energies

MDPI

Article

Role of -SF_5 Groups in Modulating the Stability and Energy Characteristics of Fluorinated Molecules

Jelena Tamuliene [1,*] and Jonas Sarlauskas [2,*]

[1] Physics Faculty, Institute of Theoretical Physics and Astronomy, Vilnius University, Sauletekio av. 3, LT-10257 Vilnius, Lithuania
[2] Department of Xenobiotics Biochemistry, Institute of Biochemistry, Life Sciences Center, Vilnius University, LT-10257 Vilnius, Lithuania
* Correspondence: jelena.tamuliene@tfai.vu.lt (J.T.); jonas.sarlauskas@bchi.vu.lt (J.S.); Tel.: +370-6891-2133 (J.T.)

Abstract: In this paper, we present our investigations into the detonation performance and stability variations caused by replacing the -CF_3 or -OCF_3 group with -SF_5. The widely applied DFT B3LYP/cc-pVTZ approach was employed to evaluate the HOMO–LUMO gap, cohesive energy, chemical hardness, and electronegativity. Based on these parameters, we predict the changes in chemical and thermal stability resulting from the inclusion of -SF_5 instead of -CF_3 or -OCF_3. Our results indicate that, in some cases, the density of fluorine-containing nitro compounds decreases due to the presence of the pentafluorosulfanyl group. Additionally, machine learning techniques were used to determine the detonation pressure and velocity of fluorine–sulfur-containing compounds. Our findings suggest that fluorine-containing nitro compounds exhibit better detonation performance and stability than fluorine–sulfur-containing ones. Overall, the pentafluorosulfanyl groups inclusion of aromatic polynitro compounds improved neither the stability nor the detonation properties such as -CF_3 or -OCF_3 groups.

Keywords: high-energy materials (HEM); fluorine-containing nitrocompounds; pen-tafluorosulfanyl group (SF_5); detonation properties; density; stability

Academic Editor: Peter Foot

Received: 14 February 2025
Revised: 2 April 2025
Accepted: 3 April 2025
Published: 5 April 2025

Citation: Tamuliene, J.; Sarlauskas, J. Role of -SF_5 Groups in Modulating the Stability and Energy Characteristics of Fluorinated Molecules. *Energies* **2025**, *18*, 1841. https://doi.org/10.3390/en18071841

1. Introduction

High-energy materials are widely used for mining, construction, military, and other purposes. Thus, they are exploited in increasing amounts each year, leading to increased requirements for effectiveness and safety. Currently, there are several directions being explored in modeling and synthesis to produce materials with favorable detonation performance and high resistance to any stimuli. One of these directions relies on increasing the density of potential hazards. Generally, this is achieved by including nitrogen-rich backbones such as triazole, furazan, etc. Recently performed investigations reveal that the inclusion of the fluorine-containing group to cycle nitramines could increase their densities and detonation performance while retaining good thermal stability [1,2]. These results are supported by investigations of Wang et al., which exhibited that the detonation velocity and heat of explosion of 3-Bromo-5-fluoro-2,4,6-trinitroanisole are higher and the impact and friction sensitivity are lower than those of TNT [3]. The presence of the pentafluorosulfanyl group also markedly increases the materials' densities and can provide energetic salts with improved properties [4]. Nevertheless, the synthesis of SF_5-containing high-energy materials is a challenge, and much effort is required to overcome it [5]. Despite the fact that some aromatic derivatives containing -SF_5 functional groups have already found applications in the molecular structures of pesticides, optoelectronic materials, and medicinal drugs, only

a few S-containing organic high-energy materials have been described as high-energy ones. A few existing studies discuss the computational and experimental energetic properties of these potentially interesting and useful compounds.

Notably, along with increasing the detonation performance, the thermal and chemical stability and resistance to shock stimuli must be equal to or, in beneficial cases, higher than that of the exploited high-energy materials. Jagadish et al. described the incorporation of sulfur into high-energy materials as a way to improve their thermostability and, in some cases, to decrease their sensitivity to impact, friction, and electrostatic discharge [6]. The newly synthesized C–C bonded 1,3,4-thiadiazole with pyrazine, incorporating a nitrimino explosophoric moiety, exhibits moderate to high thermal decomposition temperatures, high positive heats of formation, and good densities with strong detonation performance [7].

A study that we recently conducted reveals that the incorporation of -CF_3 and -OCF_3 fragments could increase the energetic properties of nitroaromatics, along with their stability and resistance to shock stimuli. Certain compounds, with the assignation codes CF3N2, OCF3N2, C2F6N2, 1CF2N2/O2CF2N2, and 2CF4N2/O2C2F4N2, were recommended for practical usage because they possess higher stability than tetryl and better explosive properties than TNT [8]. Views of these compounds and their full chemical names are given in Appendix A. Hence, referring to the above facts, we may state that the incorporation of sulfur and fluorine improves the stability and energetic properties of the compounds. In this context, pentafluorosulfanyl is the best candidate for a theoretical study that seeks to predict this technique's potential to improve the above properties. Thus, it is necessary to determine whether the detonation properties of the nitro-compounds are better when -SF_5 is incorporated along with the above-mentioned fluorine-containing groups. On the other hand, it remains unclear which fluorine- and fluorine–sulfur-containing groups or their combination leads to the greatest improvement. This means not only enhancing detonation properties but also significantly increasing the chemical and thermal stability of the material, as well as its impact resistance. Therefore, this study aims to predict whether replacing the -CF_3 or -OCF_3 groups in aromatic nitrocompounds with -SF_5 will enhance their energetic properties. Our study will help to estimate the significance of this replacement and indicate new directions in the design of advanced high-energy materials. Previously, only the early works of Sitzmann et al. were dedicated to pentafuorosulfanyl derivatives; they studied their physicochemical and energetic properties. However, that study only covered nitro aliphatic compounds, while nitroaromatic compounds were scarcely studied [9]. We contend that the results of this research will help to identify directions that are likely to lead to improvements in high-energy material properties. Consequently, this allows for a more efficient use of research resources and supports the pursuit of more promising strategies for performance enhancement.

