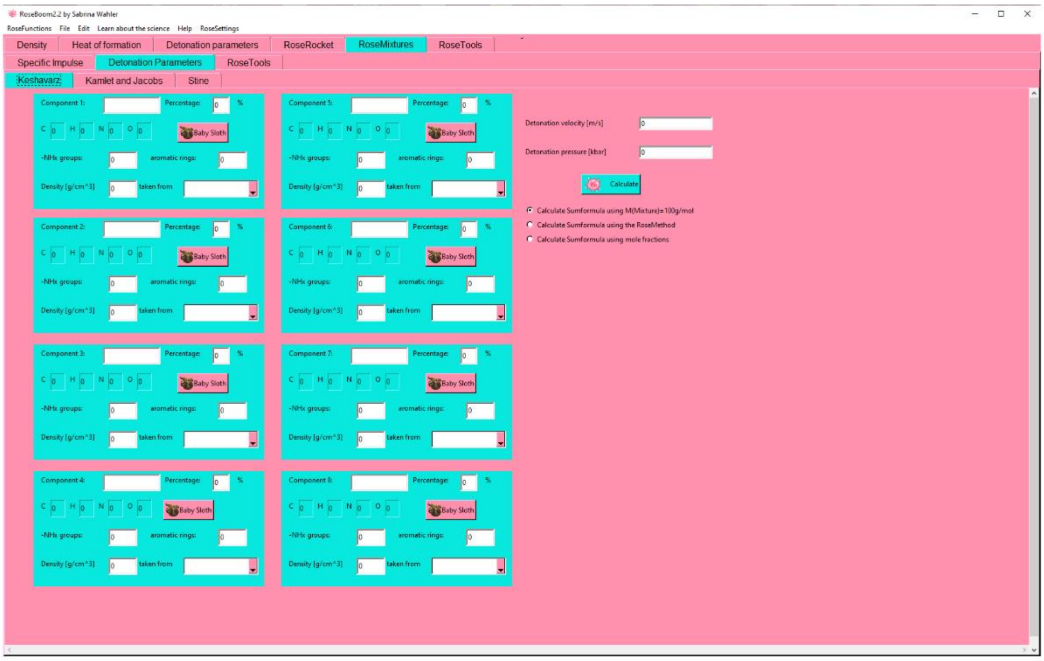
Figure 1. The physical and chemical values directly impacting the performance of energetic materials

The models implemented in RoseBoom2.2© however, have not been used in this recent study to predict the performance of energetic mixtures. These are even more time consuming for calculation in the current computer programs, because it requires the manual input of many different compounds instead of only one, and with programs like EXPLO5 [1] the computational time increases to 2 min with multiple components. Furthermore, the results are obtained in individual ".txt" files, which do not allow for a quick scan by the user for the optimum mixture or for comparing different mixtures with each other. They have to be manually converted into tables. RoseBoom2.2© allows quick and easy calculation of up to eight component mixtures with a few clicks, allowing the user to quickly find the optimum balance, as illustrated in Figure 1, because the results are given in a CSV-file that can be opened with MS Excel$^{\text{TM}}$.

2 The Program

2.1 Basic information

RoseBoom2.2© contains different empirical models to predict the detonation parameters (*e.g.* detonation velocity and pressure). With RoseBoom2.2© it is possible to calculate named detonation parameters of mixtures using the models from Kamlet and Jacobs [6], Stine [7] and Keshavarz [8] and the specific impulse using the Frem [9] and the Keshavarz models [8]. The very user-friendly graphical user interface (Figure 2), allows the user to enter Simplified Molecular Input Line Entry Specification (SMILES) into the "Baby Sloth" – function, which automatically reads the required data for the component from the input (Figure 2).



Component 1: Percentage: 0 %
C 0 H 0 N 0 O 0
-NH₂ groups: 0 aromatic rings: 0
Density [g/cm^3] 0 taken from

Detonation velocity [m/s] 0
Detonation pressure [kbar] 0

● Calculate Sumformula using M(Mixture)=100g/mol
○ Calculate Sumformula using the RoseMethod
○ Calculate Sumformula using mole fractions

(a)

Component 1: 0 Percentage: 0 %
C 0 H 0 N 0 O 0
ΔH f 0 [kJ/mol] 0 taken from

Specific Impulse [s] 0

Use the following density: Provided in .csv
Use the following Heat of Formation: Provided in .csv
List of Mixtures (up to 8 compone
*(Heat of formation and density needs to be provided in .csv)
223 of 518

(b)

Figure 2. The user-friendly interface of RoseBoom2.2© for calculating the performance of mixtures in the RoseMixture© Tab.

A new Supersloth© function is also available, which will read the information from a CSV file with an infinite number of mixtures (or single molecules) and run the calculations automatically, writing the output to another ".csv" file. The calculations presented in the results section of 518 mixtures, took three weeks computation time using EXPLO5; in RoseBoom2.2© they were run three times, using different equivalent formulas, in under 10 min with the newly developed Supersloth© function. This automation is very useful, because mixtures require the manual input of several molecules, hence it is 5 times as time-consuming to run the calculation of a five-component mixture as it is to run the calculation of a single molecule.

2.2 Computational details

All calculations for the reference dataset were performed using EXPLO5 V6.05.04. The specific impulses were calculated at 7 MPa chamber pressure and 0.1 MPa ambient pressure. An issue was encounter when calculating the equivalent formula. For the example of a 65% ammonium dinitramide (ADN, $H_4N_4O_4$) and 35% glicydyl azide polymer (GAP, $C_3H_5N_3O$) mixture, one would calculate it intuitively using Equations 1-4.

$$C = 0.65 \cdot 0 + 0.35 \cdot 3 = 1.05 \tag{1}$$

$$H = 0.65 \cdot 4 + 0.35 \cdot 5 = 4.35 \tag{2}$$

$$N = 0.65 \cdot 4 + 0.35 \cdot 3 = 3.35 \tag{3}$$

$$O = 0.65 \cdot 4 + 0.35 \cdot 1 = 2.95 \tag{4}$$

which leads to an equivalent formula of $C_{1.05}H_{4.35}N_{3.35}O_{2.95}$, but when checking with Frem's method [9] it is given as $C_{1.061}H_{3.863}N_{3.156}O_{2.449}$, and even more confusion is caused when calculating the same mixture in EXPLO5 [1], where the equivalent formula is indicated as $C_{1.208}H_{4.403}N_{3.597}O_{2.792}$. These differences are the result of Frem calculating the equivalent formula for mixtures with a fixed molar weight of 100 g/mol (Equations 5-8) and Sućeska's EXPLO5 [1] using mole fractions (Equations 9 and 10).

It was of great interest to determine in which models the accuracy is influenced by how the average sum formula is calculated, and which equivalent sum-formula gives results closest to those from EXPLO5.

The different equivalent formulas however do not affect the average density of the energetic mixtures, which is needed to predict their performance

$$C = 65 \cdot MW(ADN)^{-1} \cdot 0 + 35 \cdot MW(GAP)^{-1} \cdot 3 = 1.061 \quad (5)$$

$$H = 65 \cdot MW(ADN)^{-1} \cdot 4 + 35 \cdot MW(GAP)^{-1} \cdot 5 = 3.863 \quad (6)$$

$$N = 65 \cdot MW(ADN)^{-1} \cdot 4 + 35 \cdot MW(GAP)^{-1} \cdot 3 = 3.156 \quad (7)$$

$$O = 65 \cdot MW(ADN)^{-1} \cdot 4 + 35 \cdot MW(GAP)^{-1} \cdot 1 = 2.449 \quad (8)$$

(referred to as Method A)

$$C = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 0 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 3) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 1.208 \quad (9)$$

$$H = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 4 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 5) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 4.403 \quad (10)$$

$$N = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 4 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 3) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 3.597 \quad (11)$$

$$O = (10 \cdot 65 \cdot MW(ADN)^{-1} \cdot 4 + 10 \cdot 35 \cdot MW(GAP)^{-1} \cdot 1) \cdot (10 \cdot 65 \cdot MW(ADN)^{-1} + 10 \cdot 35 \cdot MW(GAP)^{-1})^{-1} = 2.795 \quad (12)$$

(referred to as Method B)

parameters like the detonation pressure and velocity. One would intuitively multiply the densities with the corresponding amounts in the mixture, which gives the wrong results. It is necessary to consider the volume that each component will take up in a mixture (Figure 3).

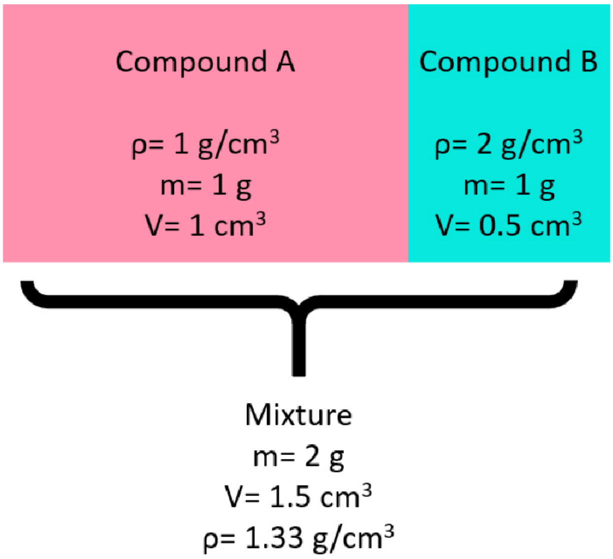


Figure 3. Graphical visualization of the problem that occurs when calculating the average densities of mixtures, with an example of two different compounds with densities of 1 and 2 g/cm^3, respectively

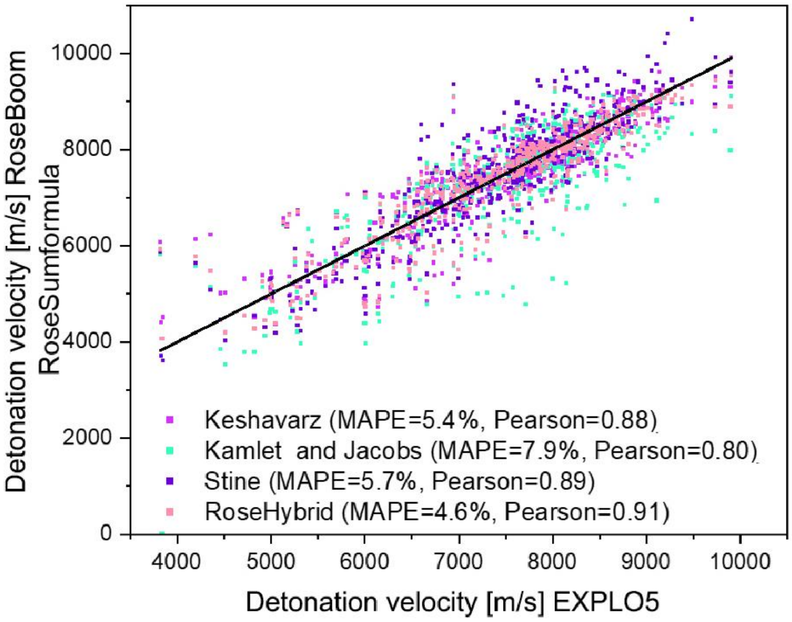
1 g of a component weighing 2 g/cm^3 will take up 0.5 cm^3, while a component weighing 1 g/cm^3 will take up 1 cm^3 (Figure 3). Therefore a mixture of 2 g (1 g of each component) will have a volume of 1.5 cm^3, which results in an average density of 1.33 g/cm^3. This rule of three can be difficult for multi-component mixtures which have several ingredients, which is why it is very useful that it can be reduced in one single step with Equation 13.

$$\rho(mixture) = \frac{1}{\sum_i^n \mathrm{X}_i \cdot \rho_i^{-1}} \tag{13}$$

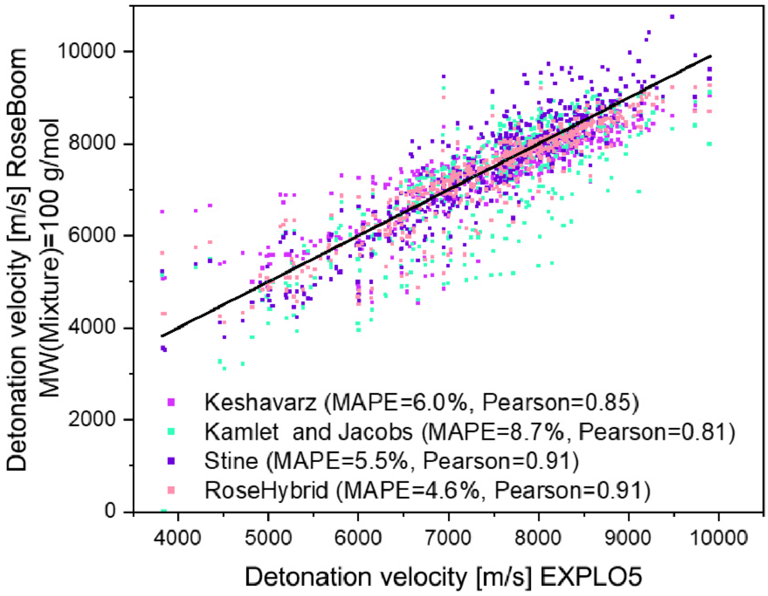
where is the amount of compound *i* and ρ_i is the corresponding density. Dividing one by the sum of the divisions of the amounts in the mixture, divided by the densities gives the average density of any mixture. This formula can be applied to mixtures with infinite amounts of components. Often energetic mixtures published in the literature contain 5 or more components in the calculation of the average densities, so the RoseDensity© formula makes it a lot easier and this is also implemented in RoseBoom2.2©.

3 Results

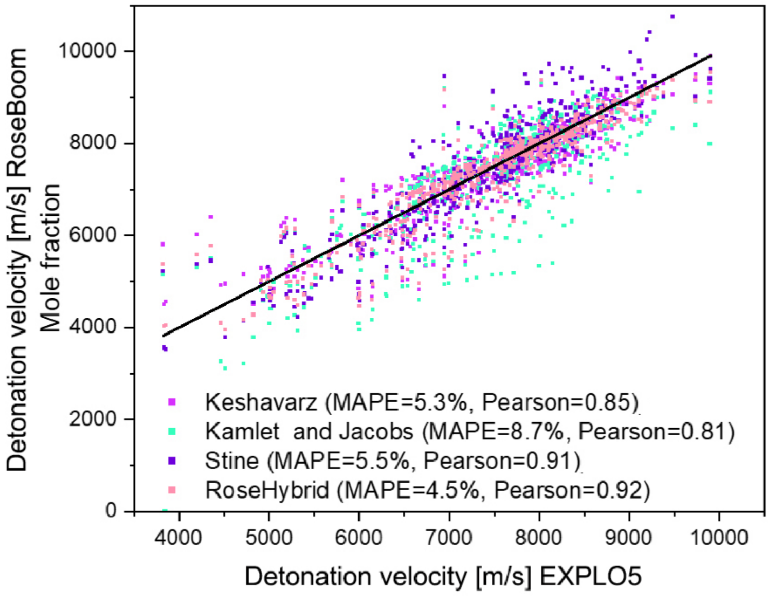
To validate the models implemented in RoseBoom2.2© a large homogenous test set was necessary. For this purpose 518 mixtures were calculated in EXPLO5 V6.05.04. These mixtures were then recalculated in RoseBoom2.2©. No studies have been published yet on a comparison of EXPLO5 values for mixtures, with experimental values. This is why, for detonation velocities, the benchmark for RoseBoom©'s predictions was 5%, because this is the deviation EXPLO5 values havefrom experimental values for pure compounds [1]. The results of the performed calculations in RoseBoom2.2© are displayed in scattering plots in Figure 4.



(a)



(b)



(c)

Figure 4. Scattering plots of the detonation velocities of the 518 mixtures investigated in this study, with RoseBoom© values using different methods of determining the sum formula, plotted against the corresponding EXPLO5 values

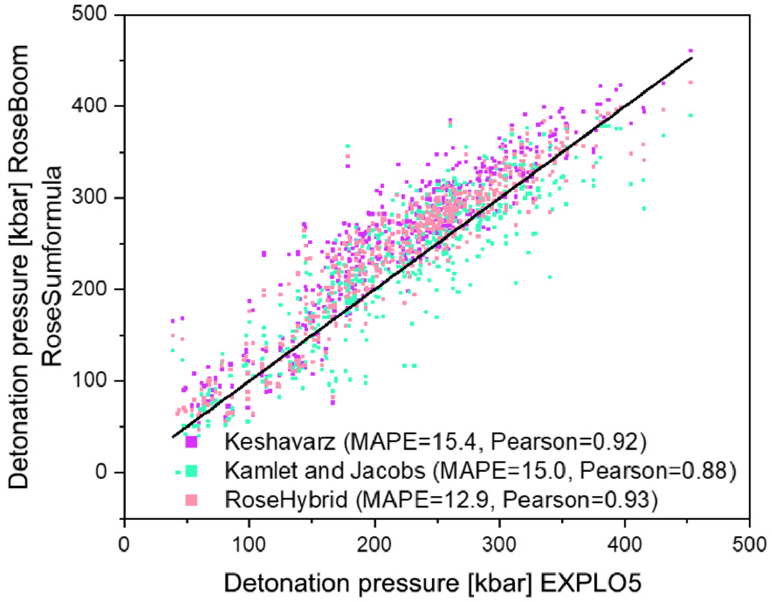
Taking a close look at the results, one can see that the benchmark of a mean absolute percentage error (MAPE) of 5% is slightly better by 0.5% when using the RoseHybrid©-values using Method B for determining the sum formula. The Pearson coefficient is slightly higher for the equivalent formula with Methods A and B. Unlike the prediction of the detonation velocity for single molecules [4], the Keshavarz method out performs those of Kamlet and Jacobs, and Stine, for mixtures using Method B for the equivalent formula (Table 1).

Table 1. Ranking of the implemented methods using the different equivalent formulas

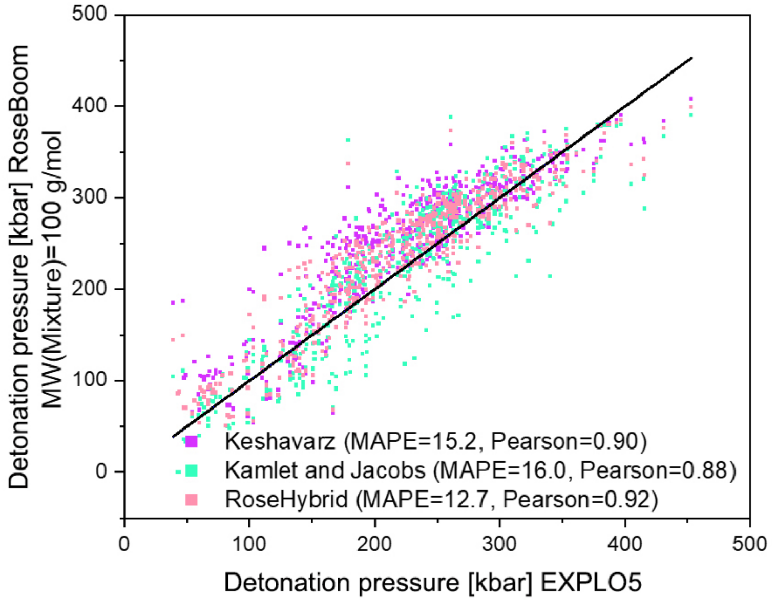
Method	Keshavarz	Stine	Kamlet and Jacobs	RoseHybrid
RoseSum formula	2	3	4	1
Method A	3	2		
Method B	2	3		

It is important to note, that it is indifferent to whether Stine's or Kamlet and Jacob's equations, Methods A or B, is used for the equivalent formula, because it is divided by the molar weight. Overall the results are satisfying, with a MAPE between 4.5-4.6% for all equivalent formulas using the RoseHybrid©-values, which is even better than the benchmark. Due to the much faster computing time and easier input, RoseBoom2.2© can be used not only to narrow down which mixtures should be further investigated, but also as an alternative to EXPLO5 to calculate the detonation velocities of mixtures.

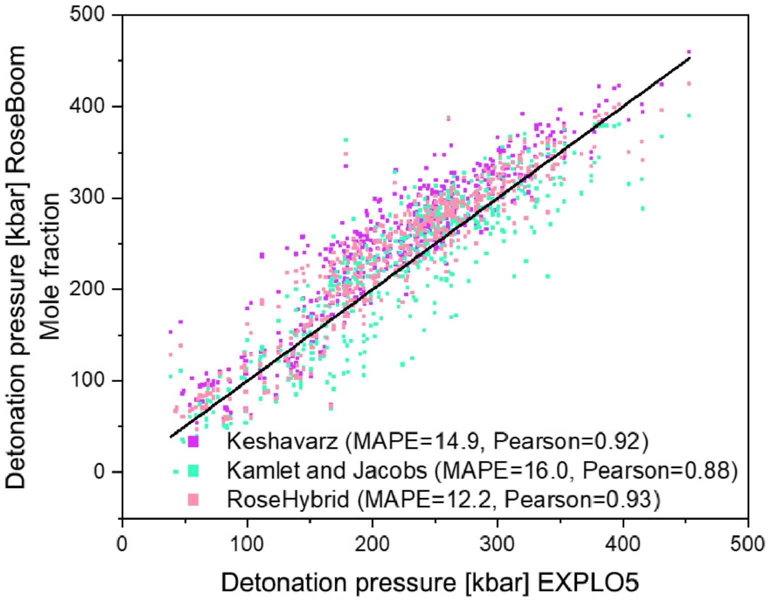
For detonation pressures, the benchmark for RoseBoom©'s predictions was 10%, because this is the deviation EXPLO5 values have from experimental values for pure compounds [1]. The results of the performed calculations in RoseBoom2.2© are displayed as scattering plots in Figure 5.


Detonation pressure [kbar] RoseBoom RoseSumformula
0
100
200
300
400
500
Keshavarz (MAPE=15.4, Pearson=0.92)
Kamlet and Jacobs (MAPE=15.0, Pearson=0.88)
RoseHybrid (MAPE=12.9, Pearson=0.93)
Detonation pressure [kbar] EXPLO5

(a)


Detonation pressure [kbar] RoseBoom MW(Mixture)=100 g/mol
0
100
200
300
400
500
Keshavarz (MAPE=15.2, Pearson=0.90)
Kamlet and Jacobs (MAPE=16.0, Pearson=0.88)
RoseHybrid (MAPE=12.7, Pearson=0.92)
Detonation pressure [kbar] EXPLO5

(b)

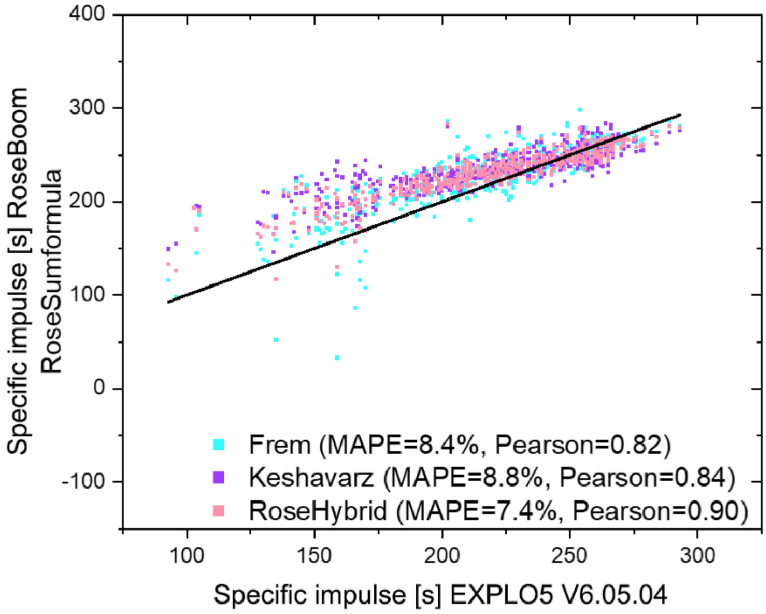


(c)

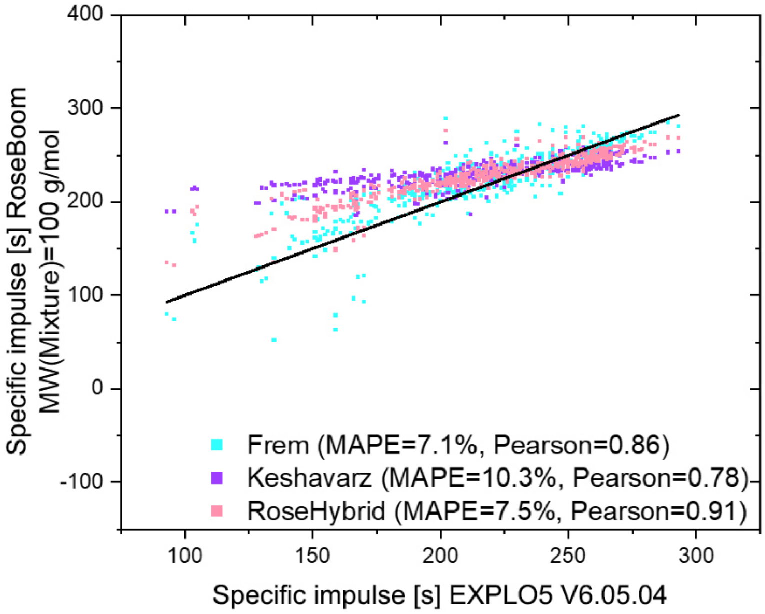
Figure 5. Scattering plots of the detonation pressures of the 518 mixtures investigated in this study, with RoseBoom© values using different methods of determining the sum formula, plotted against the corresponding EXPLO5 values

Once again, the RoseHybrid©-value showed the lowest MAPE values. Looking at the scattering plots in Figure 5, it is not difficult to tell that the Keshavarz method predicted the pressure as too high, and the Kamlet and Jacobs method too low, which is why the RoseHybrid©-value is the closest to the EXPLO5 values. Although the benchmark of 10% was slightly exceeded by 2.2% using the RoseHybrid©-value using Method B to calculate the equivalent formula, the predictions are still within a useful range. Future studies should investigate the accuracy of the models in RoseBoom© on a dataset of experimental values, for which one has to note that the different measurement techniques of detonation pressures can also deviate by up to 6% [10].

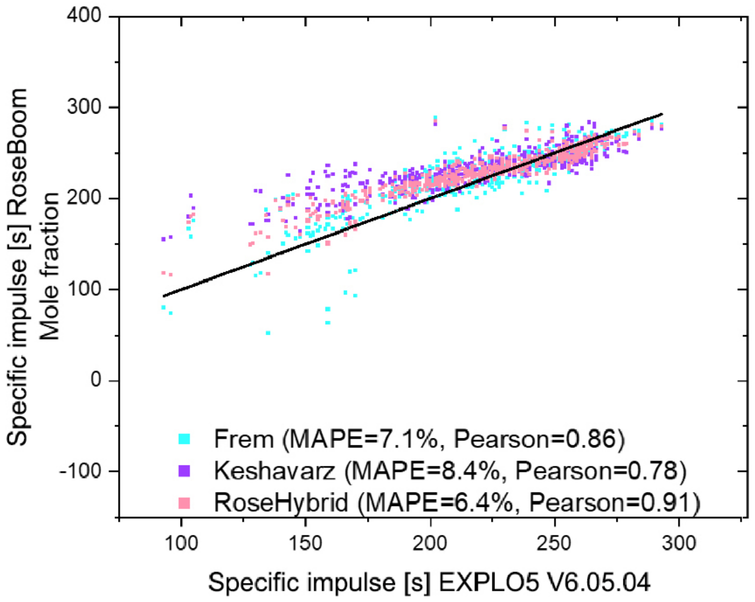
Calculating the specific impulse of energetic mixtures is also of great interest, because that is one of the key parameters for rocket propellants, for which mixtures of different materials are usually applied [11]. For the specific impulse, the goal was, as for the detonation pressure, to remain within 10% of the corresponding EXPLO5 values. The results of the performed calculations in RoseBoom2.2© are displayed as scattering plots in Figure 6.


400
300
200
100
0
-100
Specific impulse [s] RoseBoom RoseSumformula
Frem (MAPE=8.4%, Pearson=0.82)
Keshavarz (MAPE=8.8%, Pearson=0.84)
RoseHybrid (MAPE=7.4%, Pearson=0.90)
100
150
200
250
300
Specific impulse [s] EXPLO5 V6.05.04

(a)


400
300
200
100
0
-100
Specific impulse [s] RoseBoom MW(Mixture)=100 g/mol
Frem (MAPE=7.1%, Pearson=0.86)
Keshavarz (MAPE=10.3%, Pearson=0.78)
RoseHybrid (MAPE=7.5%, Pearson=0.91)
100
150
200
250
300
Specific impulse [s] EXPLO5 V6.05.04

(b)



(c)

Figure 6. Scattering plots of the specific impulses of the 518 mixtures investigated in this study, with RoseBoom© values using different methods of determining the sum formula, plotted against the corresponding EXPLO5 values

The benchmark for this value is outperformed by using the RoseHybrid©-value; with Method B for calculating the equivalent formula for the specific impulse, a MAPE of 6.4% was observed. Generally, one can say that the specific impulse, detonation velocity and pressure are best predicted using the RoseHybrid©-value with Method B. Therefore, these are the selections that should be made when calculating mixtures using RoseBoom2.2©. The Supersloth© functions allows precise computation of performance parameters for several thousand mixtures (and pure compounds) within experimental uncertainties, without much effort being required by the user.

4 The RoseFuture

- Future studies should investigate how the predicted performance parameters in RoseBoom2.2© compare to experimental values, now that it is proven that the predictions are within the uncertainties of EXPLO5 values. The prediction of RoseBoom2.2© could be even more precise than the predictions made using EXPLO5. Furthermore, the software should be expanded for other elements, especially for aluminized mixtures.

- Another emerging research field, which could be categorized as mixtures are co-crystals of energetic materials. It would be interesting to investigate if RoseBoom© can predict the different parameters of co-crystals to allow for easier evaluation of their performance before synthesis [11, 12] salts of PA have been synthesised with 2,3-diaminotoluene (PIC:23DAT).