2. Materials and Methods

As outlined above, this study aimed to demonstrate the influence of the -SF_5 group on the stability and energetic properties of fluorine-containing compounds. The methodology employed in this research aligns with that presented in our recently published work [8]. Multiple conformers of each molecule under investigation were designed to ensure reliable results. The conformers differ in the positions of substituents relative to the core structure. It is important to note that, in certain cases, steric effects allow for only one positional arrangement.

Becke's three-parameter hybrid functional approach with non-local correlation, as defined by Lee, Yang, and Parr (B3LYP), was utilized in conjunction with the cc-pVTZ basis set implemented in the GAUSSIAN software package [10–12]. This approach effectively describes various molecules' geometric and electronic structures and their derivatives [13–23].

To identify equilibrium configurations, Berny optimization was performed without applying any symmetry constraints, allowing for the optimization of bond lengths, angles, and dihedral angles. A vibrational frequency analysis confirmed that energy minima were achieved, ensuring that the structure of the most stable conformer was identified.

Initially, the calculated total energies of the conformers were compared, and the conformers with the lowest total energy were selected for further analysis. To assess and compare the thermal stability of compounds with varying chemical compositions, cohesion (*BEA*) was calculated. This parameter, which indicates the energy required to separate an atom from a system of particles, was determined using the following formula:

$$BEA = \frac{E - \sum_i E_i}{N}$$

where E is the total energy of the molecule under study, E_i is the total energy of the atoms consisting of this molecule, and N is the number of atoms. A larger value of *BEA*, the normalized energy differences, shows higher thermal stability. To evaluate the stability related to the chemical properties and aging of the compounds investigated, we calculated the HOMO–LUMO gap, chemical hardness, and electronegativity. It is known that compounds with a larger HOMO–LUMO gap and chemical hardness are more resistant to undergoing chemical reactions or to being transformed by an external perturbation, such as an applied electric field. On the other hand, a high level of electronegativity denotes a molecule's strong tendency to attract an electron; this leads to ionization and could speed up the degradation [24,25].

It is known that the density of the compounds is the main factor in increasing the detonation pressure and velocity of the compounds. Our study begins with the evaluation of the density of the generic compounds: C2F6N3, CF3N2, CF3N3, C3F9N3, O2C2F6N3, and O3C3F9N3. The density of the compounds was predicted using three approaches:

- The equations developed by Politzer et al. [26], which include the molecular mass, the volume of the 0.001 electrons/bohr^3 counter of the electronic density of a molecule, the degree of balance between positive potential and negative potential on the surface, and their sum;
- Methods implemented in ACD/ChemSketch based on the Van der Walls volumes molecular modeling program [24];
- The division of molecular weight by molar volume, obtained via B3LP/cc-pVTZ.

We used this method in order to find a more reliable approach for evaluating the density of the compounds consisting of -SF_5 substitutes. ACD/ChemSketch reliably predicts the density of known fluorine-containing compounds. For example, the experimentally obtained density of CF3N3 is 1.716–1.816 g/cm^3, while that estimated by ACD/ChemSketch is equal to 1.77 g/m^3 [24]. Based on the analysis of the calculated densities and the outlined values of the experimental measurements, the density of the -SF_5-containing compounds was calculated using the above Politizer equation. The proof of the above decision is given in the Results section.

The semi-empirical equations Kamlet and Jacobs developed focus on the $C_aH_bN_cO_d$ compounds. They are not suitable for evaluating the parameters of the derivatives consisting of fluorine and sulfur. The equations suggested by Keshavarz et al. are dedicated to the $C_aH_bN_cO_dF_e$ compounds [27,28]. The approaches implemented in Cheetah, Thermo, or EXPLO5 rely on thermodynamic databases, which may have limited or incomplete data for certain fluorine- and sulfur-containing compounds, particularly those that are newly designed and not synthesized. Therefore, we used several machine learning models to evaluate the detonation velocity and pressure. The data used for training were collected from

all available studies [28–30]. Considering that the SF_5-group is used to increase the density of these molecules, leading to better detonation performance, we obtained the dependence of the detonation pressure and velocity on the density. Another main reason for focusing solely on the density of the compound is the variability of other parameters provided alongside the detonation pressure and velocity. To ensure that we had a comprehensive dataset for training, we aimed to minimize incompleteness caused by differences in the parameters presented. Notably, the density of the compounds depends on their chemical and geometrical structures; it is, therefore, one of the factors influencing the products of detonation, which directly determines the detonation pressure and velocity [31]. Considering our aim to show how the stability and explosive properties of the fluorine-containing compounds could be changed by replacing the -CF_3 group with -SF_5, in conjunction with advanced machine learning, we hope that the above dependence is sufficient to determine the main general tendency for improving the properties of high-energy materials.

The dataset for machine learning consists of sulfur and sulfur-fluorine compounds, and it is used to obtain general equations for evaluating and determining the progress of the detonation properties, which rises due to the implementation of the -SF_5 groups. It satisfies our aim of predicting the influence of the above sulfur group on the energetic properties of the fluorine-containing compounds, i.e., when -CF_3 groups are replaced by -SF_5. As the dataset for machine learning was relatively small, we employed linear regression, polynomial regression, random forest regression, and Bayesian ridge regression, which are known to perform well in predicting numerical values. We used 80% of the generated dataset for training, reserving the remaining 20% for testing. To identify the most precise model, the models' performances were evaluated using metrics such as accuracy, the mean squared error, and the coefficient of determination (R^2). Additionally, we found that the detonation pressure mostly depends on the density of the compounds, while the detonation velocity is dependent on pressure. The metrics for assessing the accuracy of the applied machine learning methods were the best in the case of the polynomial regressions. Thus, the resulting equations of this approach were applied to calculate the detonation pressure and velocity of the newly designed fluorine- and sulfur-containing compounds. Each predicted value was validated against experimentally observed trends and anticipated limitations to ensure reliability.

3. Results

The sketches of the investigated compounds, their chemical composition, full chemical names, and assignation codes are presented in Appendices A and B. It should be noted that the hardness index of the compounds under study is higher than 0.9, which indicates their higher thermal and chemical stability. To be more specific and show how the -SF_5 group influences the thermal and chemical stability of the selected fluorine-containing compounds, we calculated the cohesion, HOMO–LUMO gap, chemical hardness, and electronegativity. The dependence of these parameters on the number of -SF_5 group is presented in Figures 1–4 and Table 1.

The study of the energetic properties began with the evaluation of the approaches used for the density calculations. Table 2 shows the values of the densities of the fluorine-containing compounds obtained using the approach implemented in ACD/ChemSketch program and the equation suggested by Politizer et al.; these values are followed by our calculation results.

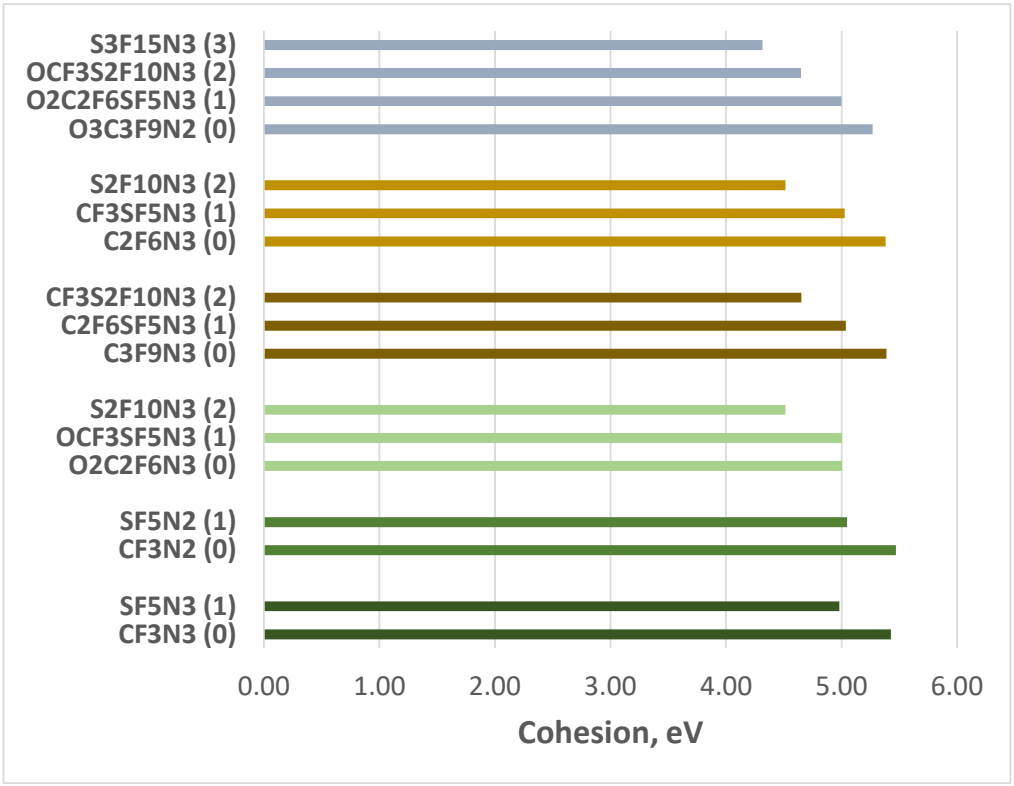


Figure 1. Dependence of cohesion on the incorporation of the -SF_5 group. The colors represent compounds derived from different parent compounds, arranged in order of the increasing -SF_5 group number presented in the bracket.