Acknowledgements

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2.3 Research output software for energetic materials based on observational modelling 2.0 (RoseBoom2.0©) – published

Author contributions

Sabrina Wahler: Development of RoseBoom©, Data collection, Manuscript Preparation

Thomas M. Klapötke: Project Supervision

Diploma for
Great Oral
Presentation

Awarded to

Sabrina Wahler

24th Seminar NTREM, April 6–8, 2022, Pardubice

Research output software for energetic materials based on observational modelling (RoseBoom©)

Title of Oral Presentation

NTREM 2022

New Trends in Research of Energetic Materials
organized by the Institute of Energetic Materials
University of Pardubice

on behalf of the Scientific Committee

Chairman of the Seminar

Chairman of the Scientific Committee

Research output software for energetic materials based on observational modelling (RoseBoom2.0)

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Abstract

*There is huge scope for the implementation of sustainable methods in the research of new energetic materials. It is certainly one of the most important aspects which must be considered and implemented in current and future modern scientific research. There are a number of ways this can be achieved, and with the development of the program "**R**esearch **o**utput **s**oftware for **e**nergetic materials **b**ased **o**n **o**bservational **m**odelling" (RoseBoom©) it is hoped that the development of new modern energetic materials will be advanced, since it aims to provide access to quick and easy prediction methods which will indicate performance parameters (e.g. the detonation velocity and pressure, the key indicator for the power of an explosive) – before they have been synthesized.*

Keyword: prediction of performance; computer program

Modern green chemistry should not only focus on aspects like atom economy[1], but also to eliminate failed synthesis attempts. Not only would it decrease the waste production and the profusion of chemicals, but it would also save a lot of time, meaning that the progress humanity makes in a certain research field is speeded up. The synthesis of energetic materials is associated with considerable risks – especially when synthesizing a new explosive with unknown sensitivity and strength. Therefore decreasing the amount of practical work in this field would also increase the safety. To achieve this, a computer program would be employed. There are many computer codes already available such as EXPLO5[2] or Cheetah 9.0[3], however, they both require an accurate density and heat of formation for the explosive as the input in order to calculate the detonation velocity and detonation pressure. Therefore, it is of great interest to find other methods for calculating the detonation velocity, detonation pressure and other related values which are more time-efficient and don't require knowledge of the density or necessitate calculation of the heat of formation for an unknown compound, which can be time-consuming to calculate, or needs to be determined experimentally. Another problem that occurs when determining many properties using experimental methods is that many of the tests require larger amounts of the explosive, which are often not available. For this reason, theoretical calculations of explosives provide not only safer working conditions for the research scientists, but can also provide information about a compound that has not or cannot be obtained experimentally.[4]

The computer program developed in this thesis, has the advantage of requiring only information that can be obtained from drawing the structure of the compound on a piece of paper and doesn't require for some of the methods included the density or heat of formation that both the EXPLO5 and Cheetah programs require (Tabelle 1)

Developing a computer program that would provide accurate predictions about the performance of an energetic materials, based only on the structural formula would already add a new aspect to the research on energetic materials. Such a predictive tool could function as an intersection between machine learning, artificial intelligence, data science tools, and synthetic work. As a proof of concept, first big steps towards this future goal have already been made in this work namely, testing the selected empirical relationships in combinations with the commonly used cheminformatic library RdKit, which is often applied in data science[5], linking the program to the isomer generator MOLGEN[6] as well as to an optical structure recognition software[7], both of which are freely available on the internet. However, before these high-tech routes can be used to optimum capability, a foundation needs to be built, which can process the generated information from currently available informatic tools. A visual representation of the gap RoseBoom© fills and the gravel in the gearbox it removes is shown in Figure 1.

Table 1. Summary of the advantages and disadvantages of the different approaches for calculation of the detonation velocity and detonation pressure of explosives.

Method	EXPLO5	Cheetah 9.0	RoseBoom©
Pros	Accurate results Results known for a large number of compounds for comparison	Accurate results Results known for a large number of compounds for comparison	Fast Requires only a sketch of the structure of the compound
Cons	Heat of formation must be calculated using composite methods which require computer cluster or determined experimentally	Only available in the US Heat of formation must be calculated using composite methods or determined experimentally	Results may be less accurate

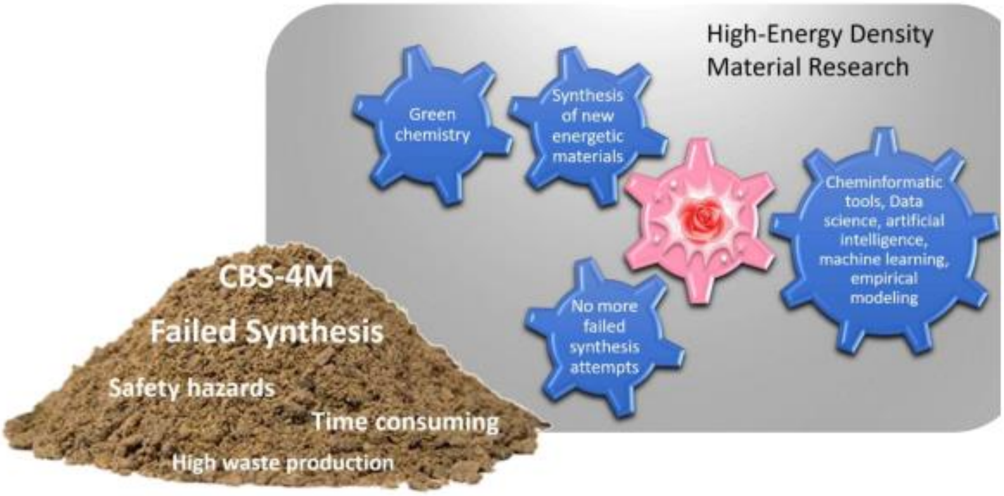

Figure 1. The position RoseBoom© is supposed to take in the future is represented by the cogs on the left. RoseBoom© should connect the synthesis of new energetic materials, green chemistry, the different computer science disciplines and the elimination of failed synthesis attempts. By this, many problems, shown by the pile of gravel on the left will be solved. By adding RoseBoom© to the high-energy density materials research field, shown as the gigantic machine, it will run smoothly without needing to twist every cog separately.

Currently, the energetic-materials community is trying to find a replacement for commonly used explosives which exhibit high toxicities such as RDX, HMX and TNT. Furthermore, to commercialize promising environmentally friendly alternatives, cheap starting materials must be used, which are then converted to the desired product, in high yields.[4] This is why modern research on energetic materials goes hand in hand with green chemistry (Figure 1). However, so far it has not been possible to combine these goals with the one dream every synthetic chemist has, in that is to obtain a compound with the desired properties in every synthesis that is attempted. The most promising method to reducing waste and emission in research in the future, is to incorporate theoretical methods like cheminformatic methods, artificial intelligence, data science and machine learning. Currently, there is a gear missing in the big machine of high-energy density materials research, which is the pink cog (Figure 1). RoseBoom© aims to connect all of these disciplines and clean out all of the gravel in the gearbox that is currently taking its place. The goal for this thesis is to build the first prototype of this cog, connecting the different aspects and disciplines of high-energy density materials research, allowing the machine to run smoothly.

During the course of this work, it was investigated wether, that reasonable predictions of detonation parameters solely based on the structural formula are possible using only empirical relationships are possible. The goal was to find different empirical relationships which allow quick and easy prediction of the density, heat of formation, detonation pressure and detonation velocity which would consequently allow a quick evaluation of a long list of candidate compounds, in order to decide which compounds should be pursued further. A schematic overview of this approach is shown in Figure 2.

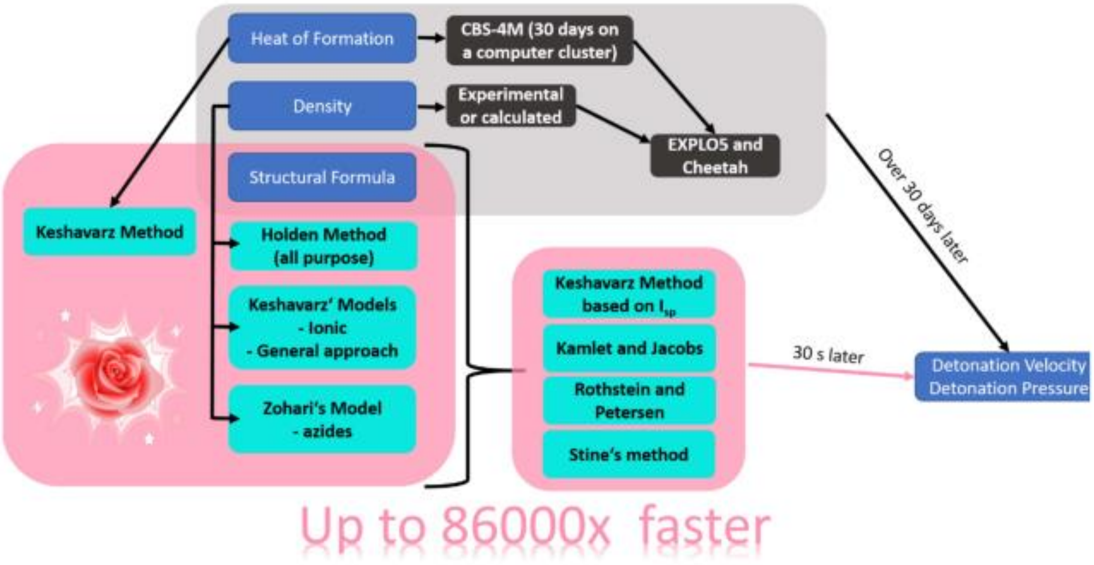

Figure 2. Schematic overview of the methods which are currently commonly used (grey) to predict the detonation parameters, as well as the approaches taken in this work (pink)[8–13], along with durations required for the two different methods.

After encoding all of the empirical relationships into the new computer program RoseBoom2.0©, the goals of this work were set even higher, and it was decided that the aim should be to be able to calculate the different parameters in 30 seconds with only the structural formula. By achieving this goal, the computational development of new energetic materials could be up to 86000 times faster – depending on the size of the energetic molecule under consideration. For a comparison: The average person works for 45 years before retiring in Germany. If one were to speed this up by 86000 times, one would need to work 0.17 ps.

Currently, scientists have to go through a long journey to find a new explosive. First a small-scale synthesis needs to be done, in order to collect first knowledge about the sensitivity. Once the sensitivities are determined, the synthesis can be upscaled. Only after these steps have be completed, a few kilograms can be synthesized for thorough evaluation. (Figure 3)

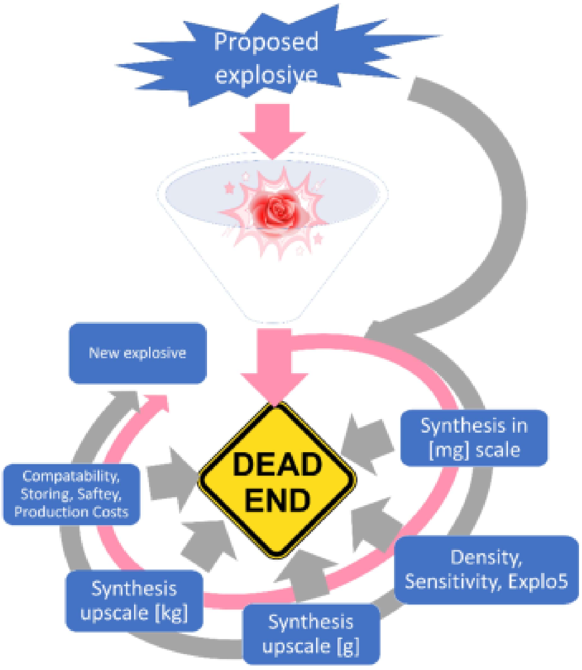

Figure 3. The treasure hunt for new energetic materials with and without RoseBoom©.

This exhausting synthetic journey could lead to failure at every step, if the end-compound doesn't have the desired properties. Additionally, the synthesis of energetic materials comes with many risks. Therefore, the future goal is to predict the properties of energetic materials with RoseBoom© so precisely, that only synthesis attempts are undertaken for compounds which have a future without failure.

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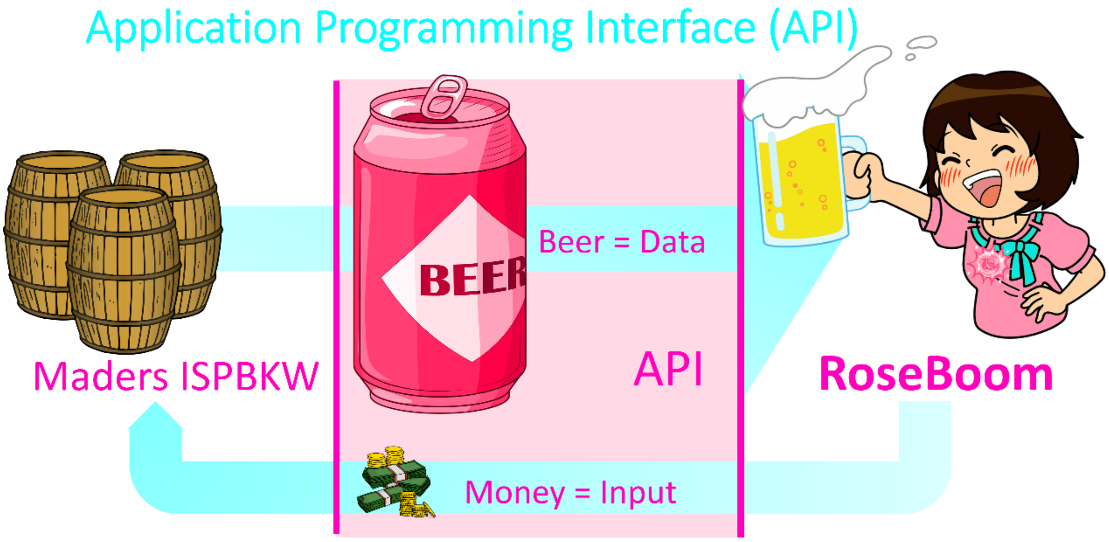
2.4 Comparison of the specific impulse calculated with the ISPBKW code, and 2 different empirical relationships encoded into the “Research output software for energetic materials based on observational modelling” (RoseBoom$^{©}$) - The RoseRocket$^{©}$ update – published, (Most Downloaded Article July 2023)

Author contributions

Sabrina Wahler: Development of RoseBoom©, Data collection, Project Planning, Manuscript Preparation, acquisition of funding

Thomas M. Klapötke: Project Supervision



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COMPARISON OF THE SPECIFIC IMPULSE CALCULATED WITH THE ISPBKW CODE AND TWO DIFFERENT EMPIRICAL RELATIONSHIPS ENCODED INTO THE RESEARCH OUTPUT SOFTWARE FOR ENERGETIC MATERIALS BASED ON OBSERVATIONAL MODELING (ROSEBOOM): THE ROSEROCKET UPDATE

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In this study, we compared the specific impulses of the ISPBKW code to two empirical models. The ISPBKW code can be easily accessed using the RoseBoom© application programming interface. For example, it took less than 3 minutes to generate all of the results presented in this paper.

KEY WORDS: *RoseBoom, RoseRocket, thermo-equilibrium, empirical modeling*

1. INTRODUCTION

The specific impulse is a critical parameter that defines the amount of energy obtained during combustion and expansion of a fuel and oxidizer. It is defined as the impulse per unit mass of propellant, and its value is dependent on the thermodynamic properties of the propellant and the combustion products (Mader, 2008).

Recent studies employing the new RoseBoom© software program have claimed that it can predict the performance of energetic parameters before synthesis without having to input any experimental data or data from composite methods (Wahler, 2022; Wahler and Klapötke, 2022). RoseBoom© can predict the density and heat of formation based on the structural formula, which then can be used in equations to calculate the detonation parameters. It can also predict the specific impulse using the Keshavarz (2008) model; however, previous studies have not focused on this value since the specific impulse was only employed to predict the detonation velocity and pressure (Wahler and Klapötke, 2022).

It is of great interest to find a quick and easy prediction method for the specific impulse because it is the key parameter used to evaluate the performance of rocket propellants (Klapötke, 2019). In this study, all of the specific impulses of a test set of compounds were calculated using the Mader (2008) ISPBKW code (Mader, 2008) and then compared to the specific impulse results obtained with the Frem (2018) and Keshavarz (2008) models. The average of these two models is referred to as the RoseHybrid model (Wahler and Klapötke, 2022).

Another obstacle that should be tackled is the user-unfriendliness of currently employed scientific software programs. Anyone who has ever worked with the Mader (2008) code or even EXPLO5 (Suceska, 2021) knows that having to manually input data is time consuming. Especially in the case of the Mader (2008) code, it is very confusing and takes a lot of time to learn how to change the BKW data file in order to obtain the desired results. The RoseBoom© application programming interface (API) resolves this issue with respect to the Mader (2008) ISPBKW code. Figure 1 illustrates the concept of an API.

2. THEORY

The ISPBKW code can model the nonideal gas behavior of mixtures of gases and solid decomposition products generated by detonation or burning. While the degree of nonideal gas behavior of propellants is small, using the ISPBKW code removes any uncertainty regarding the effect. One of the biggest uncertainties in modeling propellant performance comes from the solid products produced by burning the propellant. However, the use of the ISPBKW code allows the detailed solid product models developed for explosives to be used to calculate propellant performance (Mader, 2008).

The ISPBKW code determines the equilibrium product composition, temperature, density, energy, and entropy of a propellant at 68.94733 bar. The exhaust temperature, density, and energy (E) of the products are calculated by expanding them at constant entropy to 1.0 bar. At $\Delta H = \Delta E + P\Delta V$, enthalpies H_c and H_e can be obtained and then used to calculate the specific impulse as follows:

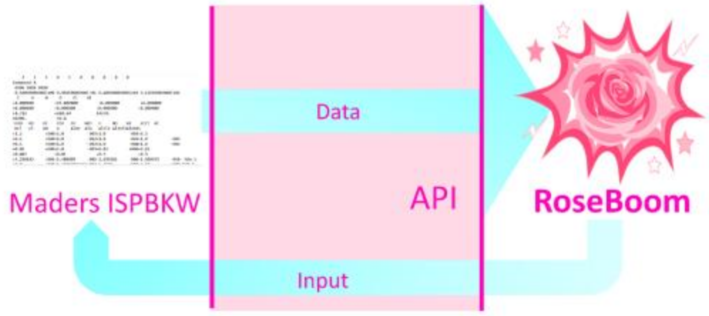

FIG. 1: Illustrative representation of an API: (right-hand side) the beer consumer sends money to the beer brewery and retrieves beer [everything taking place between the consumer and the brewery is the API (highlighted in Baker–Miller pink); translated to RoseBoom this means it sends input information to Mader's ISPBKW code and retrieves the output data (in this case, the specific impulse)]

$$I_{\mathrm{sp}} = 9.33 \times \sqrt{H_c - H_e} \qquad (1)$$

where H_c is the energy (in calories/gram) of the combustion products at 68.94733 bars. Here, H_c is the chamber energy of the decomposition products inside the rocket chamber, and H_e is the energy of the products after they have expanded and exited the rocket nozzle at a pressure of 1 atmosphere (or 1.01325 bars).

The following Keshavarz et al. (2018) equation can be used to calculate the specific impulse:

$$\begin{aligned} I_{\mathrm{sp}}(\text{aromatic}) = 2.4205 - 0.074a - 0.0036b + 0.0237c + 0.04d \\ - 0.1001(n\,\mathrm{NH}_x) - 0.1466(n\,\mathrm{Ar} - 1) \end{aligned} \qquad (2)$$

The specific impulse (I_{sp}) is given in N·s·g^{-1}, where $n\mathrm{NH}_x$ and $n\mathrm{AR} - 1$ correspond to the number of $-\mathrm{NH}_2$ or $-\mathrm{NH}$ groups and aromatic rings in the molecule, respectively; a represents the number of carbon atoms in the molecule; b represents the number of hydrogen atoms; c represents the number of nitrogen atoms; and d represents the number of oxygen atoms (Keshavarz et al., 2018).

Applying this equation gave different results for some of the test compounds compared to the results given in previous works. Correspondence with Professor Keshavarz elucidated that in there was a typo in the equation given in Keshavarz et al. (2018). Furthermore, according to Professor Keshavarz, the equations were intended to be applied as follows (Wahler, 2021):

$$\begin{aligned} I_{\mathrm{sp}}(\text{aromatic}) = 2.4205 - 0.074a - 00036b - 0.0237c + 0.04d \\ - 0.1001(n - \mathrm{NH}_x) + 0.1466(n\,\mathrm{AR} - 1) \end{aligned} \qquad (3)$$

$$I_{\mathrm{sp}}(\text{non-aromatic}) = 2.4205 - 0.074a - 0.0036b + 0.0237c + 0.04d - 0.1001(n - \mathrm{NH}_x) \qquad (4)$$

For aromatic compounds, Eq. (7) should be used and the minus sign in the Keshavarz equation should have been a plus sign [as shown in Eq. (7)]; this was the typo in Keshavarz et al. (2018). This also makes more sense because aromatic rings increase the performance of an energetic material due to the increase in the heat of formation, while the introduction of amine groups decreases the performance of an energetic material. Even more confusing is that the part marked in blue should be completely ignored for non-aromatic compounds. After solving these problems, Eqs. (7) and (8) were used for the calculations in this work (Wahler, 2021).

Kamlet and Jacobs (1968) proposed an equation to calculate the Chapman–Jouguet (C–J) point, which corresponds to the detonation pressure, from the density of the explosive ρ_0 (g/cm^3), number of moles of gas released (N), mass of gas (in grams) released by the reaction (M), and heat of the explosion (Q) [Eqs. (5) and (6)] (Kamlet and Jacobs, 1968; Klapötke, 2019):

$$p_{C-J} = K\rho_0^2\Phi, \quad K = 15.88 \qquad (5)$$

$$\Phi = N\left(M\right)^{0.5}\left(Q\right)^{0.5} \tag{6}$$

where p_{C-J} is represented in kilobars, and Φ is represented in joules per gram. Kamlet and Jacobs (1968) suggested that this detonation pressure is directly related to the detonation velocity and vice versa [see Eq. (5)] (Klapötke, 2019):

$$D = A\Phi^{0.5}\left(1 + B\rho_0\right) \tag{7}$$

where D is represented in millimeters per microsecond, $A = 1.01$, and $B = 1.30$. The equation by Dr. Dany Frem was motivated by the work of Kamlet and Jacobs (1968). The [H_2O–CO_2] arbitrary decomposition assumption was believed to have the potential to estimate the specific impulse values for propellants, given their comparable energy content and chemical composition to explosives. To test this hypothesis, a study was conducted to determine the potential influence of various parameters on the specific impulse. It was found that only the number of moles of gaseous reaction products per gram of propellant and the heat of the reaction were significant in predicting the specific impulse, which resulted in the following equations (Frem, 2018):

$$I_{\text{sp}}\left(N_{s/g}\right) = \sqrt{\left[-4.459 + 121.81\left(N_g\right) + 4.697\left(Q\right)\right]} \tag{8}$$

$$Q = \left[28.9b + 47\left(d - 0.5b\right) + \Delta H_f^0\right] / M_{\text{wt}} \tag{9}$$

$$N_g = \left(2c + 2d + b\right) / \left(48a + 4b + 56c + 64d\right) \tag{10}$$

where Q is the heat of the reaction (in kcal/g); N_g is the number of moles of gaseous products per gram of propellant; ΔH_f^0 describes the condensed phase heat of formation (in kcal/mol); and M_{wt} is the molecular weight of the composition (Frem, 2018).

The Keshavarz and Frem equations were both constructed to be used with the ISPBKW code, which is why they should be further validated on novel compounds. Therefore, in this study, we used a data set of 478 non-hydrate CHNO compounds, which mostly contain newer compound classes, to revalidate the compounds (Wahler and Klapötke, 2022).

3. METHODS

The Supersloth© function in RoseBoom© was used to run all of the molecules, since it would have been far too time consuming to calculate them manually. The API allowed simultaneously calculating the reference values from the ISPBKW code and the values obtained by the empirical relationships in RoseBoom©, which means the data presented in this study were generated in less than 3 minutes using the software developed by RoseEnergetic UG (Haftungsbeschräkt). The results are given in the Supplemental Information. The graphical user interface (GUI) of the API is shown in Fig. 2, which illustrates that the API also works with manual input of data into entry boxes or the regular sloth function. Depending on the oxygen balance of the compound, the API automatically decides whether to use the TNT or RDX parameter set in the BKW equations.

4. RESULTS AND DISCUSSION

The results obtained using the empirical Frem (2018) and Keshavarz (2008) models were compared to those obtained using the Mader (2008) thermo-equilibrium ISPBKW code. A scattering plot of the specific impulses of 478 molecules is presented in Fig. 3.

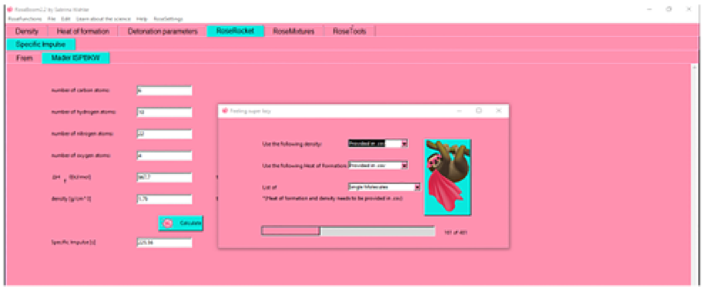

FIG. 2: GUI of the API to Mader's ISPBKW code

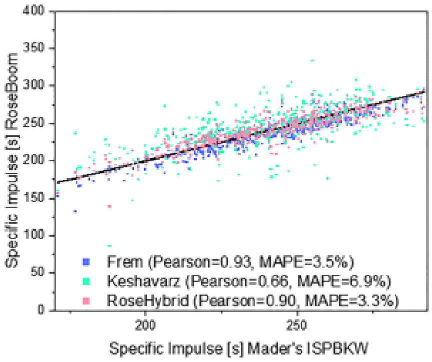

FIG. 3: Scattering plot of the obtained values for the specific impulses in RoseBoom

TABLE 1: Different compound classes and the corresponding mean absolute errors and deviations

Parameter	Keshavarz (s)	Keshavarz (%)	Frem (s)	Frem (%)	RoseHybrid (s)	RoseHybrid (%)
Neutral molecules	16.03	6.85	8.33	3.5	7.76	3.26
Aromatic	15.59	6.61	8.47	3.55	7.55	3.15
Non-aromatic	19.01	8.39	7.37	3.17	9.12	3.99
Acyclic nitramines	16.67	6.79	6.54	2.6	8.89	3.6
Molecules with nitro groups	15.39	6.46	7.33	3.01	7.73	3.21
Molecules without nitro groups	18.67	8.4	12.21	5.4	7.92	3.47
Ethers and esters	16.28	7.02	5.89	2.48	6.42	2.83
Peroxides	14.18	7.55	9.49	5.21	5.45	2.92
Molecules with –$C(NO_2)_3$ groups	17.49	6.84	9.04	3.54	10.02	3.9
Nitrate esters	17.75	7.27	6.68	2.77	7.92	3.26

Overall, all three methods performed very well. When looking at the results, it seems that the specific impulse is more strongly related to the heat of formation than the density, since the Frem model showed less scattering compared to the Keshavarz model. The RoseHybrid© value showed the smallest mean absolute percentage error, which was very closely followed by the value obtained with the Frem model. It is important to keep in mind that this might be compensated for in large data sets by the higher correlation employed in the Frem model.

In addition, it is important to remember the fact that the Frem model only requires the heat of formation and the Keshavarz model does not require external values. The ISPBKW code requires the density and heat of formation of a compound, both of which can be difficult to obtain. The fact that the Keshavarz model exhibited higher deviations in the used test set may be an indication that the heat of formation is needed to give accurate predictions, or it may be that the similarity between the ISPBKW equation, which correlates the specific impulse with the energy of the combustion products, and the Frem equation used to correlate the heat of the reactions leads to results that more closely match. One must keep in mind that the Kamlet and Jacobs (1968) equations were derived from the Ruby code, which is based on the BKW equations (Wang et al., 2014). The ISPBKW code is also based on the BKW code; therefore, the reformulating and reparameterization of the Kamlet and Jacobs (1968) equations should result in accurate predictions of the specific impulse.

Unlike with the detonation velocities, where it increased the accuracy (Klapötke and Wahler 2022), taking the average all the employed empirical equations, called RoseHybrid© did not increase the accuracy, but it rather remained the similar to Frem's equation. Initially, it was assumed that by averaging different empirical models the number of features taken into account would increase, which was not the case (Klapötke and Wahler, 2022). However, it is interesting to note that averaging the two models led to similar accuracy as obtained with the Frem model. Therefore, the results were split into categories (see Table 1) and analyzed by compound class.

Overall, splitting the data into compound classes suggests that the average of the Frem and Keshavarz models showed lower variances in the data set, which may be linked to the fact that more molecular moieties were taken into account. In addition, it was obvious that the Keshavarz model showed the highest deviations. The poor prediction of the compounds without nitro groups was likely linked to the lower oxygen balance of the compounds.

5. CONCLUSIONS

In conclusion, all of the empirical models gave accurate predictions. Thanks to the API in RoseBoom©, users can easily obtain accurate specific impulse results since all of the models can be accessed from the software program. In addition, since RoseBoom© also contains density and heat of formation predictions, various methods can be used before synthesis to evaluate if the compounds are worth investigating further or employed after synthesis with the correct density and heat of formation values (Klapötke and Wahler, 2022).

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2.5 The predictions of RoseBoom2.2© without the input of any data received from experiments or composite methods – published, Trending May 2023

Author contributions

Sabrina Wahler: Development of RoseBoom©, Data collection, Project Planning, Manuscript Preparation

Thomas M. Klapötke: Project Supervision

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The predictions of RoseBoom2.2© without the input of any data received from experiments or composite methods

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ABSTRACT
Recent studies with the new program RoseBoom© claim it can predict reliable detonation parameters only based on the structural formula, without the need of a heat of formation or density obtained using a different method. In this study, it was investigated how big the impact on the calculated detonation parameters is, when one uses the density and heat of formation predicted by RoseBoom2.2© vs. densities and the heat of formations published with the corresponding molecules. A range of traditionally used models in terms of the sensitivity to the accuracy to the input values is tested. Furthermore, it proofs the need to agree on one software for predicting the performance of energetic materials, starting with the input of values of energetic materials. Additionally, it puts further trust into the predictions by RoseBoom© and raises awareness of the uncertainty of published performance values.

KEYWORDS
Detonation parameters; empirical models; energetic materials; property prediction; RoseBoom

Introduction

Recent studies with the new software RoseBoom© claim that it can predict the performance of energetic parameters before the synthesis, not needing any experimental data or data from composite methods as input (Klapötke and Wahler 2022; Wahler 2022; Wahler and Klapötke 2022a, 2022b). The goal is to create a tool, which can tell before a synthesis whether the compound or mixture is a promising candidate (Klapötke and Wahler 2022; Wahler and Klapötke 2022a, 2022b). (Figure 1)

RoseBoom© can predict the density and heat of formation based on the structural formula, which then can be put in equations for the detonation parameters. Only studies comparing the detonation parameters to EXPLO5 (Suceska 2001) were made, using the densities and heat of formations given in the literature. However, no study has been made comparing the calculated detonation parameters, using the literature densities and heat of formations to the predicted performance parameters using RoseBoom's© density and heat of formation. The focus of this study

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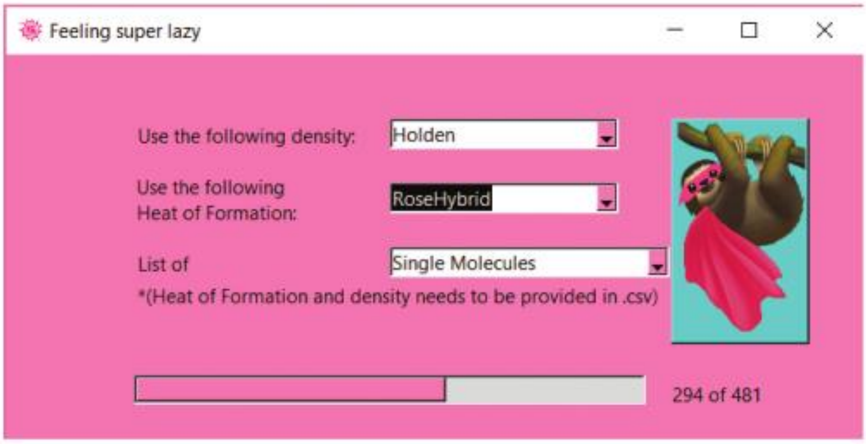
Figure 1. Metaphorical illustration of the intended use of RoseBoom©. It is supposed to act as the gold pan, when washing gold, hence searching for new energetic materials. A gold pan is an essential tool to quickly find gold in a pile of gravel.

is to investigate how well RoseBoom© really acts as a predictive tool before synthesis, without the input of values obtained from other methods.