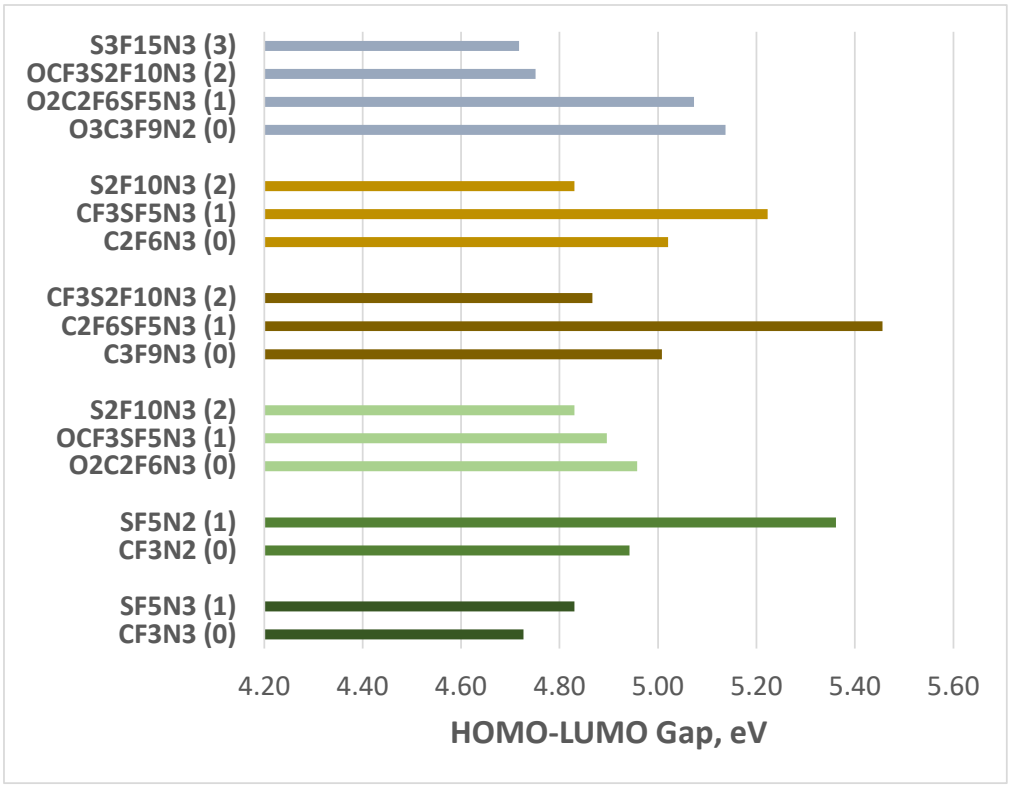


Figure 2. The figure illustrates the dependence of HOMO–LUMO on the incorporation of the -SF_5 group. The colors represent compounds derived from different parent compounds, arranged in order of the increasing -SF_5 group number presented in the brackets.

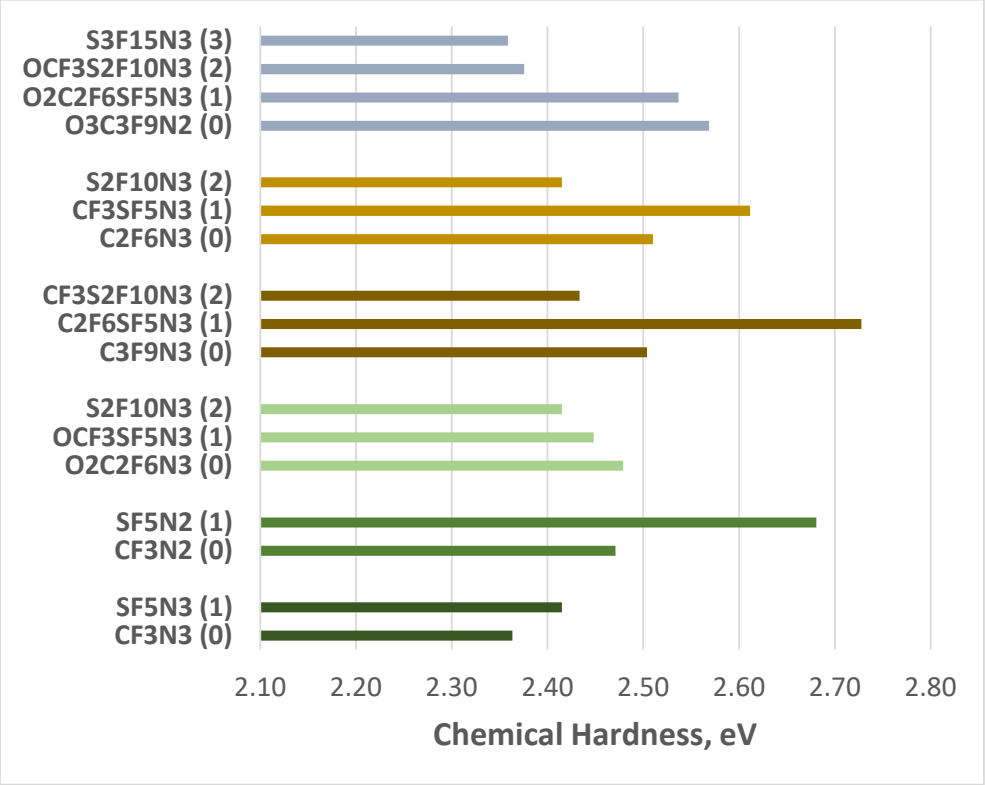


Figure 3. Dependence of chemical hardness on the incorporation of the -SF_5 group. The colors represent compounds derived from different parent compounds, arranged in order of the increasing -SF_5 group number presented in the brackets.

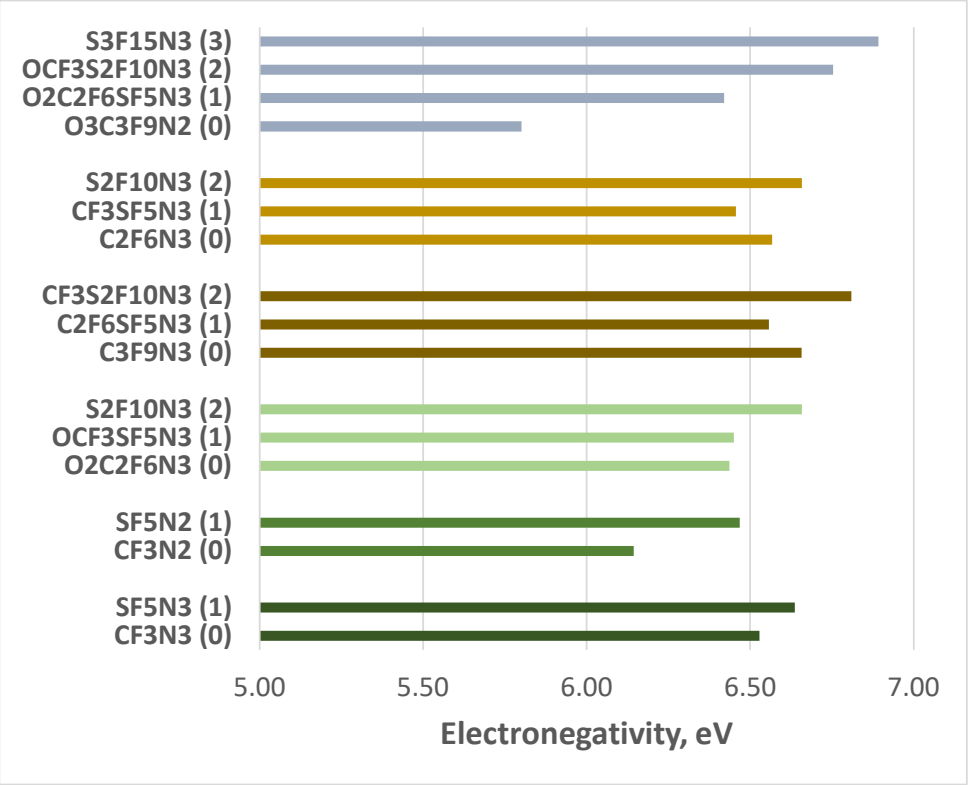


Figure 4. Dependence of electronegativity on the incorporation of the -SF_5 group. The colors represent compounds derived from different parent compounds, arranged in order of the increasing -SF_5 group number presented in the brackets.