Methods

The dataset used to validate RoseBoom2.1© (Wahler and Klapötke 2022b) was recalculated using the methods, which gave the predictions closest to literature values in RoseBoom2.1© - for the heat of formation the RoseHybrid©-method (Wahler and Klapötke 2022b) was employed and for the density the Holden method (Willer 2009) was used. The data set is given in the supporting information. With the new Supersloth©-function, which is sold as an add-on by RoseExplosive UG (haftungsbeschränkt) to the new version RoseBoom2.2©, it only took 4 min to generate the data used in this study. It allows to fully automatically run a Excel file containing the SMILES of a molecule, density, and heat of formation (if available) and the aggregate state in RoseBoom2.2©. When submitting the file, the user can select which density and heat of formation should be used to calculate the detonation parameters (Figure 2.)

The results are written in another Excel file which can be opened as an Excel Spread Sheet. With the new ChemOffice-Excel plugin, it is even possible to convert the SMILES back to chemical structures. This gives a very nice



Feeling super lazy

Use the following density: Holden

Use the following Heat of Formation: RoseHybrid

List of Single Molecules

*(Heat of Formation and density needs to be provided in .csv)

294 of 481

Figure 2. The interface of the new Supersloth©-function.

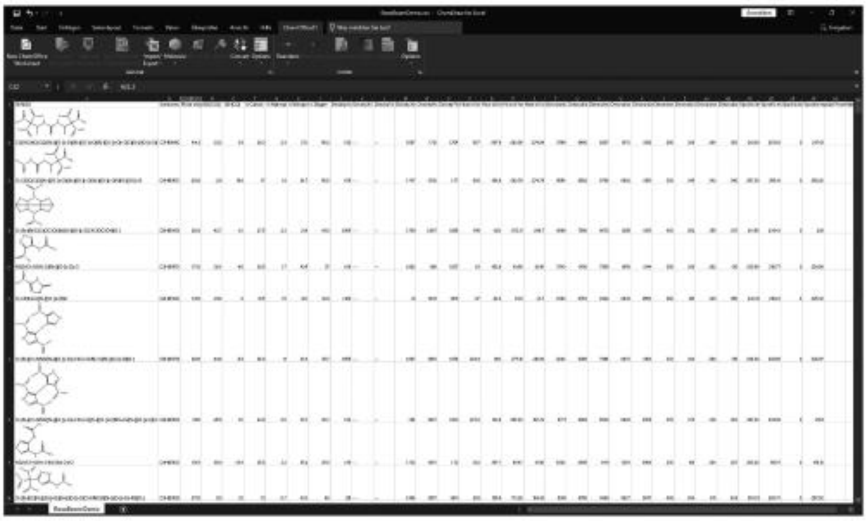


Figure 3. The result file generated by the Supersloth©-function.

overview over the calculated parameters for each individual compound. The obtained spread sheet is shown in Figure 3.

This spread sheet allows quick and easy evaluation of the calculated compounds to find the most promising candidates and unlike with the regular sloth function it is not necessary to paste the obtained data manually into such a spread sheet.

Results and Discussion

The recent study using RoseBoom© proved that the obtained densities and heat of formations are within a reasonable range. For the density, it was proven that the uncertainty lies within 4%, which is also observed between X-ray densities and pycnometer densities (Wahler and Klapötke 2022b). It was not investigated how these errors influence the predicted detonation parameters. In this study, the worst-case scenario was investigated: That the user of RoseBoom© ignores that the enthalpy of formation is not suited for ionic compounds, which are part of the test set.

The scattering plots of the values only predicted in RoseBoom© compared to the calculated results using literature values are displayed in Figures 4 and 5.

The results obtained for detonation velocities deviate between 2.2% and 3.5%. This is very low considering the uncertainties experimental measurements exhibit. Also one has to keep in mind that if RoseBoom© is employed before synthesis to investigate which compounds are worth pursuing in a synthesis, these values are not intended to be a replacement for experimental values, they are an estimation to sieve through a large pool of compounds. Therefore, a general trend of which compounds have a better performance

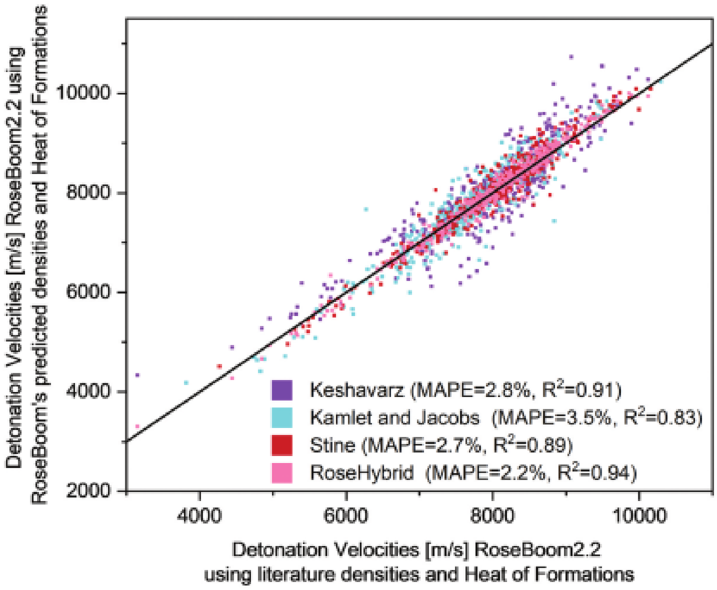


Figure 4. The comparison between the detonation velocities (Kamlet and Jacobs 1968; Keshavarz and Pouretedal 2004; Stine 1990) from RoseBoom2.2© calculated only with the predicted values for the density and enthalpy of formation.

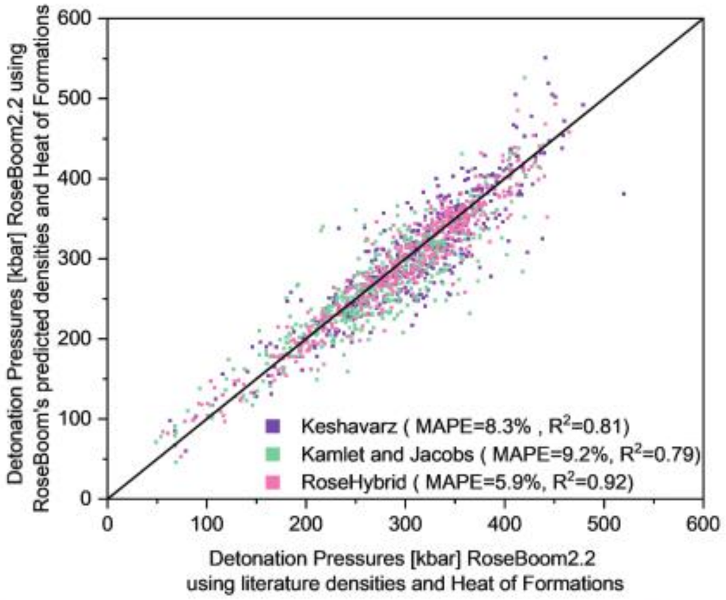


Figure 5. Scattering plot of the detonation pressures (Kamlet and Jacobs 1968; Keshavarz and Pouretedal 2004) from RoseBoom2.2© calculated only with the predicted values for the density and enthalpy of formation.

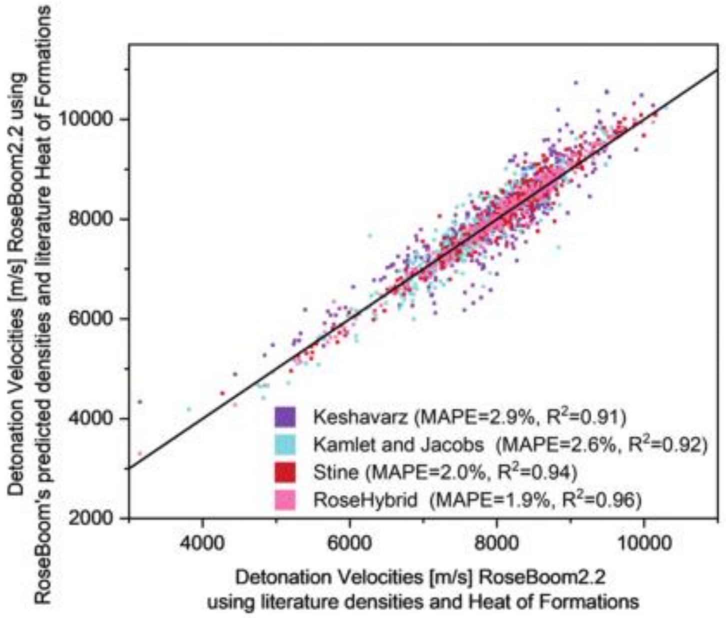


Figure 6. The comparison between the detonation velocities (Kamlet and Jacobs 1968; Keshavarz and Pouretedal 2004; Stine 1990) from RoseBoom2.2© calculated with the predicted values for the density and literature values for the enthalpy of formation.

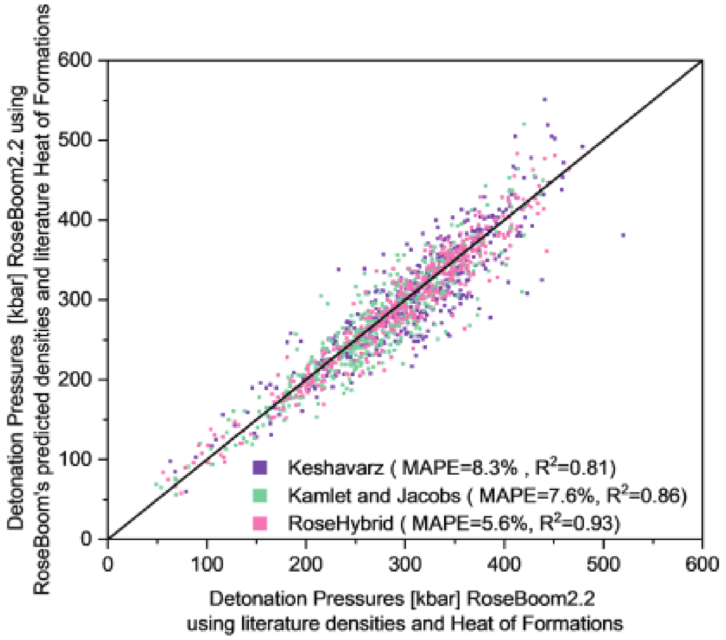


Figure 7. The comparison between the detonation pressures (Kamlet and Jacobs 1968; Keshavarz and Pouretedal 2004) from RoseBoom2.2© calculated with the predicted values for the density and literature values for the enthalpy of formation.

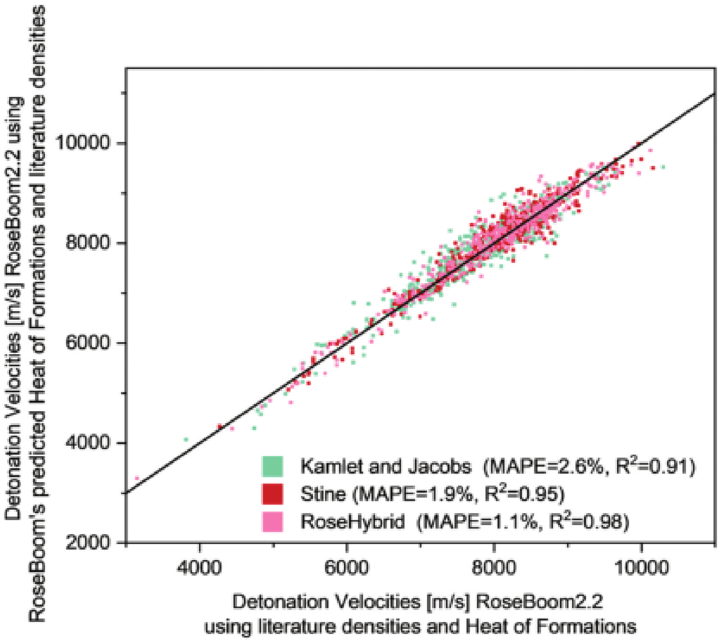


Figure 8. The comparison between the detonation velocities (Kamlet and Jacobs 1968; Keshavarz and Pouretedal 2004; Stine 1990) from RoseBoom2.2© calculated with the predicted values for the enthalpy of formation and literature values for the density.

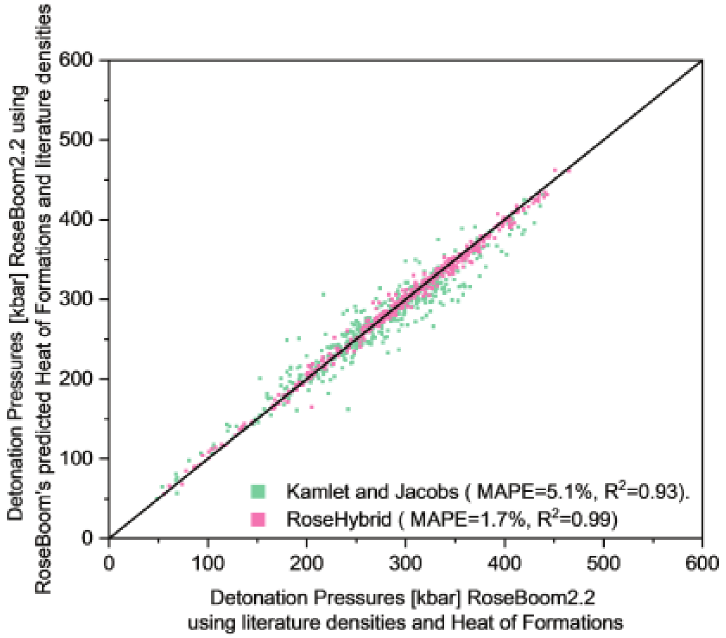


Figure 9. The comparison between the detonation pressures (Kamlet and Jacobs 1968; Keshavarz and Pouretedal 2004) from RoseBoom2.2© calculated with the predicted values for the enthalpy of formation and literature values for the density.

needs to be observed with the values predicted by RoseBoom© which is possible to see, with the neglectable error for the detonation velocities.

Looking at Figures 6 to 9 it is apparent that, the error caused by using RoseBoom's densities and heat of formations are higher for the detonation pressures. However, the range from 6.2% to 9.0% is still within the range of experimental uncertainty when measuring the detonation pressure. Detonation pressures can deviate by 7% using different methods (Pachman et al. 2018). This may question its usefulness as a parameter for the performance of an energetic material. Even though, the highest error in the prediction is caused by the deviation of the density predictions in RoseBoom© this is not too significant when using it for screening for new energetic materials, because packing density of energetic materials will vary from the theoretical maximum density (Klapötke 2019). Additionally, it is important to note that the RoseHybrid© values are less sensitive to change, as they are the average of all methods used in RoseBoom©, some of which do not require a density or heat of formation, which is favorable, for a calculation model, which different scientists may provide with varying data, depending on the source.

Conclusion

Overall, one can say that RoseBoom© is a multi-functional tool. It can be used to determine the detonation parameters of new energetic materials before a synthesis, but it has also suited to determine them after synthesis as suggested in the last study (Wahler and Klapötke 2022b). This means, it should be used as a new standard program to calculate performance parameters in the energetic materials community – RoseBoom© does not rely on parameters, which need to be determined using other methods and does not require time-consuming user-input. If the whole energetic community would agree on one software to calculate the detonation parameters, this would mean comparable results are published.

Disclosure statement

Sabrina Wahler has a commercial interest in the software used for this study.

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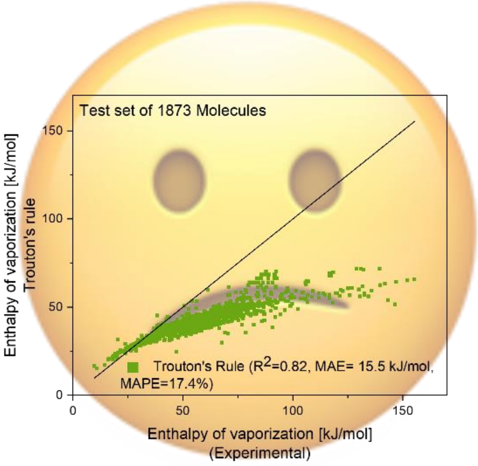
2.6 Training machine learning models based on the structural formula for the enthalpy of vaporization and sublimation and a thorough analysis of Trouton’s rules – accepted manuscript

Author contributions

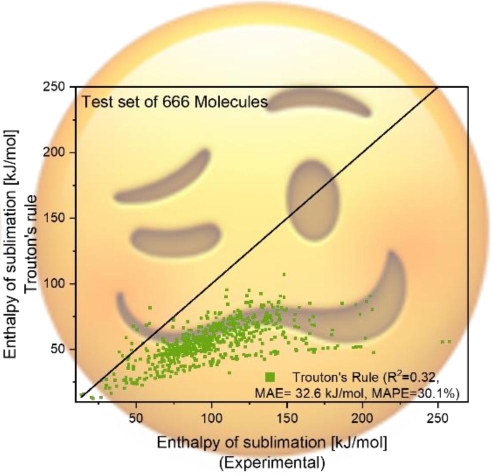
Sabrina Wahler: Development of RoseBoom©, Data collection, Project Planning, Manuscript Preparation, acquisition of funding

Peter W. Chung: Project Supervision, Manuscript Revision

Thomas M. Klapötke: Project Supervision



$\Delta H_{vap}[J/mol]=90 \cdot T_b[K]$



$\Delta H_{sub}[J/mol]=188 \cdot T_m[K]$

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Training machine learning models based on the structural formula for the enthalpy of vaporization and sublimation and a thorough analysis of Trouton's rules

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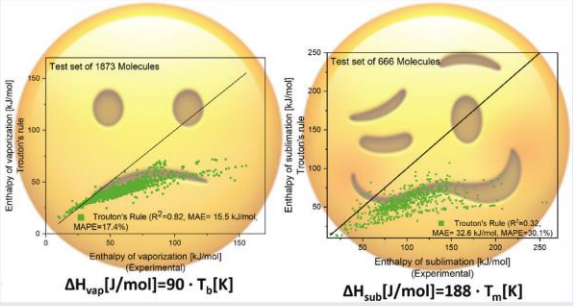
ABSTRACT
To convert a calculated value of the enthalpy of formation from the gas phase to room temperature, the enthalpy of sublimation and vaporization are needed. Numerous methods to predict the enthalpies are available, ranging from complex quantum methods to simple empirical correlations to the melting or boiling points. In this study, two machine learning models have been introduced to quickly predict the enthalpy of sublimation and vaporization. To put the results into perspective, a comparison with two empirical models correlating the named enthalpies to the melting/boiling temperature is made.



KEYWORDS
Enthalpy of sublimation; enthalpy of vaporization; machine learning; roseBoom; trouton's rule

Introduction

The enthalpy of sublimation and vaporization are both important values to know about a new material. For example, they can give information about the vapor pressure. The most common application for these values is to convert a gas phase heat of formation into solid or liquid state, depending on the aggregate state at

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room temperature. This is important for quantifying the differences in internal energy in solid and liquid states, which is required to calculate the performance of energetic materials (Klapötke 2019). The measurement of these values is rather difficult, as the sample has to be heated, which may lead to numerous problems (Reid, Sherwood, and Street 1959). This is especially problematic for energetic materials, as they can decompose or explode. The scattering of literature values for the enthalpy of sublimation is typically higher, if one looks through databases that collected values from various sources (https://webbook.nist.gov/chemistry/ n.d.). There are more sources of error when sublimating a sample than vaporizing it: the material could contain some crystal water which vaporizes; it could start melting if not heated rapidly enough, meaning an enthalpy of vaporization would be measured. Furthermore, the material could transform into a different polymorph, induced by the temperature change (Reid, Sherwood, and Street 1959). Other methods used for its determination are calculating the enthalpy of vaporization and sublimation using quantum-chemical composite methods. The issue with this is that they are very time consuming. Depending on the molecule symmetry, this can take over a month with current technologies (Omlor and Bohn 2022), which makes it very unattractive to use, as an experimental determination may be faster. This also means that these methods cannot be validated on a large dataset because of the time and resources it would take to run them. It is also important to note that different composite methods exhibit high deviations from each other as shown by Omlet and Bohn, that can be over 100 kJ/mol (Omlor and Bohn 2022; Omlor, Bohn, and Lang 2022). The other options are empirical relationships. For example, Trouton's rule, is a very simple to use, it requires a melting or boiling point that is then multiplied according to (Klapötke 2019):

$$\Delta H_{vap}[J/mol] = 90.T_b[K]$$

$$\Delta H_{sub}[J/mol] = 188.T_m[K]$$

Another recently published method refined (Muravyev et al. 2021) the formula by including the elemental composition, considering the hydrogen, nitrogen and oxygens. It was refined for energetic materials.

In this study, machine learning models which only rely on the structural formula of a molecule are developed. A simple sketch of the molecular structural formula is enough. The interest in methods which only requires a sketch of a formula is demonstrated by for example RoseBoom© ("Research output software for energetic materials based on observational modelling/machine learning") that combines various methods developed throughout the past 60 years, revalidated them on novel compound classes and made them accessible in a user-friendly format (Klapötke and Wahler 2022; Wahler n.d.; Wahler and Klapötke 2022a, 2022b). The general idea is to predict (Klapötke and Wahler 2022; Wahler n.d.; Wahler and Klapötke 2022a, 2022b) the properties of energetic materials before synthesis based on the structural formula. So far, empirical models were used like Kamlet and Jacobs (Kamlet and Jacobs 1968), Stine (Stine 1990), Rothstein and Petersen (Rothstein and Petersen 1978), Holden (Willer 2009) and numerous approaches by Keshavarz (Mohammed Hossein Keshavarz 2020).

The goal is to facilitate the calculation of enthalpies of vaporization and sublimation by using machine learning models that only require the sketch of a molecule. Additionally, the accuracy of the predictions has been improved compared to the traditionally used methods.

Computational Methods

Experimental data used in this study were collected from open source datasets focusing on organic CHNOClFBrS compounds (Chickos and Acree 2002, 2003; https://webbook.nist.gov/chemistry/ n.d.; Naef and Acree 2017). A detailed analysis of the data is given in the supplementary information (Cihan Sorkun et al. 2022; Maaten and Hinton 2008; McInnes, Healy, and Melville 2018; WOLD, ESBENSEN, and GELADI 1987).

For featurization, mmltoolkit was used (Elton et al. 2018). The E-state fingerprints, custom descriptor set and sum over bonds were selected as features. These are the “variables” the model will try to model. For modeling scikit-learn was used (https://scikit-learn.org/stable/index.html accessed on 11/17/n.d.). Five random 90:10 train-shuffle splits with the datasets were performed to validate the model on the test set. Each of the chosen features were scaled in a range between −1 and 1 for normalization. The hyperparameters were tuned using grid search. For modeling, a gaussian process regressor model is used, as it works well with small datasets. As kernel the sum of a white noise kernel and Matérn Kernel is used (Genton 2001).

Results

A dataset of 422 molecules was used as test set. One of the shuffle splits of the enthalpy of vaporization is shown in Figure 2

The test set shows high correlation $R^2 = 0.98$ as well and a mean absolute error of 2.8 kJ/mol, which is within experimental uncertainty (https://webbook.nist.gov/chemistry/ n.d.). Also, the uncertainty of 5.1% is comparable to the uncertainty bounds of the chosen regression models which is around 5% reported in other studies by Fiedler *et al.* (Fiedler, Scherer, and Trimpe 2021). Looking at Figure 3, one can tell that there is low variance between the shuffle splits, and the correlation remained similar, for all the shuffle splits and the mean and median are close together. This is a good indicator that the model was not overfitted.

After training the enthalpy of vaporization successfully, the model described in methods was trained with 2196 enthalpies of sublimation. Before training it on the full data set, a train-test split was done to prove the model is also working for the enthalpy of sublimation. The results are shown in Figure 3.

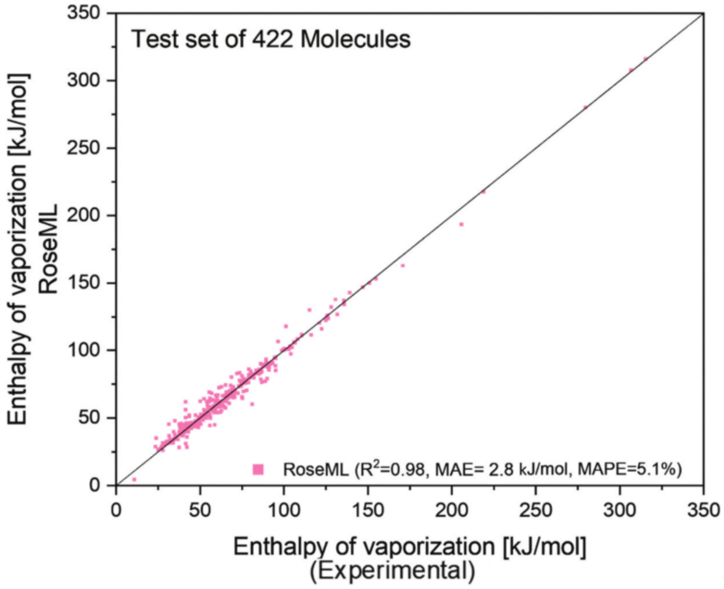


Figure 1. One test set with experimental enthalpies of vaporization plotted against the predicted values using the machine learning model referred to as "RoseML".

The model for the enthalpy of sublimation shows a lot more scattering than the enthalpy of vaporization as illustrated by the higher MAE and lower R^2 values. The reason for this could be that the dataset is smaller because less experimental values are available. The outliers circled in turquoise in Figure 3 are shown in Table 1.

Compound A is likely to be predicted with a high error because the isomeric compound 1,5-dimethyl-tetrazole is contained in the training set, which exhibits a much higher enthalpy of sublimation of 86.2 kJ/mol (Chickos and Acree 2003). Compound B is likely to be predicted to far off because in the training set of this shuffle split, there was no compound with an oxygen in an aromatic ring, which explains the poor prediction of B.

For further validation of the model, a total of five random shuffle splits were performed. The performance of the model is shown in Figure 4.

Looking at Figure 4, one can tell that there is low variance between the shuffle splits, and the correlation remained similar for all the shuffle splits, and the mean and median are close together. This is a good indicator that the model was not overfitted.

The accuracy of the selected empirical methods is discussed here. The results for the enthalpies of vaporization calculated with the Troutons rule of 1873 molecules are given in Figure 6, along with the test set of 422 molecules of the machine learning models that were not part of the training set.

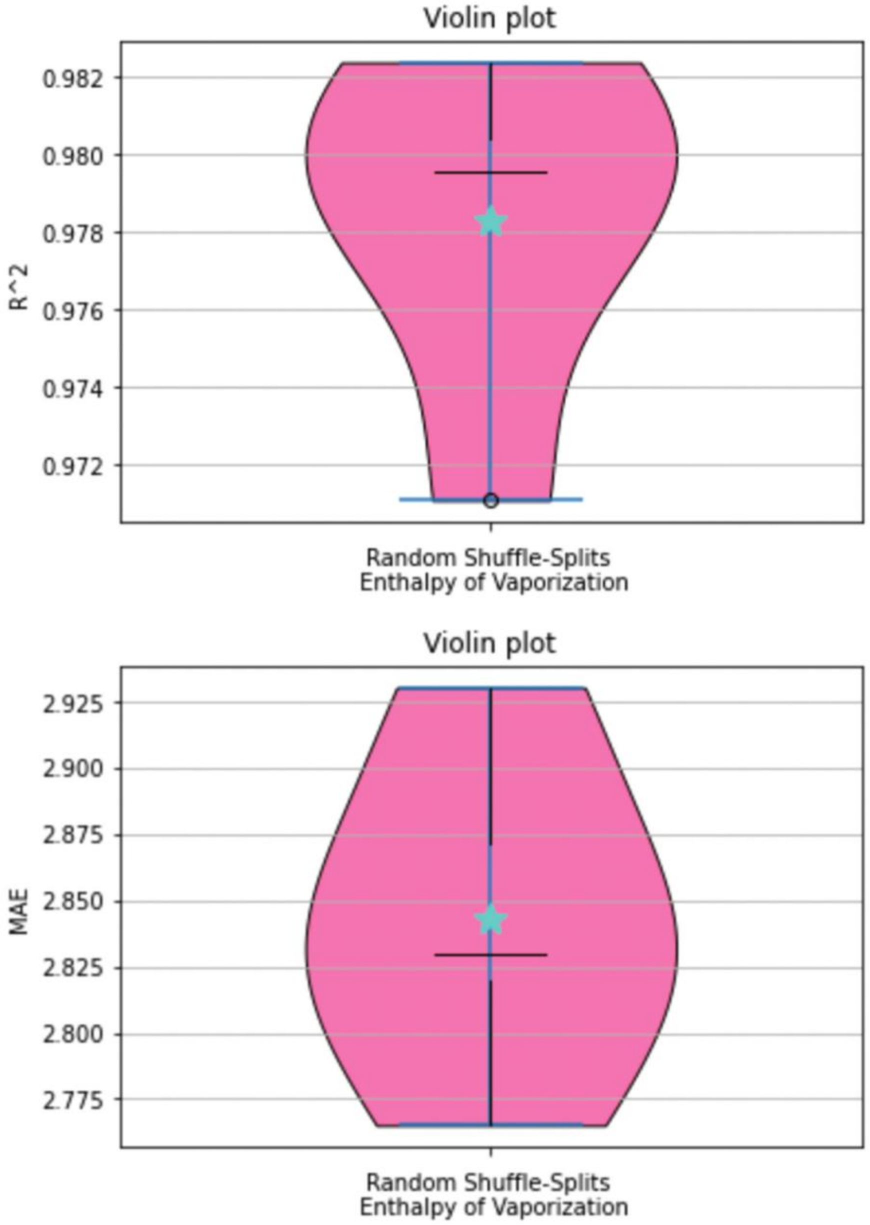


Figure 2. Boxplots of the random shuffle splits of the enthalpy of vaporization model. The mean absolute error in kJ/mol is shown at the bottom and the R2 is shown at the top. The black line shows the median, and the turquoise star shows the mean.

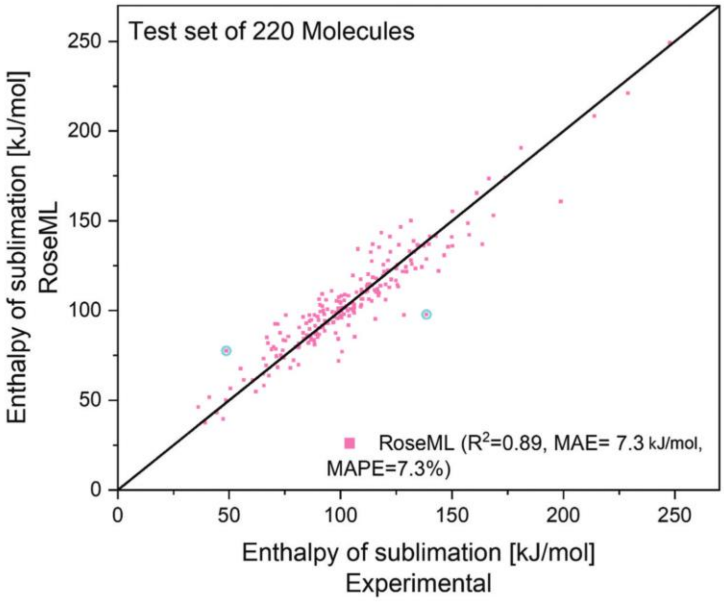
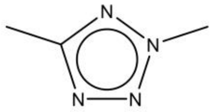
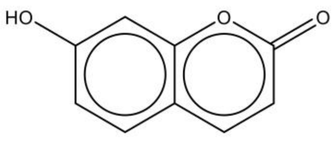


Figure 3. One test set with experimental enthalpies of sublimation plotted against the predicted values using the machine learning model referred to as "RoseML".

It is clear that the linear fit of the Trouton's rule was misfitted and the slope of the linear fit is too low (see Figure 5). As the dataset has many enthalpies of vaporization between 0 and 100 kJ/mol, the MAE is not so drastically high and the R^2 still seems to be adequate, but it is clear that it is a misfit, which just happens to correlate better for lower values. Comparing this to the machine learning model, it is clear that the correlation is much better. It is also

Table 1. Selected outliers with the experimental and predicted enthalpy of sublimation.

	Ref.	Selected outliers in the test set.	ΔH_{sub}[kJ/mol] experimental	ΔH_{sub}[kJ/mol] predicted
A	(Imamura, Murata, and Sakiyama 1988)		48.7	77.5
B	(Sousa, Matos, and Morais 2011)		133.6	97.5

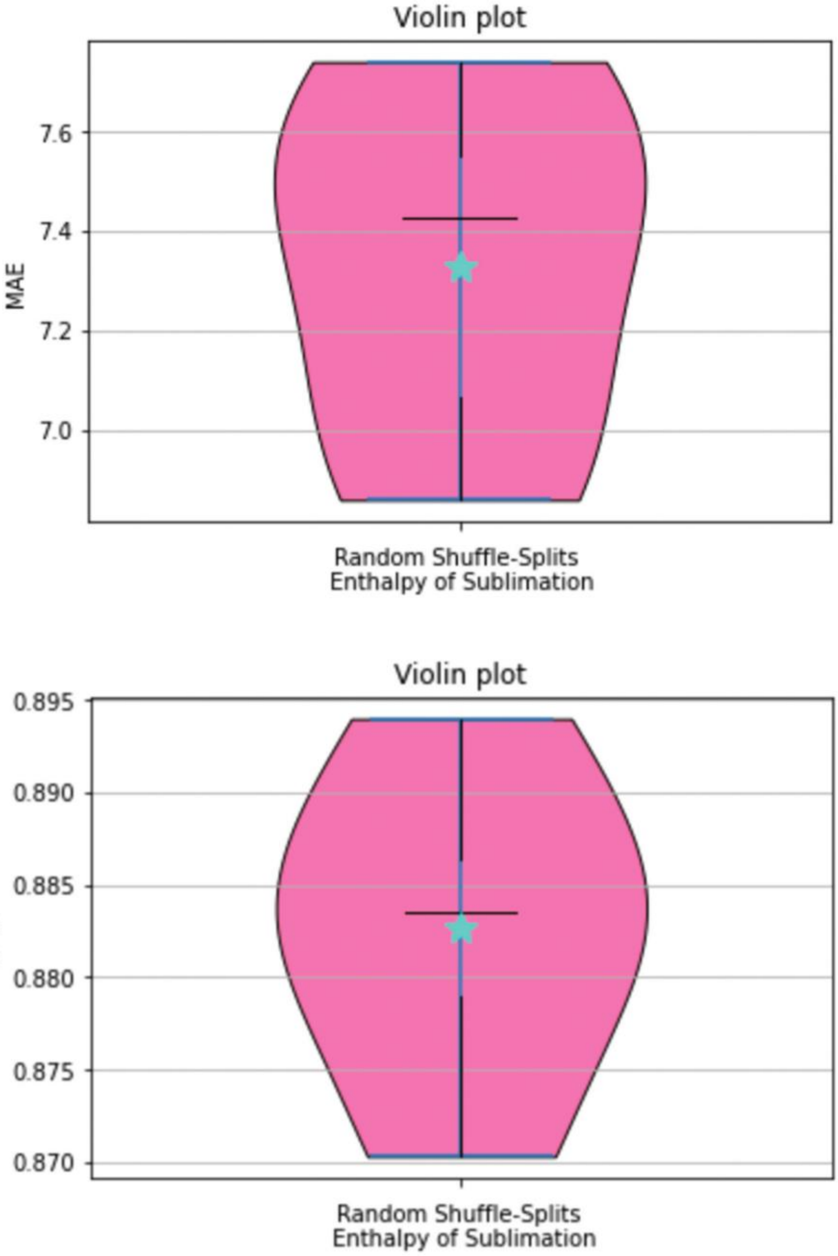


Figure 4. Boxplots of the random shuffle splits of the enthalpy of sublimation model. The mean absolute error in kJ/mol is shown at the top and the R2 is shown at the bottom. The black line shows the median, and the turquoise star shows the mean.

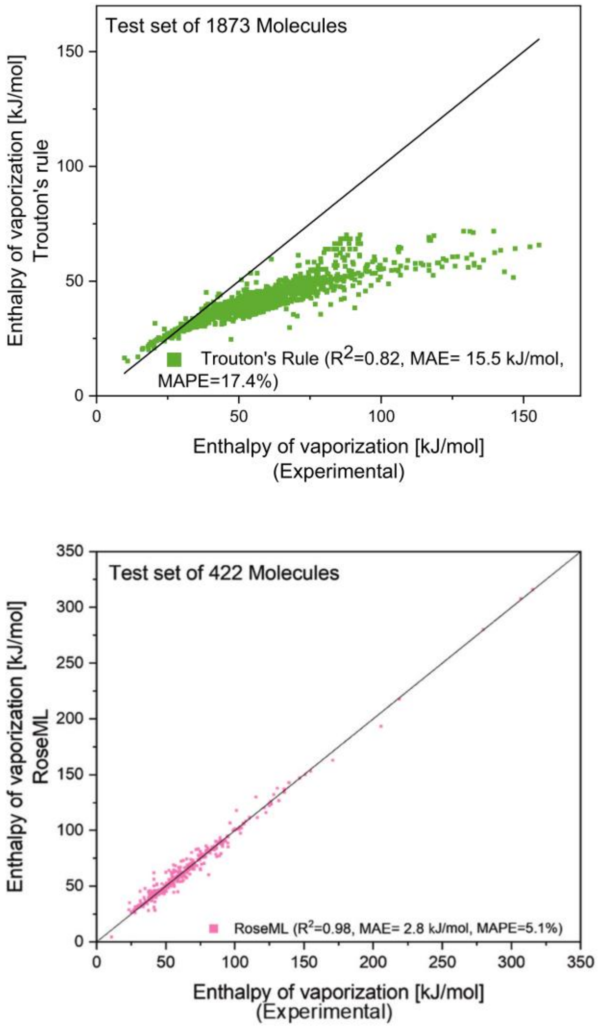
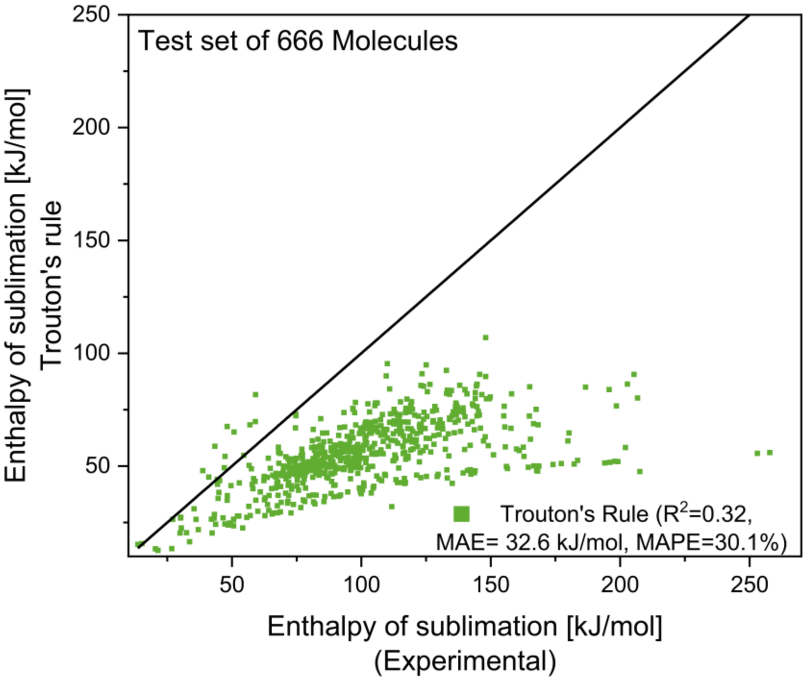


Figure 5. The enthalpies of vaporization predicted with Trouton's rule (top) and the machine learning (bottom)

important to keep in mind that as machine learning model only relies on the structural formula and does not need a boiling point, which means no prior experiments are necessary to determine the boiling point for new compounds using the models presented in this paper.

The enthalpy of vaporization varies little for most materials in the solid state. The enthalpy of sublimation, however, varies over a nontrivial range among most materials as shown in Figure 1(a) and (b). The Trouton-rule and it's reparametrized version both require on a melting point, which oftentimes cannot be obtained for numerous energetic materials, as they decompose before they melt



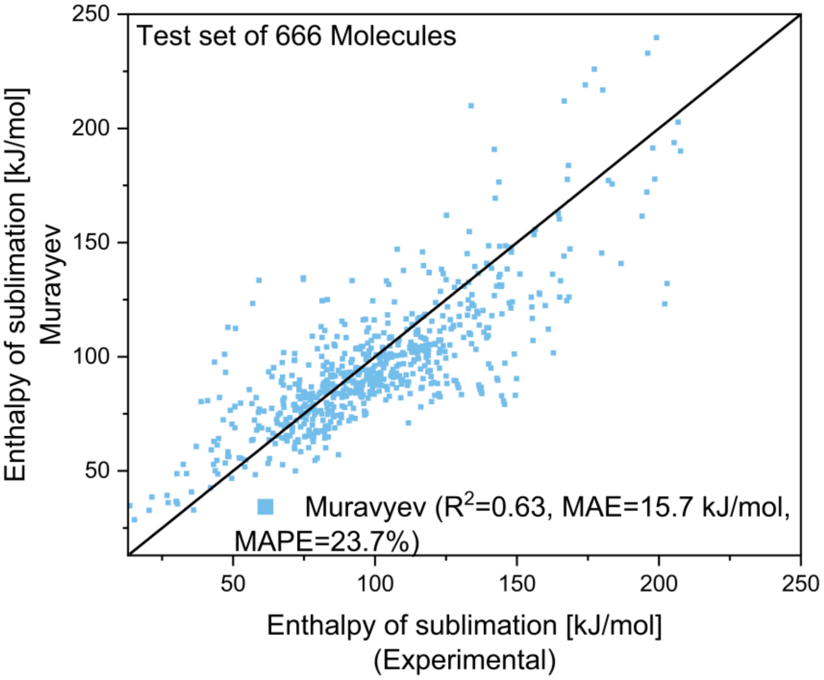


Figure 6. The enthalpies of sublimation predicted with Trouton's rule (Top right) and Muravyev's (Top left) model and one of the shuffle splits peformed with the enthalpy of sublimation test set (bottom).

(Klapötke 2021a, 2021b, 2021c). This means that the melting point would be higher than the decomposition temperature, which leads to underestimation of the enthalpy of sublimation. Therefore, the two selected models were tested on 666 molecules with melting points, where no molecules decomposed. The results are given in Figure 6, along with the 220 molecules in the test set of the machine learning models.

At first glance, it is clear to see that the machine learning model performed the best. With a low error and a higher R^2 than the empirical models. Also, the MAE is much lower across all shuffle splits (Figure 4). When comparing the models, it must be considered that Muravyev's model predicts the enthalpy of sublimation more than doubly as high as the experimental value in some cases. This means that if the model is used to convert a calculated enthalpy of formation in the gas phase into solid state, the value would be over corrected by so much that the value would be better left of in the gas phase. Therefore, scientist should rely on the Trouton-rule, even if it may have a much lower R^2-value and higher deviation because the gas phase enthalpy of formation would at least be consistently under-corrected meaning it always gets closer to the solid-state value. While when using the other empirical approach, one cannot be certain if the corrected value is closer to the solid-state enthalpy of formation. It is also important to note that as stated in the publication of the model, these models become even more imprecise if the decomposition temperature is used, if no melting point is available (Muravyev et al. 2021). This is not the case for the presented machine learning models.

Conclusion

The models presented in this paper could solve the problem of quickly assessing the enthalpies of sublimation and vaporization, if they decompose before melting or boiling. As an example how the work could benefit future works, one could take a recent example from the past into: It could also have been employed for answering the question of TKX-50's performance, as it decomposes before melting and the Trouton rule could not be applied properly, which might have been causing an overestimation of the enthalpy of formation (Huang, Shi, and Yang 2015; Klapötke, Cudziło, and Trzciński 2022). It is questionable whether quantum methods are suitable to calculate enthalpies of sublimations of compounds where it is impossible to collect experimental information accurately. Therefore, machine learning models may be more precise and reliable, if they are backed up by larger datasets of experimentally obtained data. In general, machine learning models, can easily be retrained and adjusted to new data and compound classes, which makes them attractive to use. But this raises the philosophical question, if a standardized method/model would not be better, as more comparable results are published and machine learning models should just be revalidated on new data instead of retraining them every time new data is available.

The results of this paper show that it clearly makes no sense to refine our detonation parameter predictions because the accuracy of the input data must be improved. This is most certainly not done, by refining equations for a small set of molecules, like in the case of Muravyev's model (Muravyev et al. 2021). Adjusting other parameter predictions based on these does not improve the model. Oftentimes, calculating an enthalpy of formation calculation using composite methods can take over 30 days (Wahler and Klapötke 2022b) for a single molecule, which just shows how many resources are needed. Putting this time, effort, and resources to get an accurate prediction should not be undone by using the empirical relationships discussed in this publication.

As a conclusion, one can say that the new models have numerous advantages over the empirical approaches presented in this paper. One of them being no experimental data is required, instead only a sketch of a molecule is needed to estimate the molecules properties. Hence, the already obtained experimental data can be used to reduce experimental work in the future. The other advantage is the greater accuracy than the empirical approaches. Now scientist have the option to use machine learning models for the enthalpies of vaporization and sublimation that predict the values within experimental uncertainty.

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Disclosure statement

The intellectual property of the presented machine learning models and data belongs to RoseEnergetic UG.

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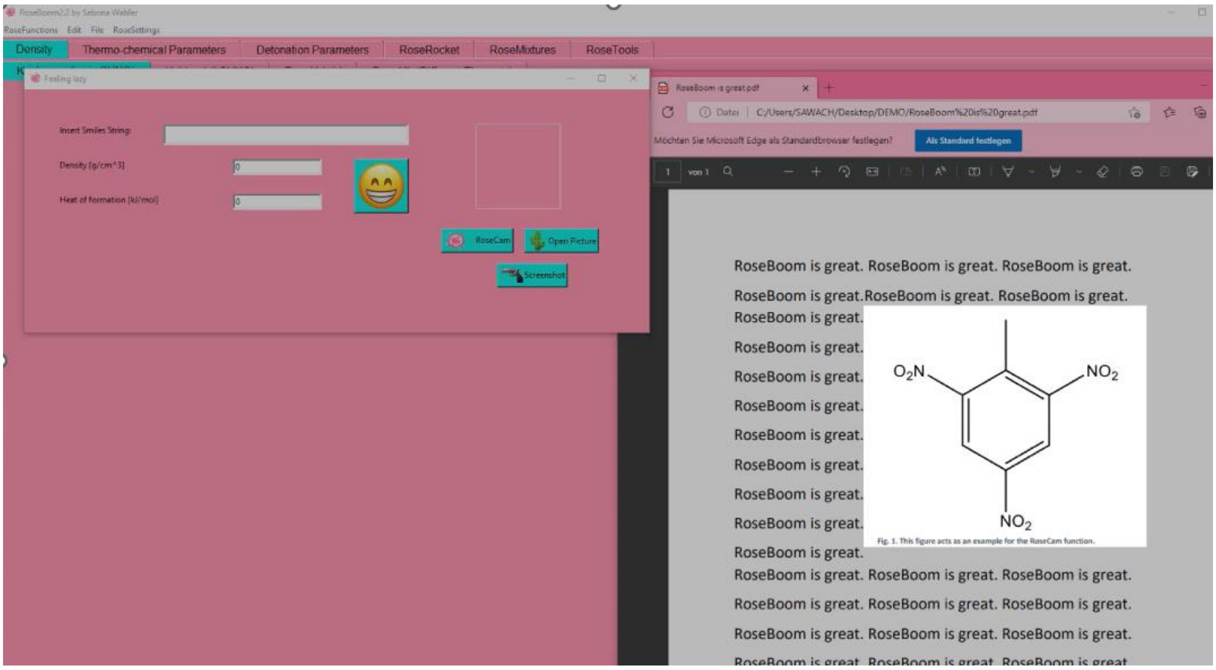
2.7 RoseBoom2.3© (“Research output software for energetic materials based on observational modelling/machine learning") – published

Author contributions

Sabrina Wahler: Development of RoseBoom©, Data collection, Project Planning, Manuscript Preparation, acquisition of funding

William G. Proud: Supervision, Manuscript Revision

Thomas M. Klapötke: Project Supervision



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Heat of formation [kJ/mol] 0

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Fig. 1. This figure acts as an example for the RoseCam function.

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Adding Machine Learning approaches to RoseBoom2.3© ("**R**esearch **o**utput **s**oftware for **e**nergetic materials **b**ased **o**n **o**bservational **m**odelling/ **m**achine learning")

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Abstract

When looking through literature, various methods are used to predict the properites of energetic materials, often with questionable precision, for key values such as the enthalpy of formation deviating by upto 200 kJ/mol. In this article artificial intelligence is used to improve the precision of values predicted by RoseBoom2.3. The programme uses values harvested from the literature and structural recognition, to convert strcuture into a machine readable format. This allows values to be calculated in a short period of time, to obtain a consistent basis for such values which is important when comparing different molecules.

Keyword: prediction of performance; computer program

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1 introduction

Recent studies using the new software RoseBoom© have stated that it can predict performance of energetic parameters of a compound before synthesis, without requring any molecule-specific experimental data or data from composite methods[1–4]. The goal is to create a tool, which can tell before a synthesis whether the compound or mixture is a promising candidate. [1,2,5] Given the range and complexity of many energtic materials it can be difficult to find the good candidates within the wide range of possible materials. This is analogous to looking for a few gold nuggets in a pile of dirt (Figure 1)

Figure 1. Metaphorical illustration of the intended use of RoseBoom©. It is supposed to act as the gold pan, when washing gold, hence searching for new energetic materials. A gold pan is an essential tool to quickly find gold in a pile of gravel.

RoseBoom© can predict the density and heat of formation based on a structural formula which can be put into a equations for the detonation parameters. A variety of methods are employed: machine learning, empirical models and a thermo-equilibirum code. Recent improvements have been made to this process by employing machine learning models, giving predictions which are within experimental uncertainty for known molecules and well-established parameters. The software combines empirical models, a thermo-equilibrium code and machine learning models, harvesting data auitomatically from the wide range of existing published data from the literature. This combined strategy makes this one of the most powerful software's for predicitve energetic material modelling.

This recalculation using data grafted from Natural Language Processing (NLP) is a promising technique when it comes to data collection and working through the extensive and ever-growing scientific literature. It can be used to quickly generate a large dataset of material properties that could further be used in training machine learning tools.[6,7] NLP seems especially promising to work through older sources, giving the knowledge hidden in them new life. It also seems like a helpful tool to work through new literature, as keeping up to date with the amount of literature published on a certain topic poses a greater challenge. Knowledge is easily accessible; however, one must keep an overview and identify promising material for which NLP tools could be employed.[8] There are, limitations, however as processing chemical structure poses a great challenge.[7] In this study Optical structure recognition tools were to convert pictures of molecules into Simplified Molecular Input Line Entry System (SMILES), focussing on new literature about nitrogen rich energetic materials[9].

Open-source tools which have the source code published. The reason for this is a concern about cyber security, especially important in the world of energetic materials. As useful as open-source tools are, they can pose a significant threat in defense research, as artificial intelligence approaches often require models to be downloaded from a server when running the source code e.g. DECIMER[10]. One approach, common in the commercial world, is to rely on paid tools, which come with a user-agreement, non-disclosure agreements and liability for data breaches.

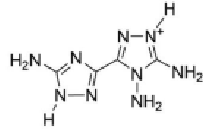
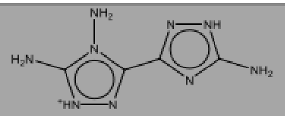
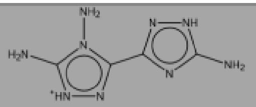
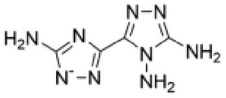
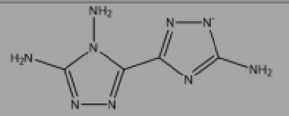
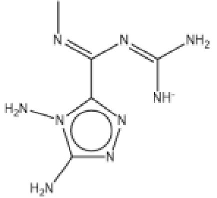
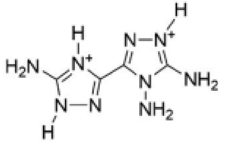
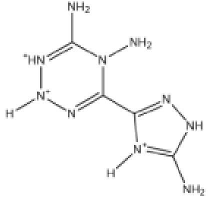
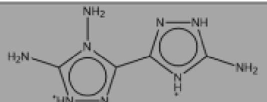
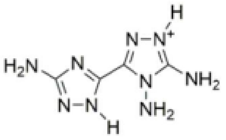
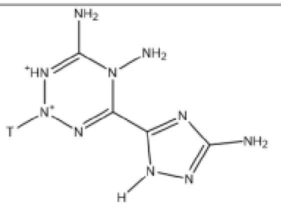
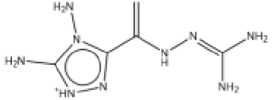
2 Computational Methods

For convenience the online version of OSRA[11] was used and compared to the DECIMER2.1[12] to convert molecular structures from three example papers containing a variety of nitrogen rich materials including triazoles, tetrazoles, azides and polymers.[13–15]

3 Results

The results obtained from recognizing molecular structures are obtained in Table 1-3. Molecules highlighted in grey were successfully recognized, molecules in white were not successfully recognized.

Table 1. Table 1. Structures recognized from “Parisi, E., Landi, A., Fusco, S., Manfredi, C., Peluso, A., Wahler, S., Klapötke, T. M., Centore, R., *Inorg. Chem.* **2021**, *60*, 16213–16222.”

	Original picture[13]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
1		C1(=NN(C(=N1)N)[3H])C2=N[N+]([NH+]=C(N2N)N)[3H]		Nc2nc(c1n[nH+]c(N)n1N)n[nH]2	
2		C1(=N[N-]C(=N1)N)C2=NN=C(N2N)N		C/N=C(\N=C(N)/[NH-])/c1nnc(N)n1N	
3		C1(=NNC(=[N+]1[H])N)C2=N[N+]([NH+]=C(N)N2N)[H]		Nc2[nH]nc(c1n[nH+]c(N)n1N)[nH+]2	
4		C1(=NC(=NN1[H])N)C2=N[N+]([NH+]=C(N2N)N)[3H]		C=C(N/N=C(N)/N)c1n[nH+]c(N)n1N	

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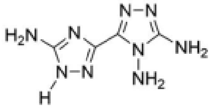
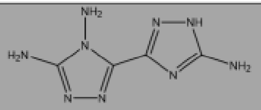
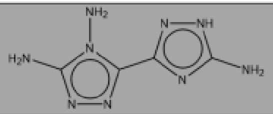
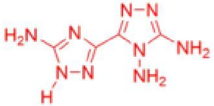
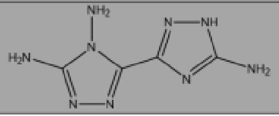
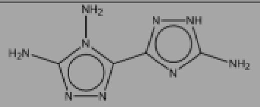
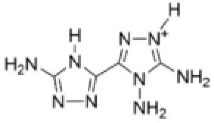
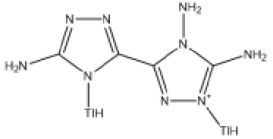
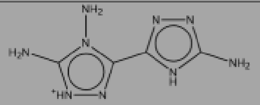
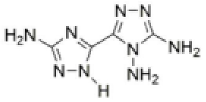
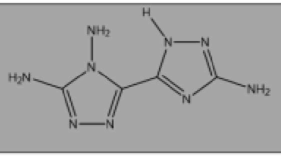
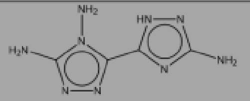
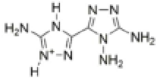
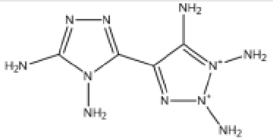
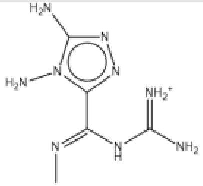
5		[3H]N1C(=NC(=N1)C2=NN=C(N2N)N)N		Nc2nc(c1nnc(N)n1N)n[nH]2	
6		C1(=NNC(=N1)N)C2=NN=C(N2N)N		Nc2nc(c1nnc(N)n1N)n[nH]2	
7		C1(=NN=C(N1[TlH])N)C2=N[N+](=C(N2N)N)[TlH]		Nc2nnc(c1n[nH+]c(N)n1N)[nH]2	
8		C1(=NC(=NN1[H])N)C2=NN=C(N2N)N		Nc2n[nH]c(c1nnc(N)n1N)n2	
9		C1(=N[N+]([N+](=C1N)N)N)C2=NN=C(N2N)N		C/N=C(NC(N)=[NH2+])/c1nnc(N)n1N	

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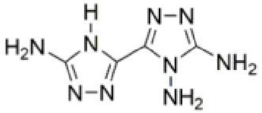
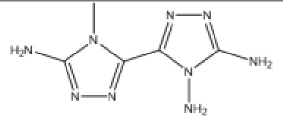
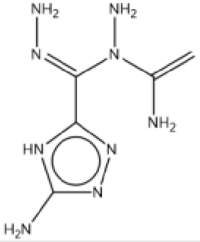
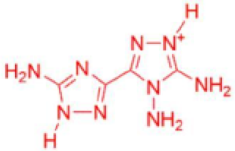
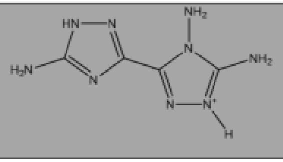
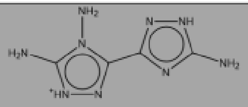
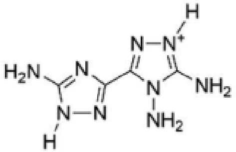
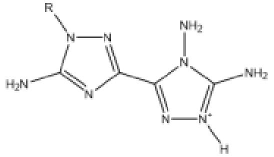
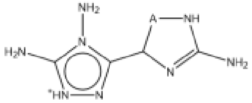
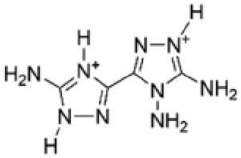
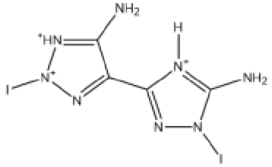
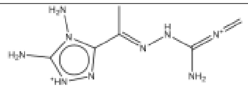
10		CN1C(=NN=C1N)C2=NN=C(N2N)N		C=C(N)N(N)/C(=N\N)c1nnc(N)[nH]1	
11		C1(=NNC(=N1)N)C2=N[N+]([H])=C(N)N2N		Nc2nc(c1n[nH+]c(N)n1N)n[nH]2	
12		C1(=NN(C(=N1)N)[R])C2=N[N+]([H])=C(N)N2N		N/C2=N/C(c1n[nH+]c(N)n1N)*N2	
13		C1(=NN(C(=[N+]1[H])N)I)C2=N[N+]([NH+]=C2N)I		C=[N+]=C(N)N/N=C(C)/c1n[nH+]c(N)n1N	

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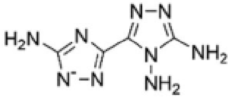
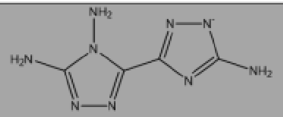
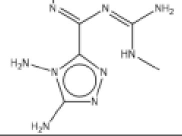
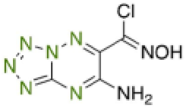
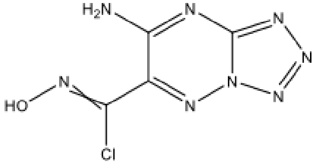
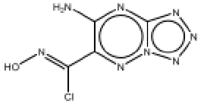
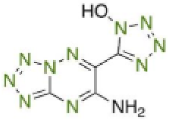
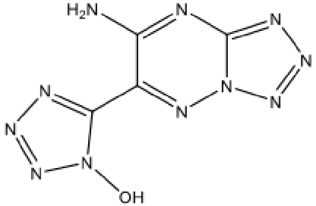
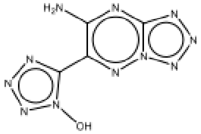
14		C1(=N[N-]C(=N1)N)C2=NN=C(N2N)N		C/N=C(\N=C(N)/NC)/c1nnc(N)n1N	

Table 2. Table 2. Molecules from “Cleveland, A. H., Imler, G. H., Snyder, C. J., Chavez, D. E., Parrish, D. A., *Propellants, Explos. Pyrotech.* **2022**, *47*, 1–7.”