Table 1. The obtained values for cohesion (*BEA*), the HOMO–LUMO gap (Gap), chemical hardness (CH), and electronegativity (ELN). The parameters of some compounds are repeated several times because they are the results of the complete replacement of -CF_3 or -OCF_3 groups by -SF_5.

Compounds	*BEA*, eV	Gap, eV	CH, eV	ELN, eV
C2F6N3	5.38	5.02	2.51	6.57
CF3SF5N3	5.02	5.22	2.61	6.46
S2F10N3	4.51	4.83	2.41	6.66
CF3N2	5.47	4.94	2.47	6.14
SF5N2	5.05	5.36	2.68	6.47
CF3N3	5.43	4.73	2.36	6.53
SF5N3	4.98	4.83	2.41	6.64
C3F9N*/	5.39	5.01	2.50	6.66
C2F6SF5N3	5.04	5.45	2.73	6.56
CF3S2F10N3	4.65	4.87	2.43	6.81
O2C2F6N3	5.00	4.96	2.48	6.44
OCF3SF5N3	5.00	4.90	2.45	6.45
S2F10N3	4.51	4.83	2.41	6.66
O3C3F9N2	5.27	5.14	2.57	5.80
O2C2F6SF5N3	5.00	5.07	2.54	6.42
OCF3S2F10N3	4.65	4.75	2.38	6.75
S3F15N3	4.31	4.72	2.36	6.89

Table 2. The density of the fluorine-containing compounds obtained using the approach implemented in the ACD/ChemSketch program (ρ_{AC}), with Gaussian ρ_G, and that suggested by Politizer et al. (ρ).

Compound	ρ_{AC}, g/cm^3	ρ_G, g/cm^3	ρ, g/cm^3
CF3N2	1.74	1.98	1.60
C2F6N3	1.82	2.34	1.79
CF3N3	1.77	2.07	1.83
C3F9N2	1.85	2.09	2.02
O3C3F9N2	1.79	2.11	1.80
O3C3F9N3	1.89	2.05	1.95

It is observed that the values obtained using the equation proposed by Politzer et al. are generally higher than those calculated using the ACD/ChemSketch program but lower than those derived from calculations performed with the Gaussian program. Moreover, the density of the CF3N3 compound obtained by the equation coincides with the experimentally determined density of 1.82 g/cm^3. The calculated densities of the other presented compounds also fall in the range of representative values [1.6–2.4 g/cm^3] of the experimentally measured ones for fluorine-containing compounds [32]. The above equation along with the approach implemented in ACD/ChemSketch was used to evaluate the fluorine–sulfur-containing compound's density. The density is presented in Table 3.

The presented values of SF_5-containing compounds range from 1.30 (gas state) to 2.08 g/cm^3, although, in some cases (for example, in concentrated forms), these values can approach or exceed 2.40 g/cm^3 and reach 2.86 g/cm^3 [29–31]. Referring to the results presented in Table 3, we may assume that the approach implemented in the ACD/ChemSketch program is dedicated to evaluating the density of the sulfur–fluorine-containing compounds in concentrated forms. On the other hand, the values obtained using the equation of Politizer et al. represent a more general density of these types of compounds. We used these values of the densities for the evaluation of derivatives representing energetic

properties to avoid overestimating them, considering the potential of the sulfur–fluorine-containing compounds.

Table 3. The density of the sulfur–fluorine-containing compounds obtained using the approach implemented in the ACD/ChemSketch program (ρ_{AC}) and that suggested by Politizer et al. (ρ).

Compound	ρ_{AC}, g/cm^3	ρ, g/cm^3
CF3SF5N3	2.35	2.09
SF5N2	2.19	1.41
SF5N3	2.20	1.88
C2F6SF5N3	2.26	2.03
CF3S2F10N3	2.84	2.40
CF3SF5N3	2.35	1.89
OCF3SF5N3	2.41	1.76
S2F10N3	2.26	1.60
O2C2F6SF5N3	2.27	2.07
OCF3S2F10N3	2.41	1.76
S3F15N3	2.48	2.05

As mentioned above, we used several machine learning models to find the one that is the most suited to the present investigation. The highest accuracy, lowest mean squared error, and coefficients of determination of 0.70 for evaluating the dependence of detonation pressure on density and 0.90 for that of detonation velocity on the pressure were achieved using the polynomial regression model. Thus, this model was used to evaluate the detonation velocity and pressure. The obtained values are presented in Table 4.

Table 4. The detonation pressure (P) and velocity (D) of the sulfur–fluorine-containing compounds obtained using a polynomial regression model within a machine learning framework.

Compound	P, kbar	D. km/s
CF3SF5N3	297.8	7.55
SF5N2	160.4	6.41
SF5N3	295.6	7.53
C2F6SF5N3	325.2	7.73
CF3S2F10N3	369.9	7.99
OCF3SF5N3	335.2	7.79
S2F10N3	222.9	6.97
O2C2F6SF5N3	332.0	7.77
OCF3S2F10N3	267.3	7.99
S3F15N3	286.7	7.47

4. Discussion

The results of the density variations caused by replacing fluorine-containing groups by -SF_5 are presented in Figure 5.