	Original picture[13]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
1		C1(=NN2C(=NN=N2)N=C1N)C(=NO)Cl		Nc2nc1nnnn1nc2/C(Cl)=N/O	
2		C1(=NN2C(=NN=N2)N=C1N)C3=NN=NN3O		Nc2nc1nnnn1nc2c3nnnn3O	

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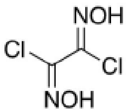
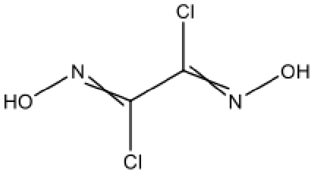
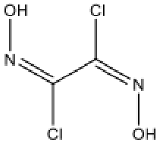
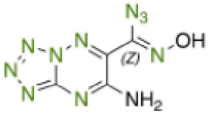
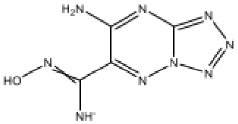
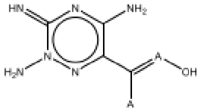
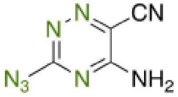
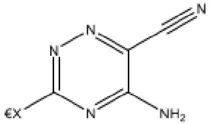
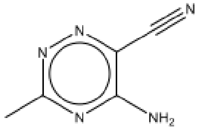
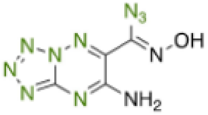
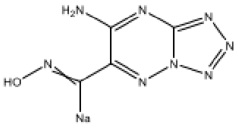
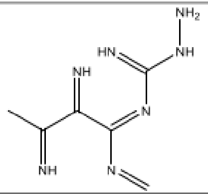
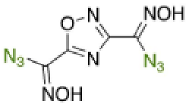
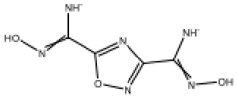
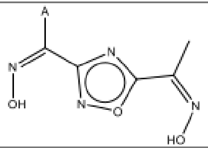
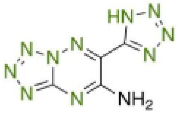
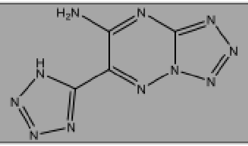
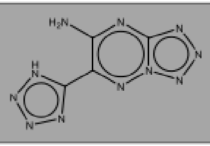
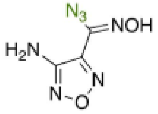
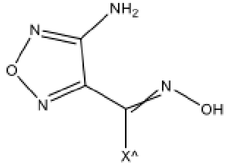
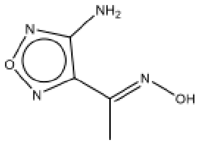
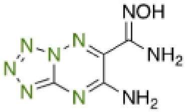
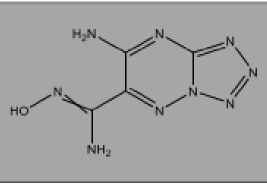
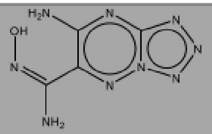
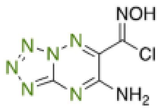
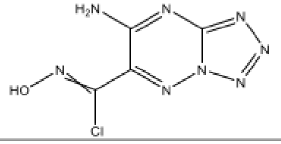
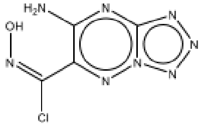
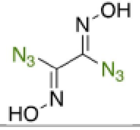
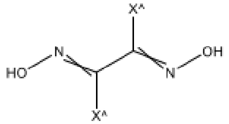
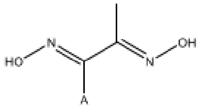
3		C(=NO)(C(=NO)Cl)Cl		O/N=C(Cl)\C(Cl)=N/O	
4		C1(=NN2C(=NN=N2)N=C1N)C(=NO)[NH-]		*/C(=*\O)c1nn(N)c(=N)nc1N	
5		C(#N)C1=NN=C(N=C1N)[X€]		Cc1nnc(C#N)c(N)n1	
6		C1(=NN2C(=NN=N2)N=C1N)C(=NO)[Na]		C=N/C(=N/C(=N)NN)C(=N)C(C)=N	
7		C1(=NOC(=N1)C(=NO)[NH-])C(=NO)[NH-]		*/C(=N/O)c1noc(/C(C)=N\O)n1	

	Original picture[13]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
8		C1(=NN2C(=NN=N2)N=C1N)C3=NN=NN3		Nc2nc1nnnn1nc2c3nnn[nH]3	
9		C1(=NON=C1N)C(=NO)[X^]		C/C(=N\O)c1nonc1N	
10		C1(=NN2C(=NN=N2)N=C1N)C(=NO)N		N/C(=N/O)c2nn1nnnc1nc2N	
11		C1(=NN2C(=NN=N2)N=C1N)C(=NO)Cl		Nc2nc1nnnn1nc2/C(Cl)=N\O	
12		C(=NO)(C(=NO)[X^])[X^]		*/C(=N\O)/C(C)=N/O	

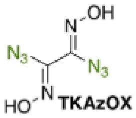
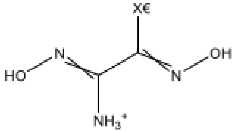
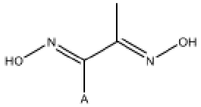
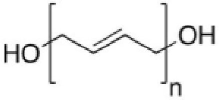
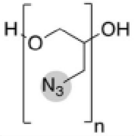
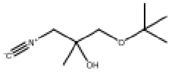
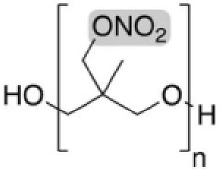
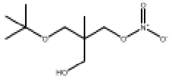
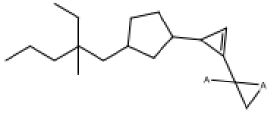
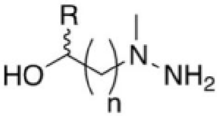
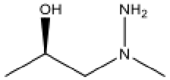
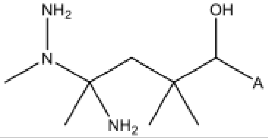
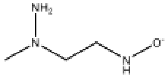
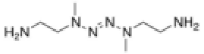
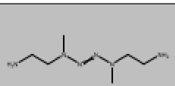
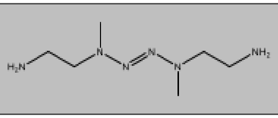
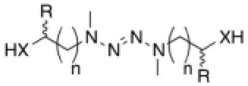
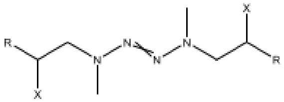
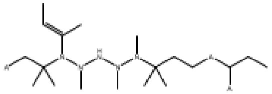
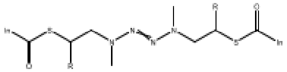
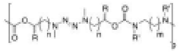
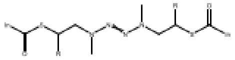
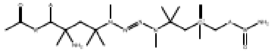
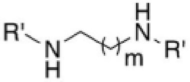
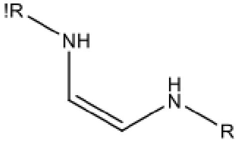
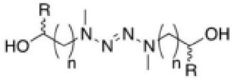
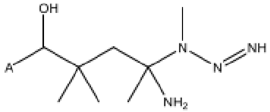
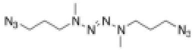
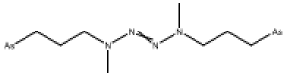
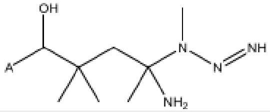
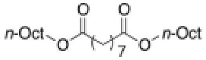
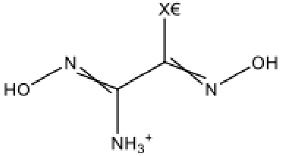
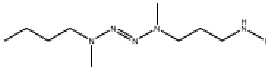
	Original picture[13]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
13	 **TKAzOX**	C(=NO)(C(=NO)[X€])[NH3+]		*/C(=N\O)/C(C)=N/O	

Table 3. Table 3. Eymann, J., Joucla, L., Jacob, G., Raynaud, J., Darwich, C., Lacôte, E., *Angew. Chemie - Int. Ed.* **2021**, *60*, 1578–1582.

	Original picture	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
1		CC(C)(/C=C/CO)O		No structure recognized	No structure recognized
2		CC(C)(C)OCC(C)(C[N+]#[C-])O		No structure recognized	No structure recognized
3		CC(C)(C)OCC(C)(CO)CO[N+](=O)[O-]		*C3(/C1=C/C1C2CCC(CC(C)(CC)CCC)C2)*C3	
4		C[C@H](CN(C)N)O		*C(O)C(C)(C)CC(C)(N)N(C)N	

	Original picture	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
5		CN(CCN[O-])N		No structure recognized	No structure recognized
6		CN(CCN)N=NN(C)CCN		CN(CCN)/N=N/N(C)CCN	
7		CN(CC([X])[R])N=NN(C)CC([X])[R]		*CC(C)(C)N(/C(C)=C/C)N(C)NN(C)N(C)C(C)(C)CC*C(*)CC	
8		CN(CC([R])SC(=O)[In])N=NN(C)CC([R])SC(=O)[In]		No structure recognized	No structure recognized
9		CC(C)(C)C(=O)OC(C)(C)CN(C)N=NN(C)CC(OC(=O)N(CC(C)(C)N(C(C)(C)C[R])[R£])[R])[R]	*Unable to display in Chemdraw*	**(*)N(*)C(C)(C)CC(C)(C)CN(*)C(=O)OC(*)C(C)(N)CC(C)(C)N(C)/N=N/N(C)C(C)(N)CC(C)(C)C(*)OC(=O)C(*)(*)C	
10		CN(CC([R])SC(=O)[In])N=NN(C)CC([R])SC(=O)[In]		*C(*C(C)=O)C(C)(N)CC(C)(C)N(C)/N=N/N(C)C(C)(C)C[C+](	

	Original picture	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
				=C)(C)C**(N)=O	
11		C(=C/N[R!])/N[R]		No structure recognized	No structure recognized
12		CN(CC(O)[R])N=NN(C)CC(O)[R].[Na+].[Na+].O.O	*Unable to display in Chemdraw*	*C(O)C(C)(C)CC(C)(N)N(C)N=N	
13		CN(CCC[As])N=NN(C)CCC[As]		*C(O)C(C)(C)CC(C)(N)N(C)N=N	
14		C(=NO)(C(=NO)[X€])[NH3+]		CCCCN(C)/N=N/N(C)CCCNI	

4 Discussion

From these tables it is clear that the current state of OSR gives patchy results, with some materials classes being identified clearly, while others are not. Taking these results in more detail and looking at Table 1, OSRA recognized one molecule more in total than DECIMER2.1. Hence Osra recognized 60% of the triazoles correctly while DECIMER2.1 only recognized 50%. From an statistical perspective the limited number of molecules chosen is not high enough to make an absolute statement on both software's, however, hits limited study illustrates the significant room for improvement.

In Table 2. both software's recognized the same molecules correctly and incorrectly. However, one must mention that DECIMER2.1 did a much better job on Molecules 6, Table 2 and Molecule 10, Table 2 because as it recognized the aromatic system. This means it is much closer to being accurate than OSRA.

Additionally, one must keep in mind, that it is much more difficult for a reader to distinguish a faulty recognition apart from a correct one, without independently reviewing the material. This defeats the reason for using automated systems and could also be considered a burden at this stage, when assembling databases.

Looking at Table 3. It becomes apparent that none of the tools worked on for depictions of polymers. Molecule 6 and 13 they are monomers, with very similar structure, the only difference in Molecule 6 there is an amine group at the end and in Molecule 13 there is an azido group. Molecule 6 was recognized properly by both software's while molecules 13 wasn't. Looking across Table 2 it becomes clear, that both software are unable to recognise azido groups if they are drawn as '-N_3 ' as is the cases in Molecules 5, 7, 9 and 12 in Table 2.

Abbreviations for molecular groups like -n-Oct (Molecule 14, Table 3) or -Im (Molecule 10, Table 3) gave wrong results, in the vast majority of cases, when recognized by the software. Commonly used conventions such as brackets symbolizing the repetitive units couldn't be processed properly. Finally, in this set OSRA showed difficulties recognizing that there were molecular structures present in some of the data used.

5 Conclusion

It turns out, that these open-source tools are rather far away to be employed for data mining and need improvement. Especially, difficult are structures which are mostly correctly recognized, but are wrong in one group or atoms. This makes it more difficult for the human eye to identify faulty results, leading to the reproduction of errors. One option to make chemical data more accessible is to start putting a computer readable representation of each molecule presented as a sketch into scientific works. Therefore, further improvements have to be made before employing these tools to recalculate a large amount of molecules using RoseBoom©.

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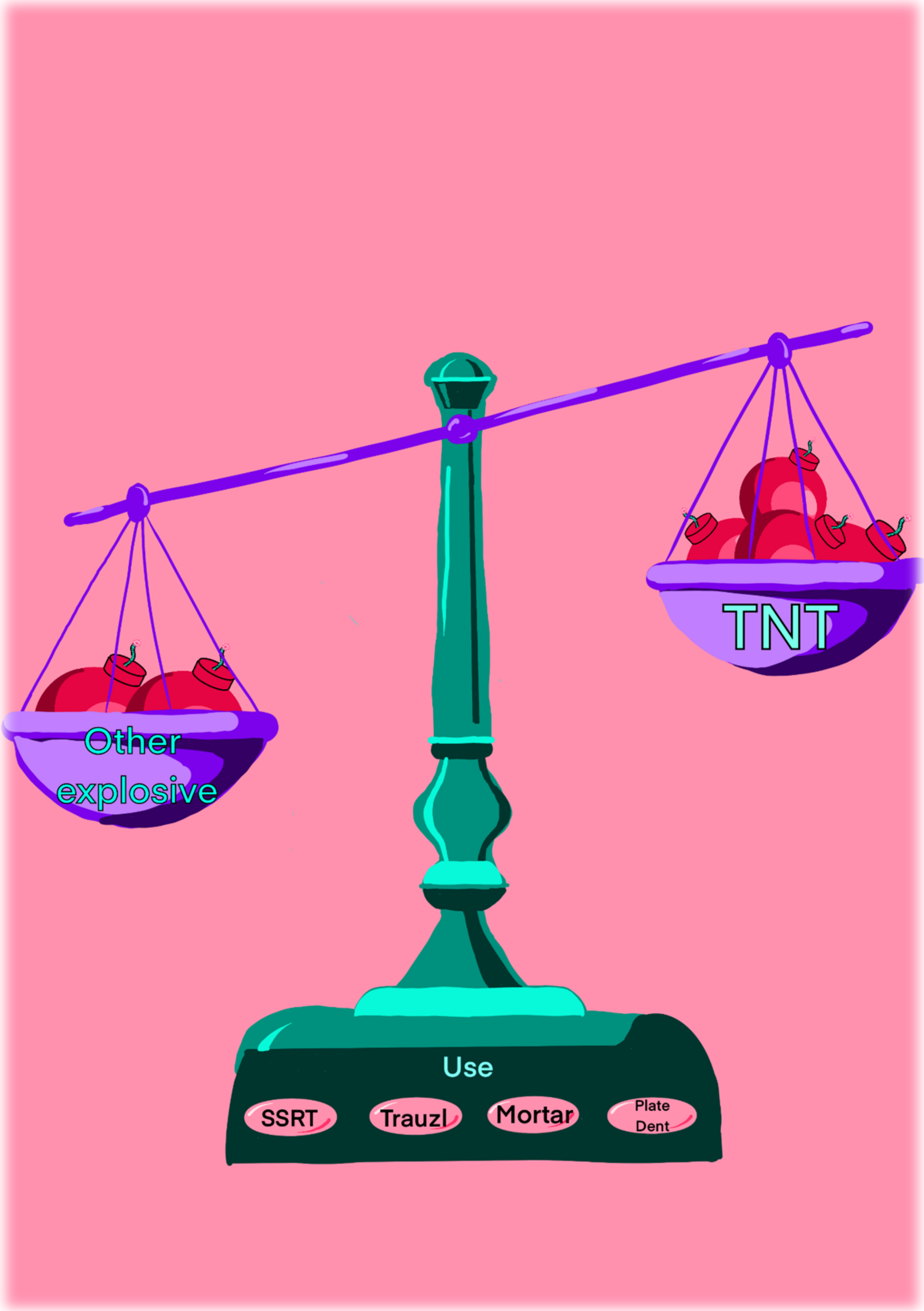
3 Investigation of TNT equivalents

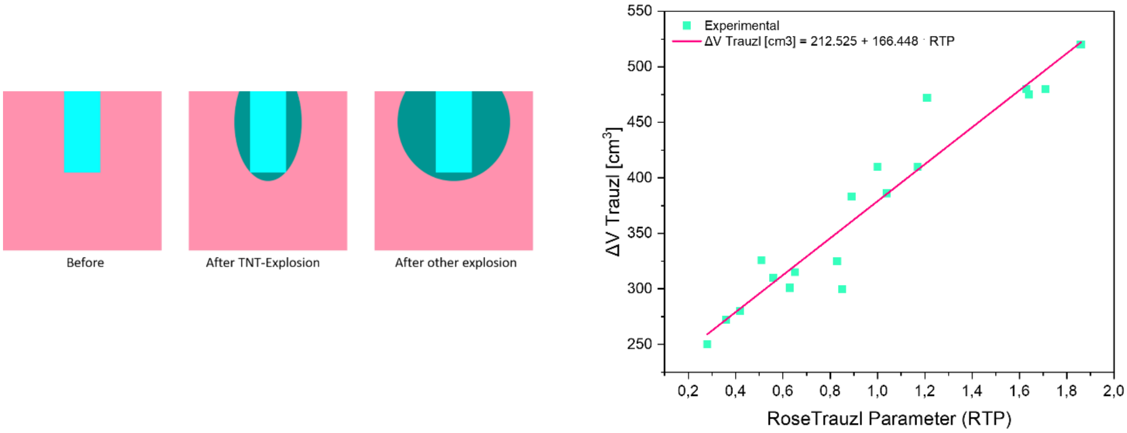


3.1 RoseTrauzl-Equation – a universal equation to predict the strength of an explosive in a Trauzl-test – published

Author contributions

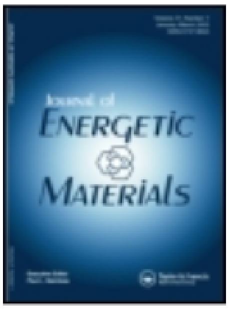
Sabrina Wahler: Development of the model, Data collection, Project Planning, Manuscript Preparation

Thomas M. Klapötke: Project Supervision



$$\text{RoseTrauzl-Parameter (RTP)} = -\,\Delta_{ex}U^{\circ\,3} \cdot V^{0} \cdot \rho^{1/9} \cdot 10^{-14}$$

$$\Delta V\ \text{Trauzl}\ [\text{cm}^3] = 212.525 + 166.448 \cdot \text{RTP}$$



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RoseTrauzl-Equation – a universal equation to predict the strength of an explosive in a Trauzl-test

Sabrina Wahler & Thomas M. Klapötke

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BRIEF REPORT

RoseTrauzl-Equation – a universal equation to predict the strength of an explosive in a Trauzl-test

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ABSTRACT
A simple correlation between the resulting volume in the Trauzl-test and the heat of detonation, density and volume of detonation gases is given in this paper. This universally applicable correlation could be used as an alternative to the Trauzl-test to determine the strength of an energetic material.

KEYWORDS
EXPLO5; detonation parameters; strength; lead block

1 Introduction

There are numerous tests to assess the power of an explosive. There is the Koenen-Test, which has to be conducted, to receive an Interim Hazard Classification and Transport Permit (Klapötke and Wahler 2021). Another standardized test is the Trauzl Test: For this, a lead block with a hole is filled with 10 g of explosive. After the ignition of the explosive, the volume of the resulting cavity is measured with sand (Figures 1 and 2) (Klapötke 2019).

Many attempts to predict the outcome of such tests have been made, however very few were done to predict the outcome of the Trauzl-test. Namely, by Keshavarz *et al.* correlating the outcome of the Trauzl-test to different molecular moieties occurring in molecules (Jafari et al., 2015). A different and simpler approach has been published by Afanasenkov correlating the strength of an explosive measured by a Trauzl-test in relation to Ammatol, to the heat of detonation and the volume of detonation gases (Afanasenkov 2004). But this correlation ignores the density of a compound which should be considered when determining its strength, which was shown by the Koenen-parameter (Klapötke and Wahler 2021). Also, the brisance is defined by equation 1(Klapötke 2019):

$$\mathrm{B} = \rho.\mathrm{F}\ \mathrm{VoD} \tag{1}$$

Where the force F of an energetic material is calculated by the general equation of state, and the density of the material and the detonation velocity is accounted for (Klapötke and Wahler 2021). Hence, it might be less precise

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Before After TNT-Explosion After other explosion

Figure 1. Schematic representation of the Trauzl-test: Lead block (color: Baker-Miller-Pink), cavity filled with explosive (color: turquoise), hole additional to the cavity filled with explosive (color: petroleum green).

Figure 2. Lead block cut in half after the Trauzl-test.

to only consider the heat of detonation and the volume of detonation gases like Afanasenkov (Afanasenkov 2004).

2 Results

Plotting the Koenen parameter K (Klapötke and Wahler 2021) against the volume of the cavity in the Trauzl test showed very little correlation. Therefore, the RoseTrauzl-Parameter (RTP) is introduced, which is shown in equation 2:

$$\mathrm{RoseTrauzl} - \mathrm{Parameter}\ (\mathrm{RTP}) = -\ \Delta\ \mathrm{ex}U^{\circ 3}\, V^{0}\, \rho^{1/9}\, 10^{-14} \tag{2}$$

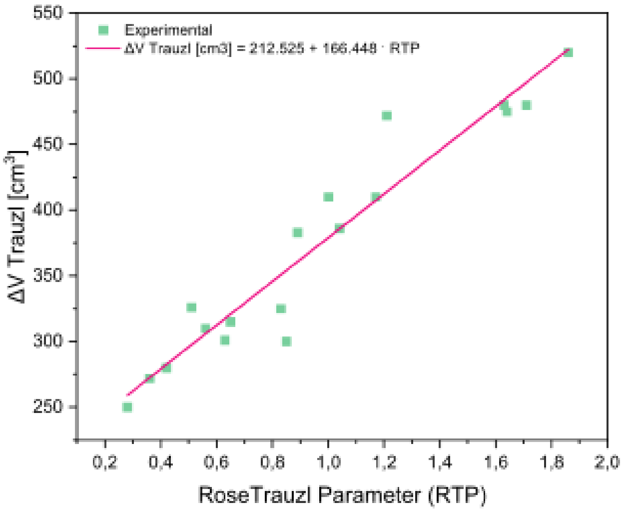

Figure 3. ΔV Trauzl [cm3] plotted against the RoseTrauzl parameter (RTP).

With this RoseTrauzl-Parameter, where the heat of detonation – $\Delta_{ex}U°$[kJ/kg] to the power of three, is multiplied by the ninth root of the density [g/cm^3] and by the Volume of detonation gases V^0 [L/kg] it is now possible obtain an estimation of the resulting Volume in the Trauzl-test with equation 3:

$$\Delta V\ \text{Trauzl}\ \left[\text{cm}^3\right] = 212.525 + 166.448\ \text{RTP} \tag{3}$$

The correlation is fitted very well by a linear function with a coefficient of determination of $R^2 = 0.92$ and a Pearson value of 0.96. The fitted plot is shown in Figure 3.

$-\Delta_{ex}U^{\circ\ 3} \cdot V^0 \cdot \rho^{1/9} \cdot 10^{-14}$.

Overall, the scattering could also be considered experimental uncertainties as there are a number of possible errors that can occur when measuring the Trauzl-test.

3 Computational Details

All calculations were carried out with the thermochemical equilibrium code EXPLO5 (version 6.05.04) and the densities and heat of formation were taken from the EXPLO5 database (Tables 1 and 2) (Suceska 2021). The heats of detonation ($-\Delta_{ex}U°$) and volumes and detonation gases (V^0) from EXPLO5 were used in the calculation of the RoseTrauzl-Parameter (RTP) along with the densities and heat of formations taken form the EXPLO5 database.

1. DNB: 1,3-dinitrobenzene, 2. Hexyl: hexanitrodiphenylamine, 3. HNS: hexanitrostilbene, 4. HMX: octogen, 5. RDX: hexogen, 6. PETN: nitropenta, 7. PA: picric acid, 8. TNT: trinitrotoluene 9. UN: uronium nitrate. 10. DDNP: 6-Diazo-2,4-dinitro-2,4-cyclohexadien-1-one, 11. AP: Ammonium picrate, 12.

Table 1. The experimental volumes in the Trauzl-test (ΔV Trauzl), the heats of detonation ($-\Delta_{ex}U°$), the heats of formation, densities and volumes of detonation gases used in the calculation of the RoseTrauzl-Parameter (RTP) in the training set.

	Acronym	Lit.	ΔV Trauzl [cm^3]	$-\Delta_{ex}U°$ [kJ/kg]	$\Delta H°_f$ [kJ/mol]	ρ [g/cm^3]	V^0 [L/kg]	RoseTrauzl-Parameter (RTP)	ΔV RoseTrauzl [cm^3]
1	DNB	(Jafari et al., 2015,Suceska 2001)	250	3567	−36.0	1.58	589	0.28	262
2	Hexyl	(Jafari et al., 2015,Suceska 2001)	325	4995	+41.4	1.77	626	0.83	354
3	HNS	(Jafari et al., 2015,Suceska 2001)	301	4612	+78.3	1.74	600	0.63	320
4	HMX	(Jafari et al., 2015,Suceska 2001)	480	5837	+74.8	1.905	763	1.63	487
5	RDX	(Jafari et al., 2015,Suceska 2001)	475	5807	+79.1	1.806	782	1.64	488
6	PETN	(Jafari et al., 2015,Suceska 2001)	480	5995	−533.66	1.778	743	1.71	500
7	PA	(Jafari et al., 2015,Suceska 2001)	315	4604	−216.34	1.767	629	0.65	324
8	TNT	(Jafari et al., 2015,Suceska 2001)	300	5033	−63.2	1.654	633	0.85	357
9	UN	(Jafari et al., 2015,Suceska 2001)	272	3348	−546.7	1.66	910	0.36	275
10	DDNP	(Jafari et al., 2015,Suceska 2001)	326	4229	60	1.63	637	0.51	300
11	AP	(Jafari et al., 2015,Suceska 2001)	280	3869	−387	1.72	680	0.42	285
12	NG	(Jafari et al., 2015,Suceska 2001)	520	6092	−370.8	1.6	782	1.86	525
13	DEGDN	(Jafari et al., 2015,Suceska 2001)	410	4866	−430	1.39	837	1.0	382
14	DINA	(Jafari et al., 2015,Suceska 2001)	472	5174	−329	1.49	833	1.21	417
15	EDNA	(Jafari et al., 2015,Suceska 2001)	410	5029	−104	1.75	862	1.17	410
16	TNB	(Jafari et al., 2015,Suceska 2001)	325/386	5256	24	1.73	676	1.04	389
17	TNA	(Jafari et al., 2015,Suceska 2001)	310	4333	−100	1.76	646	0.56	309
18	2,2-NP	(Jafari et al., 2015,Suceska 2001)	383	4621	−189	1.30	873	0.89	364

Table 2. The experimental volumes in the Trauzl-test (ΔV Trauzl), the heats of detonation ($-\Delta_{ex}U°$), the heats of formation, densities and volumes of detonation gases used in the calculation of the RoseTrauzl-Parameter (RTP) in the test set.

	Acronym	Lit.	ΔV Trauzl [cm^3]	$-\Delta_{ex}U°$ [kJ/kg]	$\Delta H°_f$ [kJ/mol]	ρ [g/cm^3]	V^0 [L/kg]	RoseTrauzl-Parameter (RTP)	ΔV RoseTrauzl [cm^3]
1	PZhV-20	(Afanasenkov 2004)	278	4207	−340.5	1.71	979	0.77	344
2	MF*	(Headquarters 1971)	153	2013	267.8	4.42	212	0.02	219
3	Black powder*	(Lorimer 1946)	180	2489	−299.7	0.87	382	0.06	225

NG: Nitroglycerin, 13. DEGDN: Diethyleneglycoldinitrate, 14. DINA: Dioxyethylnitraminedinitrate, 15. EDNA: Ethylene dinitramine, 16. TNB: 1,3,5-Trinitrobenzene, 17. TNA: 2,4,6-Trinitroaniline, 18. 2,2-NP: 2,2-dinitropropan.

1) PZhV-20: 80%/20% Ammonium nitrate/Trinitrotoluene 2) MF: Mercury fulminate 3) Black powder: KNO_3:74%/Sulfur:10.4%/Charcoal:15.6%

* Calculated from equivalents given in the corresponding publication

4 Discussion

Overall, the results obtained with the RoseTrauzl-equation are very satisfying, especially considering the high experimental uncertainty that comes with it. The compounds and composition in test set of this study were selected to be as far as possible away from the training set in terms of density and elemental composition. This gives confidence, that the model can universally describe the strength of an explosive.

Even if empirical equations usually are not meant to replace proper experiments, in the case of the Trauzl-test the RoseTrauzl-equation could or rather should replace a Trauzl test. Anyone who has hands on experience with Trauzl tests knows that it is very difficult to melt the large amount of lead and during tests the lead block may crack, which means that it is not possible to determine the exact volume. Also, when one melts a large amount of lead, in the laboratory, it is difficult to ensure that all of the lead is melted. Another problem arises when no proper tempering program is used to cool down materials: When cooling the lead at different cooling rates, it is impossible to ensure unified conditions for every test, unlike with the Koenen test where one buys the steel sleeves. The tempering of a material is crucial for its mechanical properties, as shown in numerous studies on other materials (Headquarters 1971; Lorimer 1946; Luo et al. 2010, Matsuda et al., 2013). With bad tempering conditions, one may get material defects or varying crystallinity which lead to errors because the ductility differs and/or the before mentioned cracking of the lead block. Since the Trauzl-test is usually used to compare the strength of different explosives, one should consider relying on a calculated uniform value and not an experimental value which is not uniform with current techniques. Therefore, to predict the TNT-equivalents the RoseTrauzl-Equation should be used instead of performing a Trauzl-test. This is also why the density of a material should be considered in this correlation. Even if the contribution is rather low, ranging from 3% to 7% in the dataset presented in this study, it still has an impact on the prediction and is used to fine tune the predictions. In the future, this correlation should be embedded into a computer program like the "Research output software for energetic materials based on observational modelling" (RoseBoom)(Klapötke and Wahler 2022; Wahler 2022; Wahler and Klapötke 2022a, 2022b) to allow maximum userfriendliness.

Disclosure statement

No potential conflict of interest was reported by the authors.

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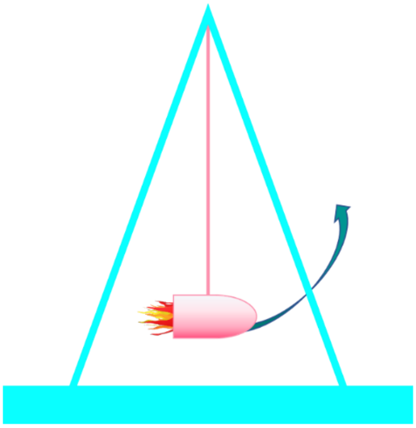
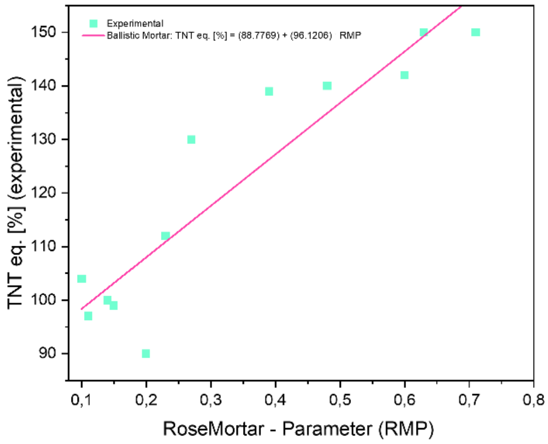
3.2 RoseMortar-Equation – a universal equation to predict the strength of an explosive in a ballistic mortar test – published, Most Viewed May 2023

Author contributions

Sabrina Wahler: Development of the model, Data collection, Project Planning, Manuscript Preparation

Thomas M. Klapötke: Project Supervision





$$\textbf{RoseMortar-Parameter (RMP)} = -\Delta_{ex}U^{\circ\,3} \cdot V^{0} \cdot \rho^{1/3} \cdot p_{c\text{-}j} \cdot 10^{-17}$$

$$\textbf{Ballistic Mortar: TNT eq. [\%]} = (88.7769) + (96.1206) \cdot \text{RMP}$$

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ROSEMORTAR EQUATION – A UNIVERSAL EQUATION TO PREDICT THE STRENGTH OF AN EXPLOSIVE IN A BALLISTIC MORTAR TEST

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A facile correlation between the resulting volume in the ballistic mortar test and the heat of detonation, density, and volume of detonation gases is presented. This correlation can be used as an alternative to the Ballistic Mortar to determine the strength of an energetic material, which describes the energy it can release.

KEY WORDS: *detonation parameters, strength, ballistic mortar, empirical correlation*

1. INTRODUCTION

There are numerous tests to assess the strength of an explosive, which is important when comparing the power of different explosives, as this is the amount of energy released by an explosive (Industries Limited Imperial Chemical, 1956). There is the Koenen test, which is a compulsory test to receive an Interim Hazard Classification and Transport permit. The Trauzl test is used to determine the TNT equivalent of an explosive (Klapötke and Wahler, 2021; Afanasenkov, 2004). In the Ballistic Mortar test, a pendulum is filled with an explosive, which is then ignited. The height of the pendulum beat is measured, from which the TNT equivalent is determined (Fig. 1).

When the explosive is ignited, the mortar swings upward in a circular motion. The deflection angle is measured, by which the height of the pendulum beat is indicated. This deflection angle is used to determine the TNT equivalent (USAMC, 1971).

Approaches to approximate the strength of an explosive have been made by Keshavarz and Seif (2013), where the power is correlated to different molecular moieties in a molecule. Generally, this approach of correctional group methods comes with the problem that only a limited number of molecules can be described, which makes it difficult to apply them to new compound classes because they cannot account for these new groups. The correlation given by Keshavarz and Seif (2013) shows a correlation coefficient of 0.80, especially when considering that it does not require an enthalpy of formation or density. But considering that a ballisitic mortar test is usually of interest after a material has been thoroughly investigated and synthesized, more in-depth information than just the structural formula is usally needed for the compound of interest.

2150–766X/22/$35.00

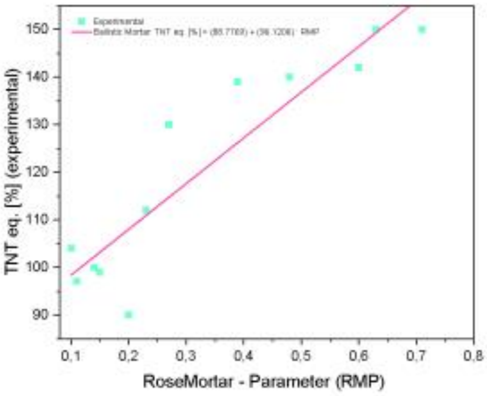

FIG. 2: TNT equivalents plotted against the RMP

TABLE 1: The TNT equivalents in the ballistic mortar test, the heats of detonation ($-\Delta_{ex}U$), the heats of formation, densities and volumes of detonation gases, and the detonation parameters used in the calculation of the RMP (USAMC, 1971; Suceska, 2001)

	Acronym	**TNT eq. [%]**	$-\Delta_{ex}U$ **[kJ/kg]**	ΔH_f **[kJ/mol]**	ρ **[g/cm^3]**	V^0 **[L/kg]**	$p_{c\text{-}j}$ **[kbar]**	**RMP**
1	HMX	150	5837	+74.8	1.905	763	378	0.71
2	RDX	150	5807	+79.1	1.806	782	336	0.63
3	PETN	142	5995	–533.66	1.778	743	308	0.6
4	PA	112	4604	–216.34	1.767	629	308	0.23
5	DDNP	97	4229	60	1.63	637	191	0.11
6	AP	99	3869	–387	1.72	680	308	0.15
7	NG	140	6092	–370.8	1.6	782	234	0.48
8	DEGDN	90	4866	–430	1.39	837	190	0.2
9	TNA	100	4333	–100	1.76	646	221	0.14
10	Tetryl	130	5144	33.6	1.73	671	249	0.27
11	NGu	104	3361	–39	1.44	1002	228	0.1
12	EDNA	139	5029	–104	1.75	862	295	0.39
13	DATB	100	4134	–118	1.84	656	245	0.14

(1) HMX: octogen, (2) RDX: hexogen, (3) PETN: nitropenta, (4) PA: picric acid, (5) DDNP: 6-Diazo-2,4-dinitro-2,4-cyclohexadien-1-one, (6) AP: ammonium picrate, (7) NG: nitroglycerine, (8) DEGDN: diethylene glycol dinitrate, (9) TNA: 2,4,6-Trinitroaniline, (10) tetryl, (11) NGu: guanidinium nitrate, (12) EDNA: ethylene dinitramine, (13) DATB: 1,3-Diamino-2,4,6-Trinitrobenzene

rich and highly sensitive 1-Diazidocarbamoyl-5-azidotetrazole (C_2N_{14}) (Klapötke et al., 2011) and the even more sensitive and nitrogen-richer 2,2′-Azobis(5-azidotetrazole) (C_2N_{16}) (Benz et al., 2022). These compounds are so sensitive, one can barely handle them without ignition. But thanks to the RoseMortar equation, their TNT equivalents can be approximated (Table 2).

This proves how the RoseMortar equation can provide knowledge about a compound which otherwise would not have been accessible.

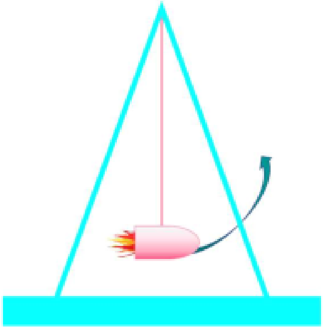

FIG. 1: Schematic representation of a ballistic mortar

Therefore, the aim of this study is to provide a better equation with a higher correlation coefficient, even if it involves parameters that need to be predicted using other methods.

2. RESULTS

Plotting the Koenen parameter K (Klapötke and Wahler, 2021) against the results of the ballistic mortar tests, very little correlation is shown. As the ballistic mortar is a measure for the energy release of an explosive, the heat of detonation must be considered. Therefore, the RoseMortar parameter (RMP) is introduced, which is given in Eq. (1):

$$\text{RMP} = -\Delta_{ex}U^3 \times V^0 \times \rho^{1/3} \times p_{c\text{-}j} \times 10^{-17} \tag{1}$$

where $\Delta_{ex}U$ [kJ/kg] is the heat of detonation, ρ is the density [g/cm^3], $p_{c\text{-}j}$ is the detonation pressure [kbar], and V^0 is the volume of detonation gases [L/kg]. With this RMP, it is now possible to obtain an estimation of the resulting TNT equivalents in the ballistic pendulum with Eq. (2):

$$\text{Ballistic mortar: TNT eq. [\%]} = (88.7769) + (96.1206) \times \text{RMP} \tag{2}$$

The correlation is fitted by a linear function with a coefficient of determination of $R^2 = 0.86$ and a Pearson value of 0.92. The fitted plot is shown in Fig. 2.

3. COMPUTATIONAL DETAILS

All calculations were carried out with the thermochemical equilibrium code EXPLO5 (version 6.05.04), and the densities and heat of formation were taken from the EXPLO5 database (Table 1) (Suceska, 2021).

4. DISCUSSION

It is important to have good approximations of the outcome of large-scale tests for energetic compounds. Not only does this allow scientists to approximate the strength of an explosive before synthesis, but it also enables scientists to approximate the strength of explosives that cannot be synthesized on a larger scale because of their high sensitivity. This is of academic interest but also of technical importance when substituting explosives. A perfect example for this is the nitrogen-

TABLE 2: The TNT equivalents in the ballistic mortar test calculated with the RoseMortar equation of C_2N_{16} (Klapötke et al., 2011) and C_2N_{14} (Benz et al., 2022), the heats of detonation ($-\Delta_{ex}U$), the heats of formation, densities and volumes of detonation gases, and the detonation parameters used in the calculation of the RMP

Compound	$-\Delta_{ex}U$ **[kJ/kg]**	ΔH_f **[kJ/mol]**	**ρ [g/cm³]**	V^0 **[L/kg]**	$p_{c\text{-}j}$ **[kbar]**	**RMP**	**TNT eq. [%] with the RoseMortar equation**
C_2N_{16}	6705	1700.7	1.803	788.5	366	1.06	191%
C_2N_{14}	6632	1495.0	1.679	777.7	300	0.81	166%

5. CONCLUSION

The RoseMortar equation is a useful correlation when it comes to comparing the power of energetic materials with each other. Considering the high uncertainty of the experimental determination of the power of an explosive, one should rely on calculated values. It is nearly impossible to provide uniform conditions for the ballistic mortar test because the temperature must be standardized, as a temperature change will make the mortar expand or shrink. For safety reasons, it is often performed outside, which makes it prone to weather changes; wind especially changes the outcome. As the apparatus is usually stored outside, it will weather, meaning it collects rust and dust, which impacts the measurement. Also, the apparatus always should be properly greased, which might not be the case in practice.

In the future, scientists could rely on these models to evaluate which compounds are worth pursuing. This will save time and resources and should lead to more comparable results.

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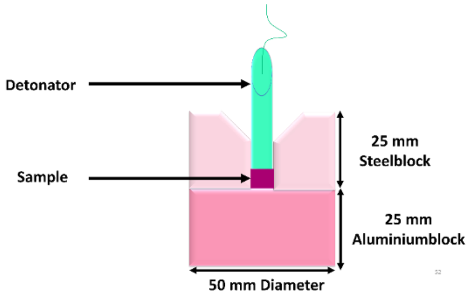
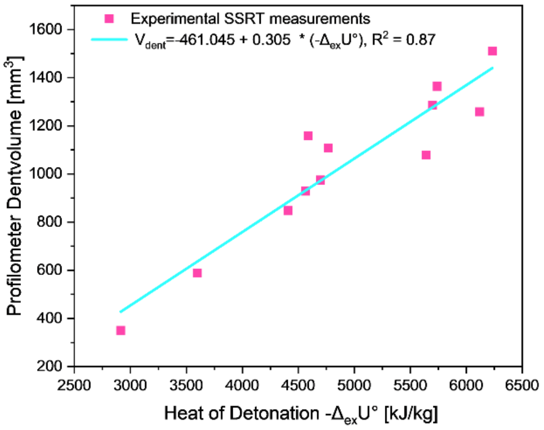
3.3 RoseSSRT-Equation – a simple linear correlation between the dent volume in a small scall-shock reactivity test and the heat of detonation –published, Most Viewed June 2023

Sabrina Wahler: Development of the model, Data collection, Project Planning, Manuscript Preparation

Thomas M. Klapötke: Project Supervision





$$\mathbf{SSRT\text{-}Dent\ [mm^3] = = (-461.045) + (0.304992) * (-\ \Delta_{ex}U^{\circ}[kJ/mol]\ )}$$

International Journal of Energetic Materials and Chemical Propulsion 22(3):1–4 (2023)

ROSE SMALL-SCALE SHOCK REACTIVITY TEST (SSRT) EQUATION—A SIMPLE LINEAR CORRELATION BETWEEN THE DENT VOLUME IN A SSRT AND THE HEAT OF DETONATION

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A simple linear correlation between the resulting dent volume in the small-scale shock reactivity test (SSRT) and the heat of detonation is presented. This correlation can be used as an alternative to the SSRT to determine the energy a material can release. It also proves that the SSRT can be replaced by a calorimetric determination of the heat of detonation.

KEY WORDS: *detonation parameters, strength, small-scale shock reactivity test, empirical correlation*

1. INTRODUCTION

Previous research efforts have been conducted with the aim of finding universally applicable correlations to approximate the strength of explosives in Koenen (Klapötke and Wahler, 2021), ballistic mortar (Wahler and Klapötke, 2022a), and Trauzl (Wahler and Klapötke, 2022b) tests. In our study, we continued the investigation of this series of correlations. In this paper, we present the Rose small-scale shock reactivity test (SSRT) equation, which can be used to predict the outcome of a SSRT using only the heat of detonation. The SSRT can be used to assess the strength of an explosive. It is a good alternative to the Trauzl test since no toxic lead is needed to perform it. Another advantage of the SSRT is that the sample size is much smaller than the required size for a Trauzl or ballistic mortar test. Hence, it is a cheaper, safer, and quicker alternative compared to the other aforementioned tests. To perform it, only a few hundred milligrams of sample are needed, compared to the Trauzl or ballistic mortar test, both of which require several hundred thousand milligrams. A schematic representation of the experimental setup for a SSRT is shown in Fig. 1 (Bauer et al., 2022).

The experimental setup consists of a steel block on top of an aluminum block. There is a hole in the steel block, which is packed at the bottom with the sample. A detonator is placed on top of the steel block. Traditionally, the resulting dent has been gravimetrically measured by filling it with sand and then weighing the sand (Klapötke, 2019). However, this method leads to rather large measurement errors. Therefore, a recent study was conducted to obtain uniform measurements using a profilometer (Bauer et al., 2022), which was used as a training set in this study.

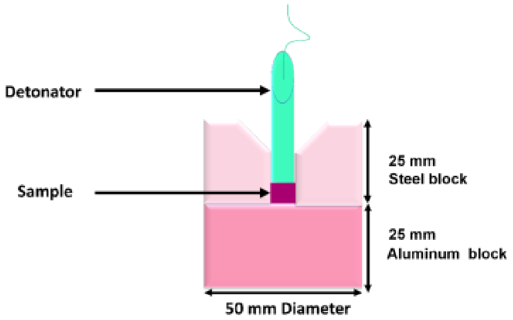

FIG. 1: The experimental setup of a SSRT consisting of a detonator, aluminum block (Baker–Miller pink), steel block (baby pink), sample (fuchsia), and detonator (turquoise) (adapted from Bauer et al., 2022)

2. RESULTS

Plotting the Koenen *K* (Klapötke and Wahler, 2021), Rose mortar (Wahler and Klapötke, 2022a), and Rose Trauzl (Wahler and Klapötke, 2022b) parameters against the results of the SSRTs, showed very little correlation. Since the SSRT is a measure of the energy release of an explosive, the heat of detonation must be considered. Therefore, we attempted to correlate the resulting dent only to the heat of formation as given by the following Rose SSRT equation:

$$\mathrm{SSRT}_{\mathrm{dent}} = (-461.045) + (0.304992) \times (-\Delta_{\mathrm{ex}} U^{\circ}) \tag{1}$$

where the units of measurement for $\mathrm{SSRT}_{\mathrm{dent}}$ and $-\Delta_{\mathrm{ex}} U^{\circ}$ are mm^3 and kJ/mol, respectively. The correlation is fitted by a linear function with a coefficient of determination of $R^2 = 0.87$ and a Pearson value of 0.93. The fitted plot is shown in Fig. 2.

3. COMPUTATIONAL DETAILS

EXPLO5 V_6.05.04 was used to calculate the heat of detonation. As input data, the densities and heat of formations from the EXPLO5 database were chosen (Suceska, 2021). Except for bis-(hydroxylammonium) 5,5′-bistetrazole-1,1′-diolate (TKX-50), where the recently published more precise values were chosen (Klapötke et al., 2022). In addition, bis-(hydroxylammonium) 3,3′-dinitro-5,5′-bis-(1,2,4-triazole)-1,1′-diolate (MAD-X1) was added (Klapötke, 2021) since it was not present in the database.

A high-quality data set published by Bauer et al. (2022) was chosen, where the indentation was measured using a profilometer to eliminate the error from gravimetric determination using sand. The average of all of the blasts performed in the study was used (Bauer et al., 2022). From the published data set, bis(1,2,4-oxadiazole), bis(methylene) dinitrate and bis(trinitropyrazoyl) methane were removed due to a variance of over 200 mm^3 between the blasts. Since we could not find a trustworthy enthalpy of formation for 3,4-dinitro-1-nitratomethylpyrazole and an error in the enthalpy of formation would have been reproduced in the heat of detonation, it was left out as well. The results are given in Table 1.

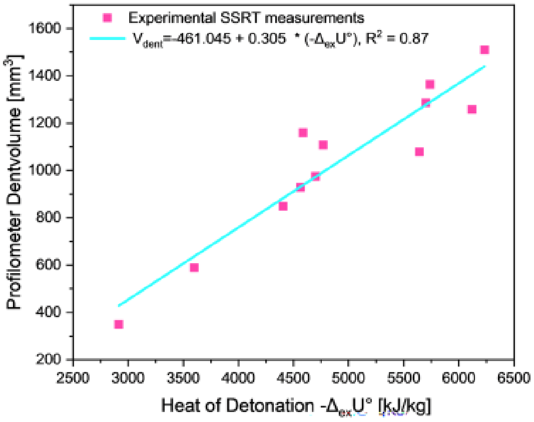

FIG. 2: The fitted function (turquoise line) and experimental values (fuchsia squares)

TABLE 1: Selected experimental and calculated Profilometer dent volumes, along with the calculated Heat of detonation

Compound	Profilometer dent volume average (mm^3)	Profilometer dent volume calculated (mm^3)	Heat of detonation, $-\Delta_{ex}U°$ (kJ/mol)
BCHMX	1258	1406	6120
PETN	1108	1375	6021
TKX-50	975	99	4768
HNS	929	972	4699
PA	588	932	4566
Tetrazole	1510	637	3600
CL-20	1079	1440	6232
MAD-X1	1364	1260	5643
RDX	848	1289	5739
TNT	1286	883	4406
HMX	1159	1277	5699
FOX-7	350	938	4588
NTO	1258	428	2915

BCHMX, 1,3,4,6-tetranitrooctahydroimidazo[4,5-d]imidazole; CL-20, hexanitrohexaazaisowurtzitane; HMX, octogen, 1,1-diamino-2,2-dinitroethylene; HNS, hexanitrostilbene; MAD-X1, bis-(hydroxylammonium) 3,3'-dinitro-5,5'-bis-(1,2,4-triazole)-1,1'-diolate; NTO, nitrotriazolone; PA, picric acid; PETN, pentaerythritol tetranitrate; RDX, hexogen; TKX-50, bis-(hydroxylammonium) 5,5'-bistetrazole-1,1'-diolate; TNT, 2,4,6-trinitrotoluene.

4. DISCUSSION

It is important to have good approximations of the outcome of up-scaling tests for energetic compounds. In this paper, the results obtained on the presented correlation show that performing a SSRT could also be replaced by calorimetric determination of the heat of detonation.

Another important advantage of empirical correlations is that they provide valuable insight into the fundamental physics involved in various tests used to determine the strength of an explosive. Correlating various tests, as done in previous works, to physical parameters (Klapötke and Wahler, 2021; Wahler and Klapötke, 2022a,b) helps to choose an experimental test according to the application of energetic materials.

5. CONCLUSIONS

The Rose SSRT equation is a useful correlation when it comes to comparing the power of energetic materials. Considering the high uncertainty of the experimental determination of the power of an explosive, one should rely on calculated values. Even if the SSRT is slightly less prone to mistakes compared to the Trauzl test, there is still high variance especially between blasts, as shown by the need to further refine the data set published by Wahler and Klapötke et al. (2022b), which was measured under standardized conditions to obtain a reliable data set (Bauer et al., 2022). It is also important to keep in mind that not all research facilities have the equipment to perform upscale tests. Therefore, well-fitted universally applicable empirical correlations are a great alternative, which can be used to evaluate energetic materials when performing further testing of substances is necessary.

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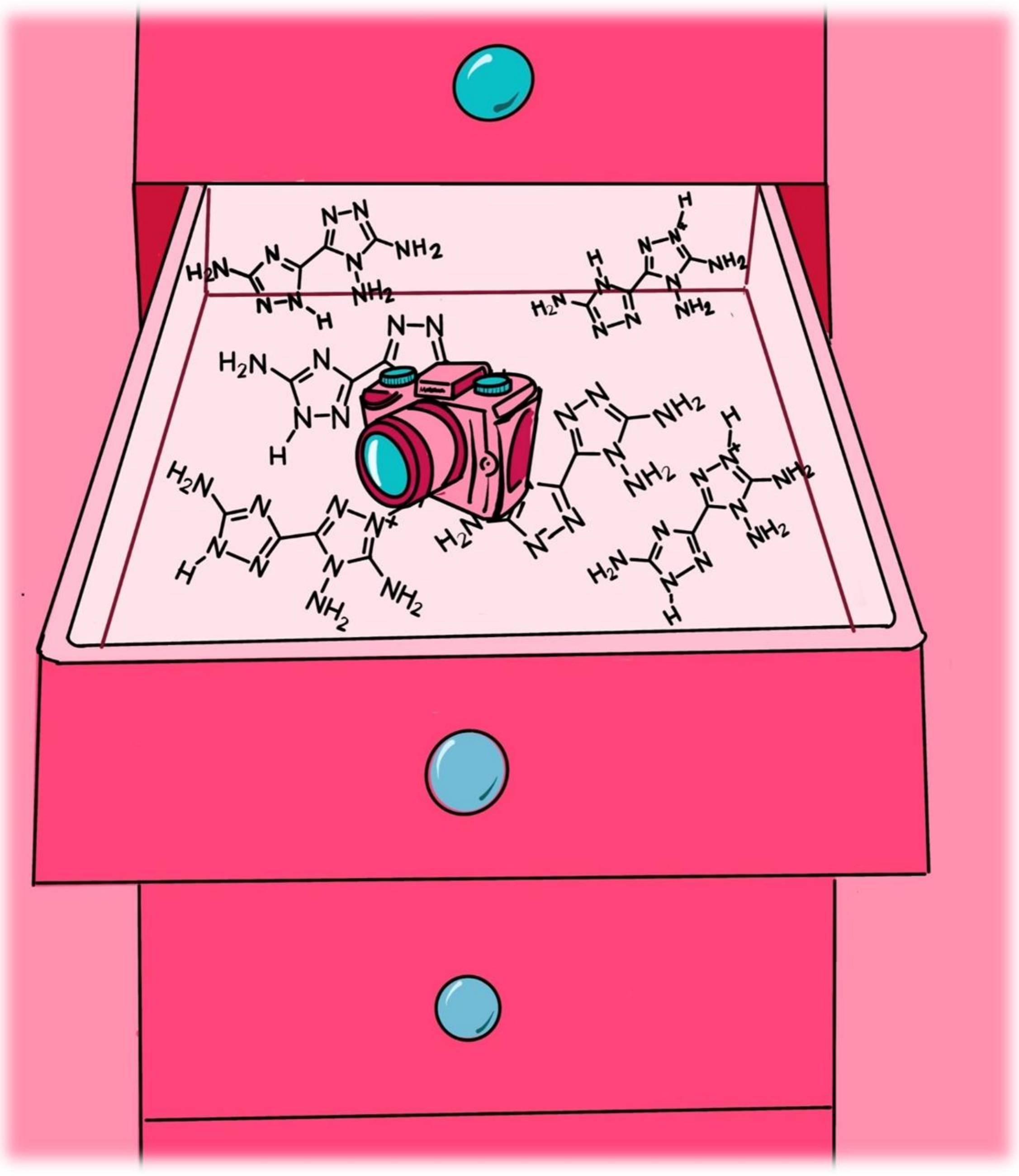
4 Miscellaneous

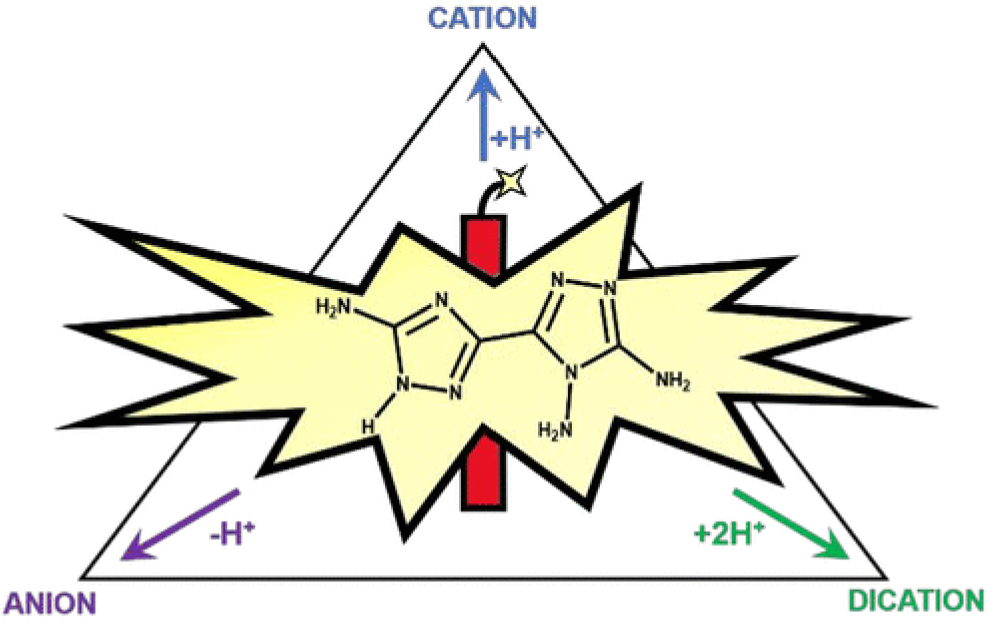


4.1 High-energy-density materials: an amphoteric N-rich bis (triazole) and salts of its cationic and anionic species – published

Author contributions

Sabrina Wahler: Calculations

Thomas M. Klapötke: Supervision and Advice



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High-Energy-Density Materials: An Amphoteric N-Rich Bis(triazole) and Salts of Its Cationic and Anionic Species

Emmanuele Parisi, Alessandro Landi, Sandra Fusco, Carla Manfredi, Andrea Peluso, Sabrina Wahler, Thomas M. Klapötke, and Roberto Centore*

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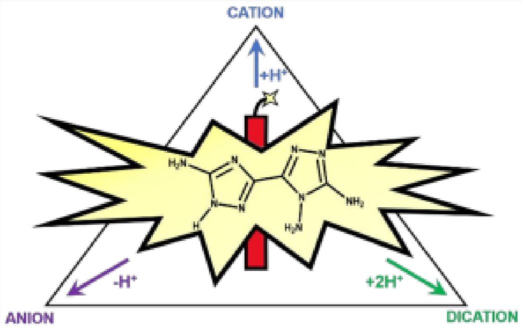
ABSTRACT: The synthesis and characterization of the N-rich bis(triazole) compound 1*H*,4′*H*-[3,3′-bis(1,2,4-triazole)]-4′,5,5′-triamine ($C_4H_7N_9$) with a N content of 69.6% by weight is reported. The compound exhibits a rich acid−base behavior because it can accept up to two protons, forming a monocation and a dication, and can lose one proton, forming an anion. Measurement of the acid constants has shown that there exist well-defined pH intervals in which each of the four species is predominant in solution, opening the way to their isolation and characterization by single-crystal X-ray analysis as salts with different counterions. Some energetic salts of the monocation or dication containing oxidizing inorganic counterions (dinitramide, perchlorate, and nitrate) were also prepared and characterized in the solid state for their sensitivity. In particular, the neutral compound shows a very remarkable thermal stability in air, with T_d = 347 °C, and is insensitive to impact and friction. Salts of the dication with energetic counterions, in particular perchlorate and nitrate, show increased sensitivities and reduced thermal stability. The salt of the monocation with dinitramide as the counterion outperforms other dinitramide salts reported in the literature because of its higher thermal stability (T_d = 230 °C in air) and friction insensitiveness.



■ INTRODUCTION

High-energy-density materials (HEDMs) can store and release in a controllable manner a high amount of (chemical) energy; thus, they are widely exploited in military and civil areas.[1] When undergoing decomposition, energetic materials produce energy by oxidation processes. One basic problem with HEDMs is that compounds highly performing from the energetic side are often sensitive to external stimuli such as heat, impact, friction, and detonation, requiring some sort of stabilization to control the energy release and avoid accidents. Recently, various classes of heterocyclic compounds with high N content have attracted considerable interest for the development of HEDMs as an alternative to traditional materials because of their excellent stability, high heat of formation, and environmentally friendly conditions.[2] The average bond energy of the N−N triple bond (954 kJ/mol) is very high, which makes N-rich compounds very endothermic and, therefore, very energetic materials. Also, N-rich heterocycles generally contain N in negative oxidation states, and these materials can decompose, giving environmentally benign gases (i.e., mainly N_2). Another advantage of N-rich heterocycles is the presence of basic N atoms or acidic N−H groups, which can lead to the formation of coordination compounds or salts in which the N-rich heterocycle is present as a cation or an anion. These salts have intrinsically low volatility and an increased energy content coming from the high energy of the ionic lattice, and their properties can be tuned, in principle, by the appropriate choice of the counterion and by crystal engineering strategies.

Here we report on the synthesis and characterization of HEDMs based on the N-rich heterocyclic compound 1*H*,4′*H*-[3,3′-bis(1,2,4-triazole)]-4′,5,5′-triamine (henceforth compound **1**) shown in Chart 1. It belongs to the class of 1,2,4-triazoles, which have been widely explored in recent years,[3−9] and has a high N content (69.6%).