Generally, replacing the -CF_3 group with -SF_5 tends to increase the density of the compounds. This observation aligns well with experimentally obtained results [28]. However, this trend is not observed in the case of CF2N2 and O2CF3SF5N3. This could be the case because the molecular volume outweighs the increase in molecular weight as a result of the trigonal bipyramidal geometry of the -SF_5 groups, which is bulkier than the relatively compact tetrahedral geometry of -CF_3. Therefore, while the addition of the heavy -SF_5 group can increase the density of compounds, this effect is not consistently observed when -CF_3 is replaced by -SF_5. Despite this finding, the density of two compounds (SF5N2 and S2F10N3) is lower than that of TNT, while that of CF3SF5N3, C2F6SF5N3, CF3S2F10N3,

O2C2F6SF5N3, and S3F15N3 is higher than the density of HMX—a powerful and relatively insensitive nitroamine.

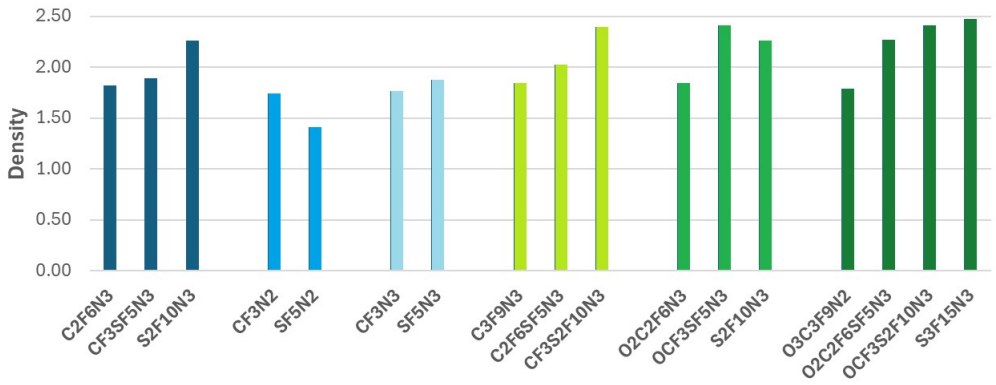


Figure 5. Changeability of the density of the CF_3-containing compounds when the group is replaced by -SF_5. The colors represent compounds derived from different parent compounds, arranged in order of increasing by one -SF_5 group number from 0 on the left to 3 or less on the right.

As mentioned above, the hardness index of the compounds under study indicated their high stability. However, the analysis of the *BEA* indicates that implementation of the -SF_5 leads to a decrease in thermal stability (Figure 1, Table 1). Indeed, the S–F and C–F bonds are some of the strongest bonds, rendering these -SF_5 and -CF_3 groups highly resistant to thermal decomposition and chemical reactions. However, the bond energy (272 kJ/mol) of the S–C bonds is lower than the 347 kJ/mol of C–C [33,34]. In some cases, the 360 kJ/ mol of the C–O bond is replaced by lower-energy C–S. This could be the main reason for the decrease in thermal stability caused by the replacement of -CF_3 with -SF_5. Based on the findings, we can predict that S–C bonds should be decomposed first during an explosion to form -CF_3 and -SF_5 and, then, if enough energy is released, these groups should degrade. Thus, after an explosion of CaHbFcNdOeSf compounds rich in -SF_5 groups, along with CO, CO_2, COS, H_2S, HF, H_2O, and N_2 gases, then SFn could also be present [35].

Referring to the results of the HOMO–LUMO gap's dependence on the -SF_5 group number, we conclude that some precise number of -SF_5 is found in the most chemically stable compounds (Figure 2; Table 1). Indeed, the HOMO–LUMO gap of the compounds with one -SF_5 group is the largest among the similar ones. More precisely, replacing one -CF_3 group with -SF_5 increases the chemical stability of nitro compounds. However, the addition of a second -SF_5 group significantly decreases stability, while the influence of additional -SF_5 groups appears negligible. The exception is O3C3F9N2, which is a highly fluorine-rich compound; thus any replacement of -CF_3 with -SF_5 leads to a decrease in chemical stability. Referring to these results, we speculate that increasing the fluorine content in nitro compounds to improve both chemical and thermal stability may be limited by two factors: there are nine fluorine atoms in the compound, and the implementation of other fluorine-containing groups worsens stability.

This tendency is confirmed by the analysis of the chemical hardness: the largest values of the parameter are the compounds possessing one -SF_5 group, except for the sulfur–fluorine compounds originating from O3C3F9N2. Thus, the most chemically stable compounds derived from different parent molecules can be ranked based on their resistance to reaction, as follows:

C2F6SF5N3 > SF5N2 > CF3SF5N3 > O3C3F9N2 > OCF3SF5N3 > SF5N3

The high electronegativity of the compounds under study is not a surprise because they consist of fluorine atoms. The values of this parameter ranged from 5.18 eV to

6.89 eV, indicating a high tendency to attract electrons, which could lead to fast aging due to ionization.

It is necessary to highlight SF5N2 and SF5N3, which differ in the number of -NO_2 groups. Previously, we demonstrated that increasing the number of -NO_2 groups in fluorine-containing compounds enhances their energetic properties. This trend is evident in these compounds: the detonation pressure and velocity of SF_5N_2, which contains two nitro groups, are lower than those of SF_5N_3, which possesses three nitro groups.