The electron-rich character of **1**, which contains three amino electron-donor groups, is compatible with a rich acid−base behavior. In principle, **1** can take up to two protons, forming a cation and a dication, while the acidic N−H H atom can be lost by reaction with bases, with formation of the anion (Chart 1). So, at variance with most of the energetic N-rich compounds studied so far, with **1**, it is possible, in principle, to prepare salts in which the N-rich heterocycle is present as a

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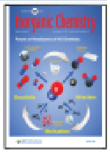


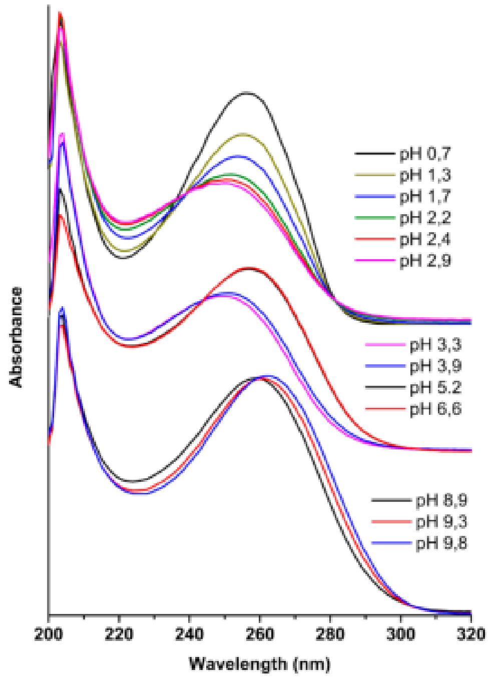


Figure 1. UV−vis absorption spectra of **1** at constant total concentration $c = 5.01 \times 10^{-5}$ M in 0.5 M NaCl recorded at $0.7 \leq pH \leq 9.8$. The spectra have been grouped into three sets of curves arbitrarily shifted along the vertical axis for easier lecture. The three sets correspond to the three equilibria involved (*vide ultra* and the SI).

Table 2. Acid Constants in the Form of pK_a (at 25 °C in 0.5 M NaCl, with Estimated Standard Deviations in Parentheses) for 1 (HL)

equilibrium	pK_a
$H_3L^{2+} + H_2O = H_3O^+ + H_2L^+$	pK_{a1} = 1.31(2)
$H_2L^+ + H_2O = H_3O^+ + HL$	pK_{a2} = 4.56(2)
$HL + H_2O = H_3O^+ + L^-$	pK_{a3} = 9.25(5)

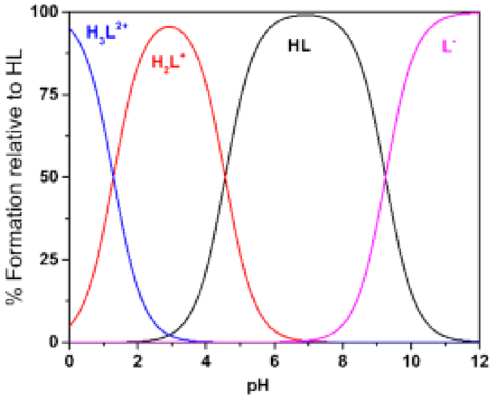
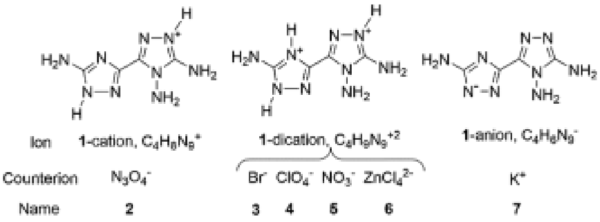


Figure 2. Distribution diagram of **1** (HL), calculated using the constants of Table 2.

equilibria is present in solution at a molar fraction of ≥90%. This should allow salts containing each of the three ionic species of **1** to be isolated from solutions.

Structural and Solid-State Analysis of 1 and Its Salts. We successfully crystallized neutral **1**, **1** monocation as the dinitramide salt, $(C_4H_8N_9)(N_3O_4)$, **1** dication as bromide, perchlorate, nitrate, and tetrachlorozincate salts, $(C_4H_9N_9)Br_2$, $(C_4H_9N_9)(ClO_4)_2$, $(C_4H_9N_9)(NO_3)_2$, and $(C_4H_9N_9)(ZnCl_4)$, respectively, and **1** anion as the potassium salt, $K(C_4H_6N_9)$ (Chart 3).

Chart 3. Composition and Numbering of Salts of 1



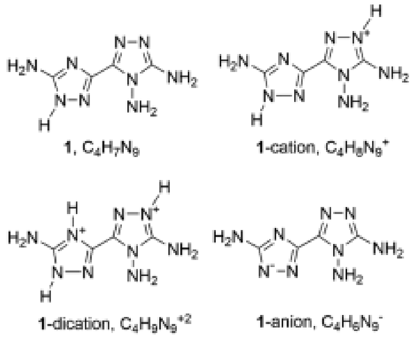
For these compounds, single-crystal X-ray diffraction analysis was performed. Remarkably, the molecular structures of all of the species involved in the acid−base equilibria have been characterized. As a general remark, we note that neutral **1** and its singly and doubly protonated species (Chart 1) are characterized by the presence of several strong H-bonding donor and acceptors on the rim of the molecule. Most of these groups, for instance, the ring N atoms and the C-NH_2 or N^+-H groups, are strong in-plane H-bonding acceptors/donors. So, a tendency toward the formation of stacked structures, in which infinite planar layers of H-bonded molecules are piled on each other, is expected for these compounds.

Neutral **1** has been crystallized as a hemihydrate, $C_4H_7N_9 \cdot 0.5H_2O$. Crystals are triclinic $P\bar{1}$ with $Z = 8$. The crystallographic analysis unambiguously indicates that the tautomer present in the crystals is 1*H* (Figure 3a). The four crystallographically independent molecules, all in the s-trans 1*H* tautomer, have a basically flat conformation, with the dihedral angle between the average planes of the two pentatomic rings ranging between 4.2(1)° for molecule A and 11.8(1)° for molecule D. The bond geometry around amino N atoms is relevant for the packing because they are H-bonding donors. The geometry is pyramidal for (N)-NH_2 atoms [the sum of the valence angles around the amino N atom ranges between 320(3)° and 327(2)° for the four independent molecules]. This result basically remains unchanged in all of the structures studied (*vide ultra*). The geometry around the (C)-NH_2 N atoms is still pyramidal, but more flat, because of conjugation with the aromatic ring, with the sum of the valence angles around the amino N atom ranging, in this case, between 341(2)° and 358(3)° for the four independent molecules.

Molecules in the crystal form infinite planar layers through H bonds involving the many N−H donor and N acceptors present in the molecules of **1** and the water molecules (Figure 3b,c). The layers are parallel to the lattice plane $2\bar{1}0$, and, in fact, reflection $2\bar{1}0$ is the most intense of the whole diffraction pattern. The stacking of the layers is achieved through H bonds between adjacent layers, and the stacking distance of the planes is rather short, $d_{2\bar{1}0}$ = 3.12 Å. The extended network of strong H bonds accounts for the relatively high density of the crystal, which is 1.629 g/cm^3 at −100 °C.

By metathesis of the perchlorate salt, $(C_4H_9N_9)(ClO_4)_2$, with potassium dinitramide (KN_3O_4), we have obtained the dinitramide salt of monoprotonated **1**, i.e., compound **2** of Chart 3. The crystal structure is shown in Figure 4.

Chart 1. Neutral, Singly Protonated, Doubly Protonated, and Deprotonated Forms of 1[a]



[a]Only one tautomeric form is shown for the neutral and cationic species. For the anion, only one resonance form is shown.

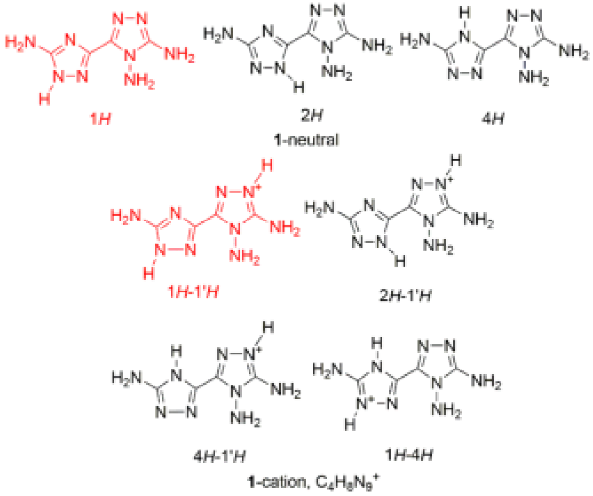
cation/dication and salts in which it is present as an anion. Indeed, those salts have been prepared and will be described in the present paper, with full characterization of their properties in the solution and solid state, including measurements of the sensitivities in the solid state for the energetic compounds. Some energetic salts of the **1** dication (nitrate and perchlorate) have recently been studied, independently from us, by the groups of Shreeve[10] and Cheng/Yang,[11] with possible application as gas-generating agents, propellants, or explosives. We note that a compound similar to **1** but containing one fewer NH_2 group (% N 67.4) was used by Shreeve in 2010,[12] while another one containing one more NH_2 group (% N 71.4) was described by us.[3,5,6]

■ RESULTS AND DISCUSSION

Tautomerism. Tautomerism is a phenomenon common to several classes of N-containing aromatic heterocycles, exhibiting many intriguing aspects that are relevant in many areas, including crystal engineering,[13] drug design,[14] energetic materials,[15] and coordination chemistry.[16,17] Of particular interest are compounds for which quasi-degenerate tautomers are possible because they can be switched between each other depending on the environment.[18,19] The N-rich system of **1** is potentially tautomeric. In Chart 2 are reported the canonical tautomers of the neutral and singly protonated species. Moreover, two different conformers can be expected for each tautomer, differing by the relative orientation of the triazole rings, which can be s-trans or s-cis if we look at the bond between the two rings.

The computed relative energies of the tautomers/conformers of Chart 2 are shown in Table 1. For the neutral molecule, the most stable predicted species, in a polar medium, is 1*H*/s-trans. The 2*H* tautomer, however, follows quite closely in energy both in the s-trans and, mostly, in the s-cis conformation. In the gas phase, 2*H*/s-cis is predicted as the most stable species, probably as a result of an intramolecular N−H···N interaction, and in a polar medium, the energy of 2*H*/s-cis is only 0.5 kcal/mol higher than 1*H*/s-trans, a value that is within the accuracy of the method used in the calculations. On the other hand, the 4*H* conformer has significantly higher energy.

Chart 2. Some Possible Tautomers of 1 and of Its Singly Protonated Cation (Only s-trans Conformers Are Shown)[a]



[a]Highlighted in red are the tautomers/conformers predicted as the most stable by computational analysis.

Table 1. Computed Relative Energies (kcal/mol) of Tautomers/Conformers of Neutral and Singly Protonated 1

	gas		water	
tautomer	s-cis	s-trans	s-cis	s-trans
1*H*	6.7	6.3	0.4	0.0
2*H*	0.0	9.2	0.5	1.3
4*H*	18.2	6.4	5.2	3.5
1*H*−1′*H*	0.4	0.0	0.5	0.0
2*H*−1′*H*	3.6	not stable[a]	3.0	7.1
4*H*−1′*H*	23.2	7.2	7.6	5.0
1*H*−4*H*	18.2	13.8	6.1	7.8

[a]Interconverts in the conformer s-cis upon geometry optimization.

Concerning singly protonated species, the data of Table 1 indicate that the tautomer 1*H*−1′*H* is the most stable both in the gas phase and in a polar medium. The other tautomers all have significantly higher energy. For the doubly protonated cation, we have not performed any computation. In fact, the tautomer shown in Chart 1 is only possible when both positive charges are on the N atoms adjacent to the C-NH_2 groups.

Acid−Base Equilibria in Solution. The acid−base equilibria of **1** in solution have been studied at 25 °C by potentiometric−spectrophotometric titrations in the constant ionic medium 0.5 M NaCl (see also the Supporting Information, SI). UV−vis absorption spectra of **1** recorded at different pH values and a constant total concentration are reported in Figure 1.

There is a nonmonotonic dependence of λ_{max} from the pH. Starting from the lowest value of the pH (pH = 0.7, λ_{max} = 257 nm), there is an initial hypsochromic shift up to pH = 2.9 (λ_{max} = 248 nm). Then, with increasing pH, the shift of λ_{max} is always bathochromic up to pH = 6.6 (λ_{max} = 257 nm) and further on to pH = 9.8 (λ_{max} = 264 nm). The changes in the absorption spectra can be accounted for by the three equilibria of Table 2 (see also the SI): neutral **1** (HL) can accept up to two protons, forming the cationic species H_2L^+ and H_3L^{2+}, and can release one proton, forming the species L^-.

The distribution diagram of the species is reported in Figure 2. It is noteworthy that there exist definite pH intervals in which each of the four species involved in the protolytic

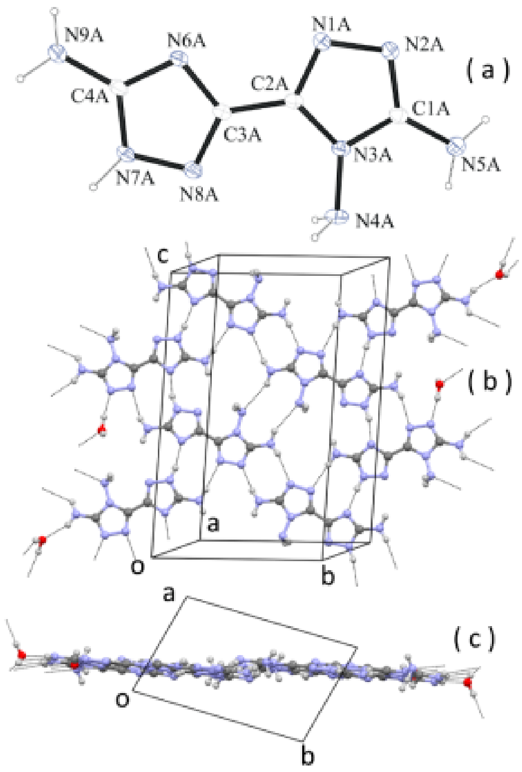


Figure 3. (a) ORTEP diagram of one of the four crystallographically independent molecules of $C_4H_7N_9{\cdot}0.5H_2O$. (b) Face view of a layer of H-bonded molecules. (c) Same layer viewed along *c*. Some H bonds are indicated by dashed lines.

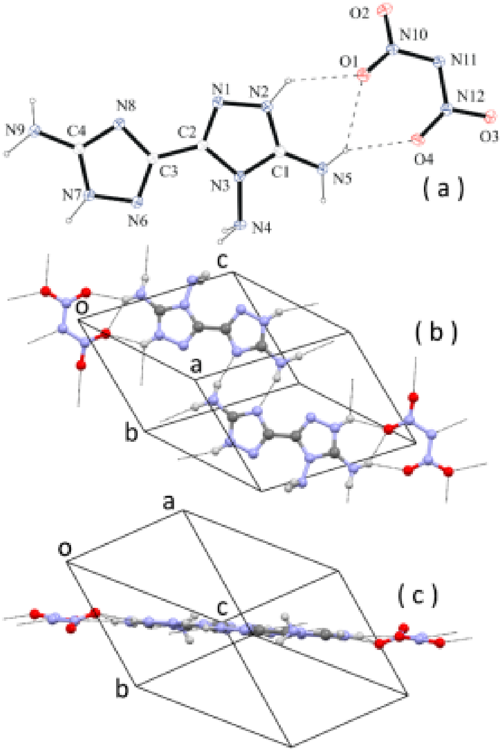


Figure 4. (a) ORTEP diagram of the crystallographic independent unit of $(C_4H_8N_9)(N_3O_4)$. (b) Face view of a layer of H-bonded molecules. (c) Edge view of the same layer. Some H bonds are indicated by dashed lines.

The cation is present as the 1*H*−1′*H* tautomer (Figure 4a), consistent with the results of computational analysis, so single protonation of **1** is observed at the triazole ring bearing two amino groups. The conformation of the cation is basically flat, with the dihedral angle between the average planes of the rings being 5.2(2)°. The geometry around the amino (N)-NH_2 atom is pyramidal [the sum of the valence angles is 319(4)°]. Compared with neutral **1**, full planarization of the geometry around the (C)-NH_2 N atoms is observed, with the sum of the valence angles being 360(5)° and 359(5)°. The packing shows similarities with neutral **1**. Also in this case, molecules form planar ionic/H-bonded layers through N−H donor and N acceptors present in the cation molecule and O and N acceptors of the dinitramide anion (Figure 4b,c). The layers are parallel to the lattice plane $\bar{1}21$ ($\bar{1}21$ is the most intense reflection of the diffraction pattern). The stacking distance of the planes is shorter than **1**, $d_{\bar{1}21}$ = 3.11 Å. The extended network of strong H bonds and the ionic interactions between cations and anions account for the significantly higher density of the crystal, which is 1.837 g/cm^3 at −100 °C.

The salts in which the triamine molecule is present as a dication, i.e., compounds **3**−**6** of Chart 3, were easily prepared by dissolving neutral **1** in a water solution of the corresponding strong inorganic acid (hydrobromic, perchloric, and nitric). In all of the salts studied, the tautomer present is 1*H*−1′*H*−4*H* s-trans (Chart 1). So, protonation (single or double) of neutral **1** is always at the ring N atoms. This is expected because the electron-donor character of the amino groups can stabilize the positive charge of the cation; as a result, the geometry around the amino (C)-NH_2 N atoms is trigonal-planar in all of the structures of the dications studied.

Some features of the crystal structure of the bromide salt are shown in Figure 5.

Again, the structure is of the stacked-layer type. The layers of ionic/H-bonded molecules (Figure 5b,c) are parallel to the lattice plane $1\bar{2}2$, with a short stacking distance of $d_{1\bar{2}2}$ = 3.13 Å. The stacking between the layers is accomplished through strong H bonds between bromide ion acceptors and N-NH_2 donors, with the formation of $R_4^2(8)$ ring patterns (Figure 5c).

The energetic perchlorate salt is interesting because in the crystal the N-rich dication is fully surrounded by oxidizing tetrahedral perchlorate anions. The conformation of the dication is again flat, with the dihedral angle between the average planes of the two rings being 5.8(2)°. The layers of ionic/H-bonded molecules (Figure 6a,b) are parallel to the lattice plane $11\bar{2}$, with a stacking distance of $d_{11\bar{2}}$ = 3.22 Å.

The same feature is also present in the packing of the energetic nitrate salt, with the dication surrounded by trigonal-planar nitrate ions (Figure 7). In the nitrate salt, however, the dication shows the maximum deviation from planarity within the set of investigated compounds. In fact, the dihedral angle between the two pentatomic rings is 15.0(2)°. The layers of ionic/H-bonded molecules (Figure 7a,b) are parallel to the lattice plane 211, with a stacking distance of d_{211} = 3.32 Å.

We have also crystallized the dication with the tetrachlorozincate complex anion (Figure 8). The crystal structure is stabilized by many N−H⋯Cl H bonds that are distributed over the full length of the N-rich molecule ion (Figure 8a). The

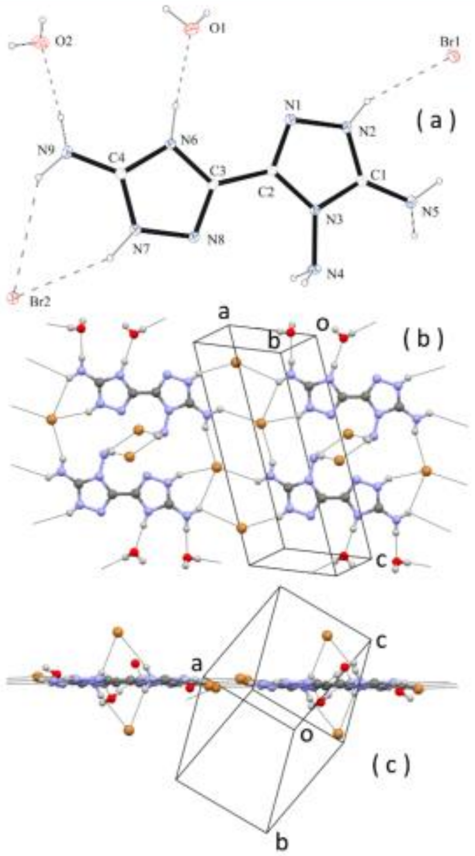


Figure 5. Crystal structure of $(C_4H_9N_9)Br_2{\cdot}2H_2O$: (a) ORTEP diagram of the crystallographic independent unit; (b) face view of a layer of ionic/H-bonded molecules; (c) edge view of the same layer. Some H bonds are indicated by dashed lines. Some hanging H bonds have been omitted for clarity.

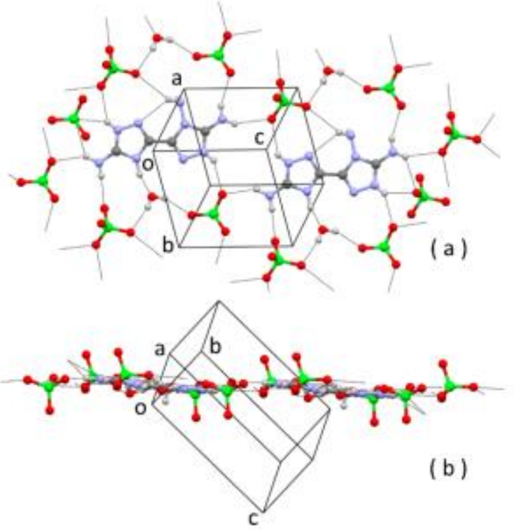


Figure 6. Partial packing of $(C_4H_9N_9)(ClO_4)_2{\cdot}H_2O$: (a) face view of a layer of ionic/H-bonded molecules; (b) edge view of the same layer. H bonds are indicated by dashed lines. Some hanging H bonds have been omitted for clarity.

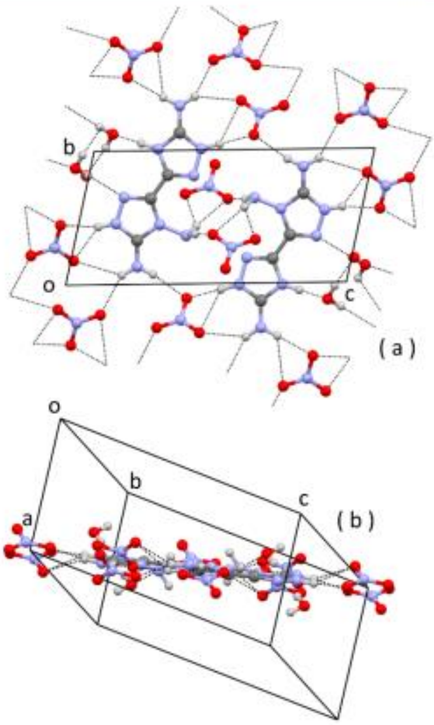


Figure 7. Partial packing of $(C_4H_9N_9)(NO_3)_2{\cdot}H_2O$: (a) face view, along *a*, of a layer of ionic/H-bonded molecules; (b) edge view of the same layer. H bonds are indicated by dashed lines. Some hanging H bonds have been omitted for clarity.

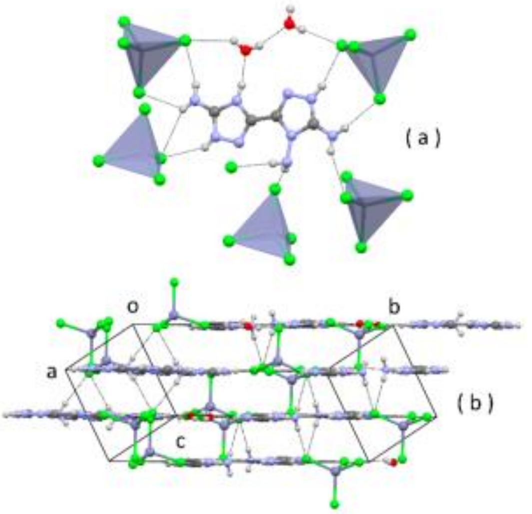


Figure 8. Crystal structure of $(C_4H_9N_9)ZnCl_4{\cdot}2H_2O$: (a) view of the cation, water molecules, and some H-bonded tetrachlorozincate anions; (b) edge view of layers of ionic/H-bonded ions. Hanging contacts have been omitted for clarity.

layers of ionic/H-bonded molecules (Figure 8b) are parallel to the lattice plane 102, with a stacking distance of d_{102} = 3.16 Å.

Thanks to the amphoteric properties of **1** (Chart 1 and Table 2), we have tried to crystallize salts of the triamine anion with inorganic cations (Na^+, K^+, and NH_4^+). As a matter of fact, neutral triamine is soluble in inorganic acids (e.g., HCl, HBr, and $HClO_4$) and inorganic bases ($NaOH_{aq}$, KOH_{aq}, and aqueous ammonia). However, crystallization of neutral **1** from aqueous ammonia yielded crystals of hydrated neutral **1**. This result can be rationalized if we observe that the product of the acid constant of **1** (K_{a3} in Table 2) and of K_b of ammonia (1.774×10^{-5} at 25 °C)[20] is almost equal to K_w, and so the equilibrium constant of the reaction between ammonia and **1** is almost unitary. On the other hand, we have successfully crystallized the sodium and potassium salts of the anion. The crystal structure of $K(C_4H_6N_9)\cdot 2H_2O$ is reported in Figure 9.

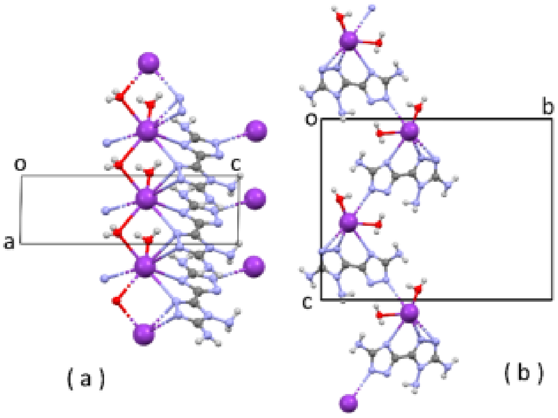


Figure 9. Partial packing of $K(C_4H_6N_9)\cdot 2H_2O$: (a) projection along *b*; (b) projection along *a*.

In the molecular structure of the anion, the geometry around the (C)-NH_2 N atom is again pyramidal [the sum of the valence angles is 337(2)° and 347(2)°], and this is expected because the electron excess of the anion reduces conjugation of the (C)-NH_2 amino groups toward the rings. The tendency toward the formation of layers is no longer observed because the packing is mainly driven by the coordination geometry of the anionic ligand to the metal ion. As is evident from Figure 9, each anion acts as a tetradentate ligand by four ring N atoms. One N atom is μ_2 between two K^+ ions, and a water molecule is also μ_2-bridging between the same K^+ ions. In this way, infinite chains running along *a* are formed by simple translation (Figure 9a). Chains are also formed running along *c*, and they are generated by the glide operation of the space group $P2_1/c$ (Figure 9b). Altogether, a 2D coordination network is generated.

Characterization of Energetic Materials. In Figure 10 is reported the thermogravimetric analysis (TGA) of **1** and of energetic salts of the **1** cation or dication with oxidizing anions [differential scanning calorimetry (DSC) analysis is reported in the SI].

The neutral compound shows a very remarkable thermal stability in air. After an initial loss of hydration water at about 80 °C, the anhydrous sample is stable up to 347 °C. Among similar N-rich triazoles reported in the literature,[6] **1** has the best thermal stability in air. The thermal stability of the salts of the dication (perchlorate and nitrate) is lower. The dinitramide salt, in which triamine is present as a monocation, has a very clean TGA curve: it is fully stable up to 230 °C, when it suddenly decomposes, losing 85% by weight, with an almost vertical TGA curve (green curve of Figure 10). Among the many N-rich dinitramide salts reported so far in the literature as energetic materials,[6] the highest thermal stability is shown by FOX-12 (*N*-guanylurea dinitramide), with T_d = 215 °C.[21] The thermal stability of nitramide **2** is significantly higher.

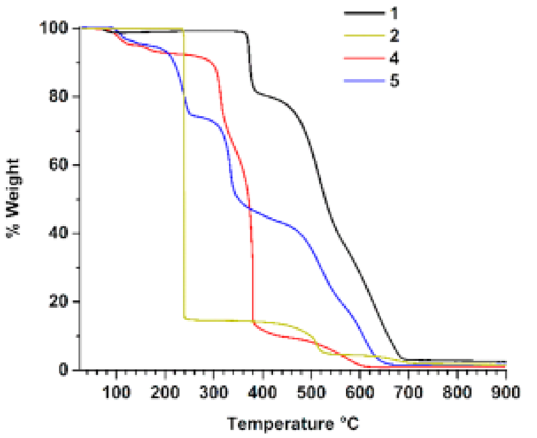


Figure 10. TGA of **1** and of some of its salts in air. Heating rate 10 K/min.

The impact (IS), friction (FS), and electrostatic discharge (ESD) sensitivities of **1** and some of its energetic salts were measured experimentally (grain size 100−500 μm) and are listed in Table 3. On the basis of the computed enthalpies of formation (see the SI), the detonation parameters (V_{oD} = velocity of detonation, P_{C-J} = detonation pressure, and Q_{ex} = heat of detonation) were calculated with the *EXPLO5* program[23] and are also reported in Table 3.

Since the development of RDX (1,3,5-trinitro-1,3,5-triazacyclohexane or cyclonite), any newly synthesized energetic compounds must face RDX, particularly in terms of the detonation pressure and detonation velocity, which are very important parameters in secondary explosives. For these reasons, the energetic properties of RDX have been added in Table 3 for a direct comparison. We have also added to Table 3 the literature data[2] for two reference energetic salts containing inorganic anions: 5-aminotetrazolium dinitramide (HAT-DN) and 5-aminotetrazolium nitrate (5-ATN). Energetic compounds should also be stable with respect to the temperature, have a high density, be safe to handle, and be cheap to synthesize. In terms of the thermal stability, both **1** and **2** surpass the 200 °C benchmark and so largely outperform RDX, as well as HAT-DN and 5-ATN. **2** slightly outperforms RDX and 5-ATN also in the detonation velocity, while its performances in terms of the detonation pressure are slightly lower. Concerning the experimentally determined sensitivities, **1** is insensitive to both impact and friction. **2** is impact-sensitive, with a measured value in the range observed for other N-rich dinitramides: ammonium dinitramide (ADN) 5 J, triaminoguanidinium dinitramide (TAGDN) 2 J,[6] and HAT-DN. On the other hand, **2** is friction-insensitive, a significant result, inasmuch as other N-rich dinitramides, including HAT-DN, have high sensitivity toward friction (ADN 72 N and TAGDN 24 N).[6] **4** is impact-sensitive and moderately sensitive to friction, while **5** is less impact-sensitive than **2** and **4** and friction-insensitive, and so it is better performing than nitrate 5-ATN. The lower impact sensitivity of **5**, compared with **2** and **4**, can be related to some of the structural features discussed above. In **5**, the dication shows the highest deviation from coplanarity of the two rings, and this produces an increase of the stacking distance between the planes of ionic/

Table 3. Energetic Properties and Detonation Parameters of Compounds 1, 2, 4, and 5 and the Reference Compounds RDX, HAT-DN, and 5-ATN

compound	ρ[a] (g/cm^3)	ρ[b] (g/cm^3)	T_d (°C)[c]	IS (J)[d]	FS (N)[e]	ESD (J)[f]	V_{oD} (m/s)[g]	P_{C-J} (kbar)[h]	Q_{ex} (kJ/kg)[i]
1	1.629	1.599	347	>40	>360	1	7681	194	−2378
2	1.837	1.803	230	4	>360	0.1	8948	311	−4496
4	1.908	1.873	270	4	192	0.1	7033	191	−1711
5	1.773	1.740	210	>25	>360	0.6	8092	246	−3289
RDX[j]	1.806		204	7.5	120	0.20	8861	345	−5845
HAT-DN[k]	1.856		117	2	20	0.75	9429	384	6186
5-ATN[k]		1.807	190	10	>324		8898	357	−4603

[a]Cystallographic density at −100 °C. [b]Calculated density at 298 K, according to ref 22. [c]Decomposition temperature (onset) for the anhydrous sample in the TGA runs of Figure 10. [d]Impact sensitivity (BAM drop hammer). [e]Friction sensitivity (BAM friction tester). [f]Electrostatic discharge sensitivity. [g]Calculated detonation velocity. [h]Calculated detonation pressure. [i]Calculated heat of detonation. [j]Data taken from ref 6. [k]Data taken from ref 2.

H-bonded molecules and a reduced density. Nitramide **2** can be considered to be the most interesting energetic material within the set investigated, although its impact sensitiveness hinders its use as main explosive. Altogether, the salt compounds described here could be of potential interest as propellant charges, as additives in propellant charges, or as gas generators.

■ CONCLUSION

We have presented the N-rich bis(triazole) compound **1** and have investigated its acid−base behavior. An interesting feature of **1** is the existence of well-defined pH intervals in which it is present in solution as neutral, singly protonated, doubly protonated, and deprotonated forms. This discloses the possibility of selective crystallization from a solution of salts containing different ionic forms of **1**, which we have experimentally realized. In fact, salts containing all of the ionic species of **1** were crystallized and structurally characterized by X-ray analysis. For some salts containing energetic counterions (nitrate, perchlorate, and dinitramide), the sensitivities were experimentally determined, and the detonation parameters were computed.

Our present study paves the way to more specific studies of energetic materials based on **1**. Because of the existence of two different protonated forms, the set of possible energetic salts of **1** to be investigated is very large in principle. As an example, further studies could be directed to a comparison of the properties of energetic salts containing the same counterion but different protonated forms of **1**.

■ EXPERIMENTAL PART

Caution! *The compounds in this work are potentially energetic materials that could explode under certain conditions (such as impact, friction, or electric discharge). Experiments should be performed on a small scale. Appropriate safety precautions, including the use of safety shields and personal protection (safety glasses, ear plugs, and gloves), are suggested at all times during handling of these compounds.*

General Procedures. All reagents were of analytical grade and were used without further purification. Melting points were determined by temperature-controlled optical microscopy (Zeiss Axioskop polarizing microscope equipped with a Linkam PR600 heating stage). TGA was performed with a PerkinElmer TGA 4000 apparatus. DSC analysis was performed with a PerkinElmer Pyris instrument. NMR spectra were recorded with a Bruker spectrometer operating at 400 MHz, in deuterated dimethyl sulfoxide (DMSO-d_6). Electrospray ionization (ESI) mass spectrometry (MS) analyses were recorded with an Applied Biosystems API 2000 mass spectrometer equipped with an electrospray source used in the positive mode. Elemental analyses were performed using a FlashEA 1112 analyzer (Thermo Fisher Scientific Inc.) and a Netsch STA 429 apparatus.

Synthesis of 1. Commercial 5-amino-1*H*-1,2,4-triazole-3-carboxylic acid (5.00 g, 4.90 × 10^{-2} mol) and diaminoguanidine monohydrochloride (6.40 g, 5.09 × 10^{-2} mol, 30% excess by mol) were finely ground in a mortar. The mixture was added in portions, under mechanical stirring, to a beaker containing poly(phosphoric acid) (40 g) at 100 °C (Scheme S1). After a few minutes, the evolution of gaseous HCl was observed from the reaction mixture. The temperature of the pasty reaction mixture was increased to 150 °C, and the mixture reacted for 5 h under stirring. Afterward, the mixture was poured into cold water (100 mL), and the pH of the resulting solution was increased to 5 by the addition of a concentrated solution of NaOH. Raw **1**, in the form of an off-white solid, was obtained, filtered, washed with cold water, and dried in an oven at 100 °C. Raw **1** (5.5 g) was suspended in water (100 mL). Concentrated HCl (37%; 20 mL) was added drop by drop under stirring, and the suspension was heated. Upon addition of the acid and heating, the suspension progressively became a clear, pale-brown solution. The solution was kept boiling under stirring until the volume reduced 50 mL. Then it was cooled to room temperature, and a white solid (the dichlorhydrate salt) formed. The solid was recovered by filtration and washed on the filter with ethanol. Then it was dried in an oven at 110 °C. A total of 4.9 g of the dichlorhydrate salt was obtained. The salt product was solved in hot water (about 100 mL). A 1 M solution of KOH was added drop by drop until the pH was 6−7. A crystalline precipitate formed. The suspension was cooled to room temperature, and the precipitate was filtered, washed with water on the filter, and dried in an oven at 110 °C overnight. In this way, 3.98 g of pure **1** was obtained. Yield: 3.98 g (45%). Mp: 347 °C (dec). ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.67 (s, 2H), 5.77 (s, 2H), 6.18 (s, 2H) 12.33 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.59, 150.58 155.47 157.24. MS (ESI, positive mode). Calcd for $C_4H_7N_9$: *m/z* 181.16. Found: *m/z* 182.0 ($M^+ \cdot H$). Anal. Calcd for $C_4H_7N_9 \cdot 0.5H_2O$: C, 25.26; H, 4.24; N, 66.29. Found: C, 25.86; H, 3.69; N, 67.00.

Synthesis of $(C_4H_8N_9)(N_3O_4)$. $(C_4H_9N_9)(ClO_4)_2$ (0.667 g, 1.75 mmol) was dissolved in 25 mL of hot water. The solution was added to another solution containing KN_3O_4 (0.508 g, 3.50 mmol) and 2 mL of water. Pale-pink prismatic crystals of the triamine monocation salt were obtained by slow cooling to room temperature from a warm water bath (70 °C) with quantitative yield. Anal. Calcd for $(C_4H_8N_9)(N_3O_4)$: C, 16.66; H, 2.80; N, 58.32. Found: C, 16.31; H, 2.43; N, 58.81.

Synthesis of $(C_4H_9N_9)Br_2$. A total of 10 drops of a HBr concentrated solution (48%, v/v) was added to a hot water solution of 30 mg of **1** (0.150 mmol). Prismatic colorless crystals of the dihydrate bromide salt were obtained by slow solvent evaporation at room temperature in 2 days, with 86% yield. Anal. Calcd for $(C_4H_9N_9)Br_2 \cdot 2H_2O$: C, 12.67; H, 3.46; N, 33.26. Found: C, 12.42; H, 3.31; N, 33.69.

Synthesis of $(C_4H_9N_9)(ClO_4)_2$. A total of 5 drops of a $HClO_4$ concentrated solution (70%, v/v) was added to a hot water solution of

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30 mg of **1** (0.150 mmol). Prismatic colorless crystals of the perchlorate salt hydrate were obtained by slow evaporation at room temperature in 2 days, with 90% yield. The sample was dehydrated by keeping it in a desiccator over $CaCl_2$ for 1 week. Anal. Calcd for $C_4H_9N_9(ClO_4)_2$: C, 12.57; H, 2.37; N, 32.99. Found: C, 12.51; H, 2.64; N, 32.38.

Synthesis of $(C_4H_9N_9)(NO_3)_2$. A total of 5 drops of a HNO_3 concentrated solution (65%, v/v) was added to a hot water solution of 30 mg of 1 (0.150 mmol). Pale-pink lozenge crystals of the nitrate salt dihydrate was obtained by slow cooling to room temperature from a warm water bath (70 °C) with quantitative yield. Anal. Calcd for $(C_4H_9N_9)(NO_3)_2{\cdot}H_2O$: C, 14.77; H, 3.41; N, 47.37. Found: C, 14.99; H, 3.75; N, 46.98.

Synthesis of $(C_4H_9N_9)(ZnCl_4)$. **1** (30 mg, 0.150 mmol) was dissolved in 1 mL of hot water. The solution was added to another solution containing $ZnCl_2$ (20 mg, 0.150 mmol), water (1 mL), and 10 drops of a concentrated HCl solution (37%, v/v). The solution was left undisturbed, and pale-brown prismatic crystals were obtained in 2 days, with 60% yield. Anal. Calcd for $(C_4H_9N_9)ZnCl_4{\cdot}2H_2O$: C, 11.24; H, 3.06; N, 29.49. Found: C, 11.71; H, 2.83; N, 28.97.

Synthesis of $K(C_4H_6N_9)$. Brown prismatic crystals of the $K(C_4H_6N_9)$ dihydrate salt were grown in 1 day by slow cooling to room temperature of a hot water solution containing 200 mg of 1 (1 mmol) and a KOH concentrated solution (2 mL) with quantitative yield. Anal. Calcd for $K(C_4H_6N_9){\cdot}2H_2O$: C, 18.82; H, 3.95; N, 49.38. Found: C, 18.23; H, 4.42; N, 49.27.

Computational Details. Quantum-chemical computations were carried with the *Gaussian 16* package by using density functional theory (DFT).[24] The B3LYP functional was employed throughout in conjunction with the 6-31+G** basis set. B3LYP has proven to give excellent performance, nearly reproducing experimental electrical and optical properties for organic molecules.[25,26] Solvent (water) effects were included by the polarizable continuum model.[27] The nature of the located stationary points was verified by checking the eigenvalues of the Hessian matrix; all of the minimum-energy structures have positive eigenvalues. For all tautomers of Chart 2, a molecular-mechanics scan based on the *Spartan* program was performed, in order to find possible conformers.

Acid−Base Equilibria. The protolytic equilibria of 1 were studied by UV−vis absorption spectroscopy in 0.5 M NaCl, as the ionic medium, following a procedure already described[8,18] and detailed in the SI. The experiments were performed as acid−base titrations at a constant total concentration of **1** (c = 5.01 × 10^{-5} M). The investigated pH range extends from 0.3 to 12. For each experimental point, the equilibrium free proton concentration was evaluated from the measured electromotive force at the ends of the galvanic cell GE/TS/RE, where TS indicates the test solution, GE is the glass electrode, and RE is a reference electrode [0.5 M NaCl|Hg_2Cl_2|Hg (Pt)] placed outside but electrically connected to TS through a salt bridge. All of the experiments were carried out in air, in a thermostat at 25.00 ± 0.03 °C. Absorption spectra were recorded with a Varian Cary 50 UV−vis spectrophotometer using a 1 cm cell. The primary spectrophotometric data (A, pH, and λ) were elaborated graphically[28] and numerically by using the *HYPSPEC 2008* program[29] for determination of the equilibrium constants in solution.

X-ray Analysis. All data for crystal structure determinations were measured on a Bruker-Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream 700 apparatus, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Reduction of data and semiempirical absorption correction were done using the *SADABS* program.[30] The structures were solved by direct methods (*SIR97* program[31]) and refined by the full-matrix least-squares method on F^2 using the *SHELXL-2015* program[32] with the aid of the program *WinGX*.[33] H atoms bonded to N atoms, which are essential in the identification of tautomers, and those bonded to O atoms in water molecules, were clearly found in difference Fourier maps as the first maxima, and in some cases, their coordinates were refined. For all H atoms, U_{iso} = 1.2U_{eq} of the carrier atom was assumed. Full crystal and refinement data are summarized in Tables S1 and S2. Analysis of the crystal packing was performed using the program *Mercury*.[34] CCDC 2092331, 2092333, 2092335, 2092337, 2092339, 2092341, and 2092342 contain the supplementary crystallographic data for this paper (see the SI).

Sensitivity Testing. The impact sensitivity tests were carried out according to *STANAG 4489*[35] modified instruction[36] using a BAM (Bundesanstalt für Materialforschung) drophammer.[37] The friction sensitivity tests were carried out according to *STANAG 4487*[38] modified instruction[39] using the BAM friction tester. The classification of the tested compounds results from the "UN Recommendations on the Transport of Dangerous Goods".[40] Additionally, all compounds were tested on the sensitivity toward electrical discharge using the Electric Spark Tester ESD 2010 EN.[41]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02002.

> Scheme of the synthesis of **1**, ^{1}H and ^{13}C NMR and mass spectra of **1**, DSC thermograms of **1** and its energetic salts, detailed description of the UV−vis and electrochemical methods used in the study of the acid−base properties, full crystallographic details, full details of the computation of the energetic properties, and geometry of DFT-optimized tautomers/conformers (PDF)

Accession Codes

CCDC 2092331, 2092333, 2092335, 2092337, 2092339, 2092341, and2092342 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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(40) Impact: insensitive, >40 J; less sensitive, ≥35 J; sensitive, ≥4 J; very sensitive, ≤3 J. Friction: insensitive, >360 N; less sensitive, 360 N; sensitive, <360 N and >80 N; very sensitive, ≤80 N; extremely sensitive, ≤10 N. According to the UN recommendations on the transport of dangerous goods.

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4.2 Testing and breaking open-source tools for optical chemical structure recognition on novel nitrogen-rich energetic materials – published

Author contributions

Sabrina Wahler: Project plan and execution, software and manuscript preparation, acquisition of funding

William G. Proud: Supervision and Manuscript revison

Thomas M. Klapötke: Supervision and Advice

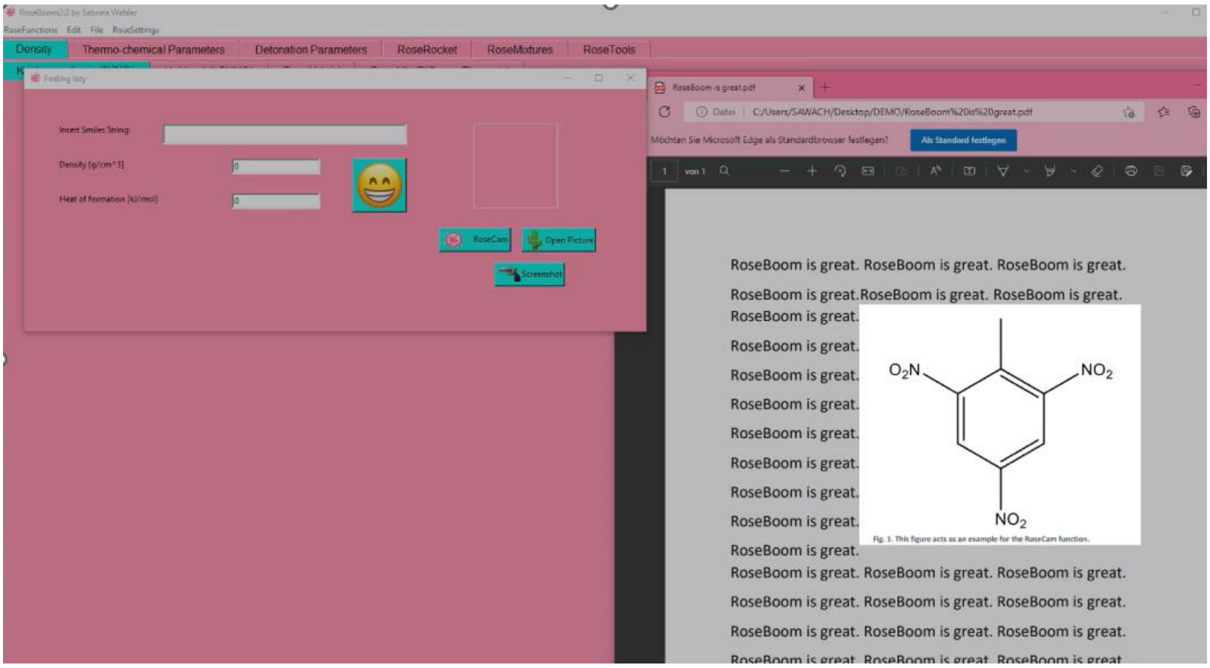

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Fig. 1. This figure acts as an example for the RoseCam function.

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Testing open-source tools for optical chemical structure recognition on novel nitrogen-rich energetic materials

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ABSTRACT

In this study, a rule-based optical structure recognition and one based on a CNN are tested on nitrogen-rich materials to see if they can be coupled to software for predicting the properties of said materials. Overall, the accuracy has been tested on three scientific publications, to see if it is possible to easily extract information from literature to assemble large databases for material property prediction.

Keywords

Optical structure recognition; high-through put; nitrogen-rich

Introduction

Natural Language Processing (NLP) is an increasingly useful technique in data collection and searching documents. This allows the generation of large datasets of material properties that can be used in training of machine learning tools (Garcia et al. 2022; Olivetti et al. 2020). NLP seems especially promising to work through older documents and materials, which have not been widely diffused so recovering the knowledge hidden in them new life. Looking forwards NLP can be applied by researchers to keep up to date with the amount of literature published on a given topic, a task which often poses a significant challenge. Such tools make knowledge easily accessible, however, one must keep an overview and identify and select promising material for which NLP tools could be employed (Elton et al. 2019). One key limitation is the processing of chemical structure, this poses a great challenge (Olivetti et al. 2020). To overcome this, optical structure recognition could be employed soon.

Optical structure recognition turns images of molecular formulas into machine-readable format. Different techniques can be applied, so far mostly rule-based recognition was applied, but there are also programs which rely on artificial intelligence (Xu et al. 2022). In this study, open-source tools which convert pictures of molecules into SMILES *(Simplified Molecular Input Line Entry System)* were evaluated on new literature about nitrogen richs energetic materials.

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For the scope of this study, open-source tools were tested, where the source code has been published. The reason for this is twofold: first to avoid the "black-box" syndrome where the analysis is hidden from the user and secondly, the concern about cyber security, which is especially important in the world of energetic materials. Data security can be breached if documents and molecular structures are run through software and analysis systems hosted on remote servers. In some cases, even when the source code is published, new artificial intelligence approaches often require models, to be downloaded from a server while running the source code, this is the case of DECIMER (Rajan, Zielesny, and Steinbeck 2021).

The converse are paid tools, which generally come with a user-agreement including options for non-disclosure agreements and liability for any data breaches.

Within the field of energetic synthesis, a wide range of nitrogen-rich materials are being synthesized with the aim of developing new propellants. This study aims to evaluate how good some common open-source optical chemical structure recognition tools are in converting commonly encountered nitrogen-rich molecules into computer readable format of the type used to train new predictive models.

Computational Methods

For convenience, the online version of OSRA (Cactus 2023) was used and compared to the DECIMER2.1 (Brinkhaus et al. 2022) to convert molecular structures from three example papers containing a variety of nitrogen-rich materials including triazoles, tetrazoles, azides, and polymers (Cleveland et al. 2022; Eymann et al. 2021; Parisi et al. 2021).

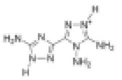
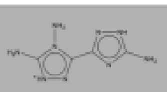
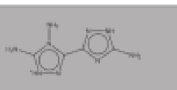
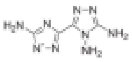
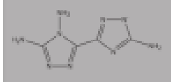
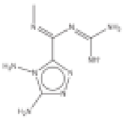
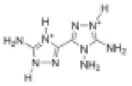
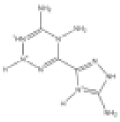
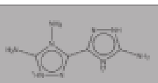
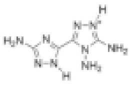
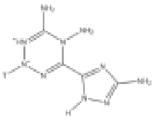
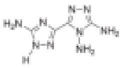
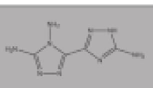
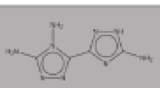
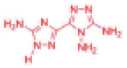
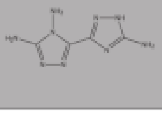
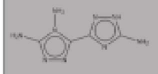
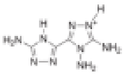
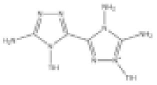
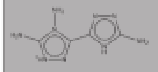
Results

The results obtained from recognizing molecular structures are obtained in Tables 1–3. Molecules highlighted in gray were successfully recognized, molecules in white were not successfully recognized.

Discussion

From these tables, the current state of OSR in this area gives patchy results, with some materials classes being identified clearly, while others are not. Taking these results in more detail and looking at Table 1, OSRA recognized one molecule more in total than DECIMER2.1. Hence, OSRA recognized 60% of the triazoles correctly while DECIMER2.1 only recognized 50%. From a statistical perspective, the limited number of molecules chosen is not high

Table 1. Structures recognized from "Parisi, E., Landi, A., Fusco, S., Manfredi, C., Peluso, A., Wahler, S., Klapötke, T. M., Centore, R., inorg. chem. 2021, 60, 16213 –16,222".

	Original picture[a]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
1		C1(=NN(C(=N1)N)[3H])C2=N[N+]([NH+]=C(N2N)N)[3H]		Nc2nc(c1n[nH+]c(N)n1N)n[nH]2	
2		C1(=N[N-]C(=N1)N)C2=NN=C(N2N)N		C/N=C(\N=C(N)/[NH-])/c1nnc(N)n1N	
3		C1(=NNC(=[N+]1[H])N)C2=N[N+]([NH+]=C(N)N2N)[H]		Nc2[nH]nc(c1n[nH+]c(N)n1N)[nH+]2	
4		C1(=NC(=NN1[H])N)C2=N[N+]([NH+]=C(N2N)N)[3H]		C=C(N/N=C(N)/N)c1n[nH+]c(N)n1N	
5		[3H]N1C(=NC(=N1)C2=NN=C(N2N)N)N		Nc2nc(c1nnc(N)n1N)n[nH]2	
6		C1(=NNC(=N1)N)C2=NN=C(N2N)N		Nc2nc(c1nnc(N)n1N)n[nH]2	
7		C1(=NN=C(N1[TlH])N)C2=N[N+](=C(N2N)N)[TlH]		Nc2nnc(c1n[nH+]c(N)n1N)[nH]2	

(*Continued*)

Table 1. (Continued).

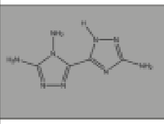
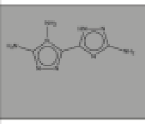
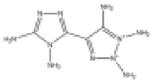
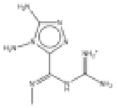
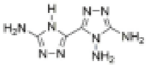
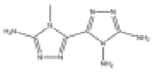
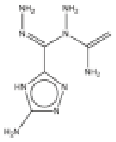
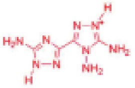
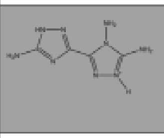
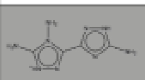
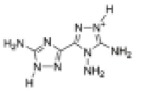
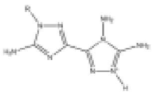
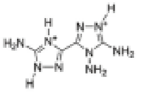
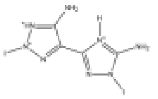
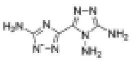
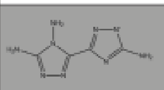
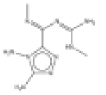
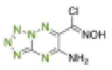
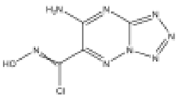
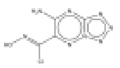
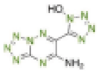
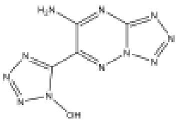
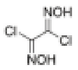
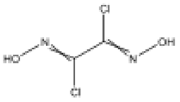
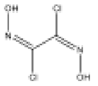
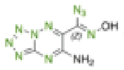
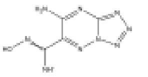
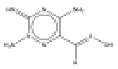
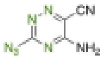
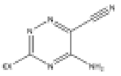
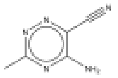
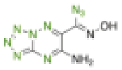
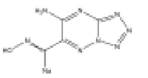
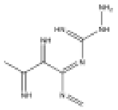
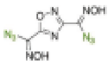
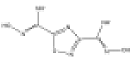
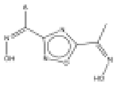
	Original picture[a]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
8		C1(=NC(=NN1[H])N)C2=NN=C(N2N)N		Nc2n[nH]c(c1nnc(N)n1N)n2	
9		C1(=N[N+]([N+](=C1N)N)N)C2=NN=C(N2N)N		C/N=C(NC(N)=[NH2+])/c1nnc(N)n1N	
10		CN1C(=NN=C1N)C2=NN=C(N2N)N		C=C(N)N(N)/C(=N/N)c1nnc(N)[nH]1	
11		C1(=NNC(=N1)N)C2=N[N+]([H])=C(N)N2N		Nc2nc(c1n[nH+]c(N)n1N)n[nH]2	
12		C1(=NN(C(=N1)N)[R])C2=N[N+]([H])=C(N)N2N		N/C2=N/C(c1n[nH+]c(N)n1N)*N2	
13		C1(=NN(C(=[N+]1[H])N)I)C2=N[N+]([NH+]=C2N)I		C=[N+]=C(N)N/N=C(C)/c1n[nH+]c(N)n1N	
14		C1(=N[N-]C(=N1)N)C2=NN=C(N2N)N		C/N=C(\N=C(N)/NC)/c1nnc(N)n1N	

Table 2. Molecules from "Cleveland, A. H., Imler, G. H., Snyder, C. J., Chavez, D. E., Parrish, D. A., Propellants, explos. pyrotech. 2022, 47, 1–7".

	Original picture[a]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
1		C1(=NN2C(=NN=N2)N=C1N)C(=NO)Cl		Nc2nc1nnnn1nc2/C(Cl)=N/O	
2		C1(=NN2C(=NN=N2)N=C1N)C3=NN=NN3O		Nc2nc1nnnn1nc2c3nnnn3O	
3		C(=NO)(C(=NO)Cl)Cl		O/N=C(Cl)/C(Cl)=N/O	
4		C1(=NN2C(=NN=N2)N=C1N)C(=NO)[NH-]		*/C(=*\O)c1nn(N)c(=N)nc1N	
5		C(#N)C1=NN=C(N=C1N)[X€]		Cc1nnc(C#N)c(N)n1	
6		C1(=NN2C(=NN=N2)N=C1N)C(=NO)[Na]		C=N/C(=N/C(=N)NN)C(=N)C(C)=N	
7		C1(=NOC(=N1)C(=NO)[NH-])C(=NO)[NH-]		*/C(=N/O)c1noc(/C(C)=N/O)n1	

(*Continued*)

Table 2. (Continued).

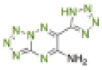
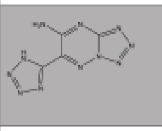
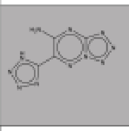
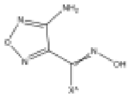
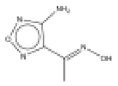
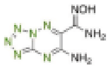
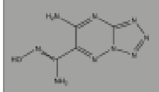
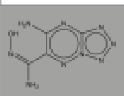
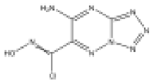
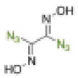
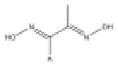
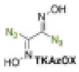
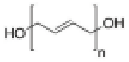
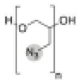
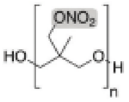
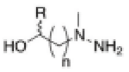
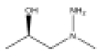
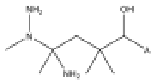
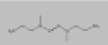
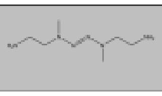
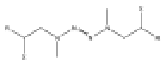
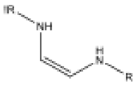
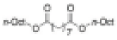
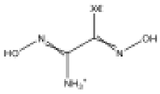
	Original picture[8]	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
8		C1(=NN2C(=NN=N2)N=C1N)C3=NN=NN3		Nc2nc1nnnn1nc2c3nnn[nH]3	
9		C1(=NON=C1N)C(=NO)[X^]		C/C(=N\O)c1nonc1N	
10		C1(=NN2C(=NN=N2)N=C1N)C(=NO)N		N/C(=N/O)c2nn1nnnc1nc2N	
11		C1(=NN2C(=NN=N2)N=C1N)C(=NO)Cl		Nc2nc1nnnn1nc2/C(Cl)=N\O	
12		C(=NO)(C(=NO)[X^])[X^]		*/C(=N\O)/C(C)=N/O	
13	 TKAzOX	C(=NO)(C(=NO)[X€])[NH3+]		*/C(=N\O)/C(C)=N/O	

Table 3. Eymann, J., Joucla, L., Jacob, G., Raynaud, J., Darwich, C., Lacôte, E., Angew. chemie - int. ed. 2021, 60, 1578–1582.

	Original picture	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
1		CC(C)(/C=C/CO)O		No structure recognized	No structure recognized
2		CC(C)(C)OCC(C)(C[N+]#[C-])O		No structure recognized	No structure recognized
3		CC(C)(C)OCC(C)(CO)CO[N+](=O)[O-]		*C3(/C1=C/C1C2CCC(CC(C)(CC)CCC)C2)*C3	
4		C[C@H](CN(C)N)O		*C(O)C(C)(C)CC(C)(N)N(C)N	
5		CN(CCN[O-])N		No structure recognized	No structure recognized
6		CN(CCN)N=NN(C)CCN		CN(CCN)/N=N/N(C)CCN	
7		CN(CC([X])[R])N=NN(C)CC([X])[R]		*CC(C)(C)N(/C(C)=C/C)N(C)NN(C)N(C)C(C)(C)CC*C(*)CC	

(*Continued*)

Table 3. (Continued).

	Original picture	SMILES (DECIMER2.1)	DECIMER2.1	SMILES (OSRA)	OSRA
8		CN(CC([R])SC(=O)[In])N=NN(C)CC([R])SC(=O)[In]		No structure recognized	No structure recognized
9		CC(C)(C)C(=O)OC(C)(C)CN(C)N=NN(C)CC(OC(=O)N(CC(C)(C)N(C(C)(C)C[R])[R£])[R])[R]	*Unable to display in Chemdraw*	**(*)N(*)C(C)(C)CC(C)(C)CN(*)C(=O)OC(*)C(C)(N)CC(C)(C)N(C)/N=N/N(C)C(C)(N)CC(C)(C)C(*)OC(=O)C(*)(*)C	
10		CN(CC([R])SC(=O)[In])N=NN(C)CC([R])SC(=O)[In]		*C(*C(C)=O)C(C)(N)CC(C)(C)N(C)/N=N/N(C)C(C)(C)C[C+](=C)(C)C**(N)=O	
11		C(=C/N[R!])/N[R]		No structure recognized	No structure recognized
12		CN(CC(O)[R])N=NN(C)CC(O)[R].[Na+].[Na+].O.O	*Unable to display in Chemdraw*	*C(O)C(C)(C)CC(C)(N)N(C)N=N	
13		CN(CCC[As])N=NN(C)CCC[As]		*C(O)C(C)(C)CC(C)(N)N(C)N=N	
14		C(=NO)(C(=NO)[X€])[NH3+]		CCCCN(C)/N=N/N(C)CCCNI	

Disclosure statement

No potential conflict of interest was reported by the authors.

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