Typically, the high-energy materials exhibit detonation velocities between 1.01 km/s and 9.89 km/s. The measured detonation velocity of TNT, usually used as a standard, is 6.9 km/s. That of RDX and HMX is 8.7 and 9.1 km/s, respectively. Hence, the detonation velocity results presented in Table 4 classify the compounds under study as high-energy materials. Moreover, the detonation velocities of only two compounds, S2F10N3 and SF5N2, are comparable to that of TNT, while the detonation velocity of the remaining compounds is higher. However, these detonation velocities are lower than RDX and HMX. A similar observation can be made when comparing the detonation pressures of TNT (~210 kbar), RDX (338 kbar), and HMX(393 kbar) with the values presented in Table 4 [7,36]. Again, the detonation pressures of S2F10N3 and SF5N2 are similar to that of TNT, while that of the others is between TNT and RDX, except for CF3S2F10N3. The detonation pressure of this compound is higher than that of RDX but lower than that of HMX. Hence, the implementation of -SF_5 groups could lead to improvements in the energetic properties of fluorine–sulfur-containing nitro compounds, but it is not mandatory (Figure 6, Table 4). Notably, the detonation pressure of the nitro compounds consisting of -CF_3 or -OCF_3 explored in this study varies from 189 to 459 kbar [8]. Their detonation velocity is also higher, ranging from 7.01 to 8.78 km/s. Based on these results, we speculate that replacing -CF_3 or -OCF_3 with -SF_5 would not improve the energetic properties of fluorine-containing nitro compounds.

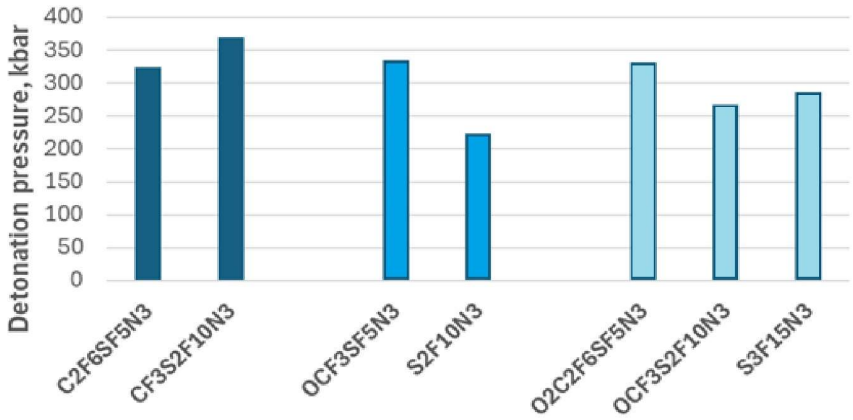


Figure 6. The dependence of detonation pressure on the incorporation of the -SF_5 group. The colors represent compounds derived from different parent compounds, arranged in order of increasing SF_5 group number from 1 on the left to 2 or 3 on the right.

That said, the results presented in Figure 6 suggest that replacing -CF_3 with -SF_5 may enhance the energetic properties of fluorine-containing compounds. However, this is not valid for compounds where -CF_3 is incorporated within oxygen. Reducing the number of oxygen atoms results in a decline in the energetic properties of the compounds consisting of -OCF_3 and -SF_5 groups.

5. Conclusions

This study aimed to predict the influence of replacing -CF_3 or -OCF_3 with -SF_5 on the stability and detonation performance of fluorine-containing nitro benzenes. Notably, all of the designed and investigated compounds are classified as high-stability and high-energy compounds.

We found that -CF_3 replacement by heavier -SF_5 groups does not necessarily increase the density of the compounds. This is because of the different intensifications in volume and molecule weights. However, the density of our proposed advanced materials, such as CF3SF5N3, C2F6SF5N3, CF3S2F10N3, O2C2F6SF5N3, S3F15N3, is higher than the density of HMX—a powerful and relatively insensitive nitroamine.

Another undesirable effect is the reduction in thermal stability caused by the inclusion of -SF_5 instead of -CF_3 or-OCF_3. Moreover, the comparison of the evaluated parameters such as the HOMO–LUMO gap, the energy of cohesion, and chemical hardness allows us to conclude that the number of fluorine atoms in the nitro compound should not be higher than nine, because surpassing this threshold leads to a decrease in the chemical and thermal stability of fluorine-containing nitro compounds. Additionally, we speculate that the compounds under study undergo rapid aging due to ionization, considering their high electronegativity.

Regarding detonation performance, no solid conclusion was reached regarding the improvement of the detonation performance due to replacing the fluorine group with pentafluorosulfanyl. The replacement of -OCF_3 with -SF_5 reduces the number of oxygen atoms, leading to a decline in the energetic properties in compounds containing both -OCF_3 and -SF_5. In contrast, replacing -CF_3 with -SF_5 produces the opposite effect, improving the detonation performance.

Based on our findings and the challenges associated with incorporating the pentafluorosulfanyl group into nitro compounds, we conclude that the practical implementation of compounds containing -SF_5, either alone or in combination with -CF_3 or -OCF_3, is unlikely to be effective or beneficial.

Author Contributions: Conceptualization, J.T. and J.S.; methodology, J.T., and J.S; formal analysis, J.T., and J.S.; investigation, J.T. and J.S.; writing—original draft preparation, J.T. and J.S.; writing—review and editing, J.T. and J.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available on request from the corresponding author due to access restrictions.

Acknowledgments: The numerical calculations conducted with the GAUSSIAN09 package were performed using the resources of the Information Technology Research Center of Vilnius University and the supercomputer "VU HPC" of Vilnius University in the Faculty of Physics location.

Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

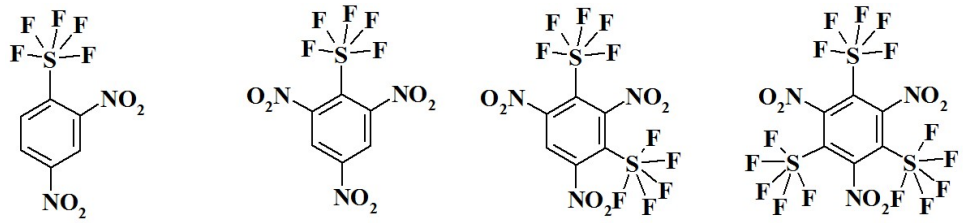
Abbreviations

The following abbreviations are used in this manuscript:

BEA	Cohesion
HOMO	The highest occupied molecular orbital
LUMO	The lowest unoccupied molecular orbital
Gap	HOMO–LUMO gap
CH	Chemical hardness
ELN	Electronegativity

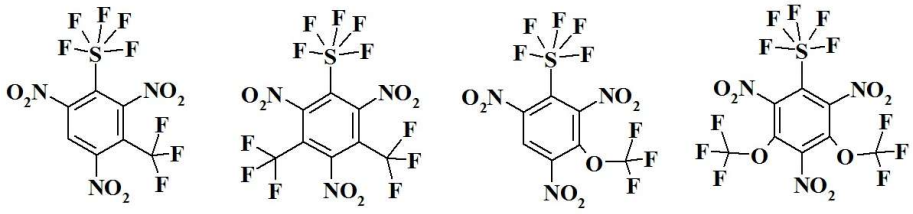
Appendix A

The view of sulfur- and fluorine-containing derivatives:



SF5N2 **SF5N3** **S2F10N3** **S3F15N3**

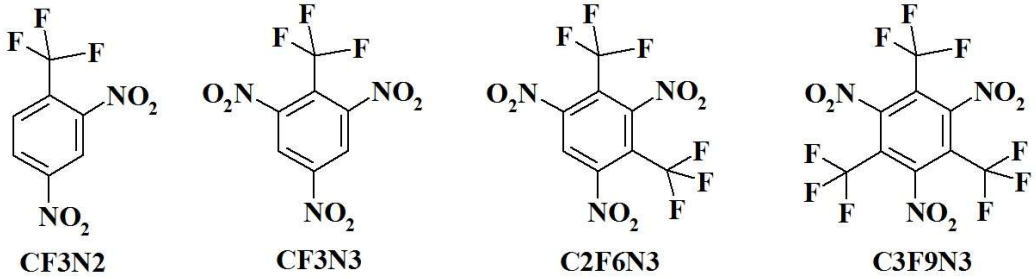
Code (Assignation) and Chemical Name:
SF5N2—*2,4-dinitro-1-(pentafluoro-lambda^6-sulfanyl)benzene;*
SF5N3—*1,3,5-trinitro-2-(pentafluoro-lambda^6-sulfanyl)benzene;*
S2F10N3—*1,3,5-trinitro-2,4-bis(pentafluoro-lambda^6-sulfanyl)benzene;*
S3F15N3—*1,3,5-trinitro-2,4,6-tris(pentafluoro-lambda^6-sulfanyl)benzene;*



CF3SF5N3 **C2F6SF5N3** **OCF3SF5N3** **O2C2F6SF5N3**

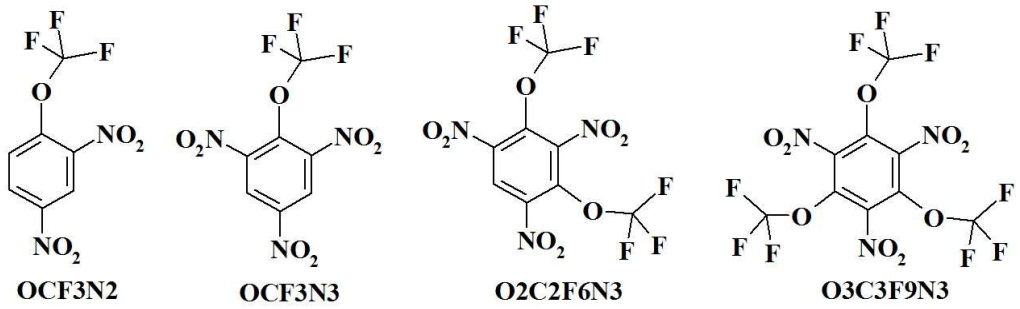
Code (Assignation) and Chemical Name:
CF3SF5N3—*1,3,5-trinitro-2-(pentafluoro-lambda^6-sulfanyl)-4-(trifluoromethyl)benzene;*
C2F6SF5N3—*1,3,5-trinitro-2-(pentafluoro-lambda^6-sulfanyl)-4,6-bis(trifluoromethyl)benzene;*
OCF3SF5N3—*1,3,5-trinitro-2-(pentafluoro-lambda^6-sulfanyl)-4-(trifluoromethoxy)benzene;*
O2C2F6SF5N3—*1,3,5-trinitro-2-(pentafluoro-lambda^6-sulfanyl)-4,6-bis(trifluoromethoxy)benzene;*

View of fluorine-containing derivatives:



CF3N2 **CF3N3** **C2F6N3** **C3F9N3**

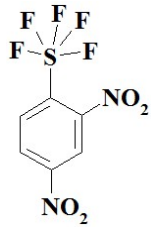
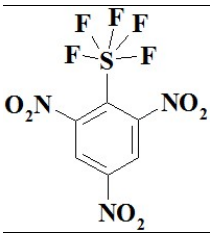
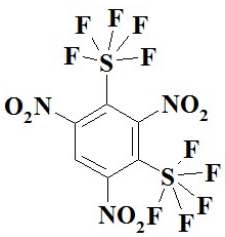
Code (Assignation) and Chemical Name:
CF3N2—2,4-dinitro-1-(trifluoromethyl)benzene;
CF3N3—1,3,5-trinitro-2-(trifluoromethyl)benzene;
C2F6N3—1,3,5-trinitro-2,4-bis(trifluoromethyl)benzene;
C3F9N3—1,3,5-trinitro-2,4,6-tris(trifluoromethyl)benzene;

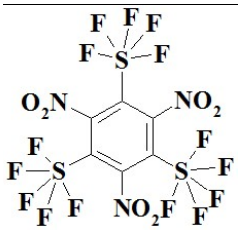
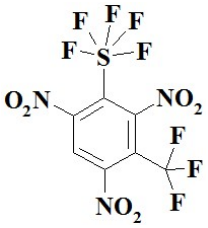
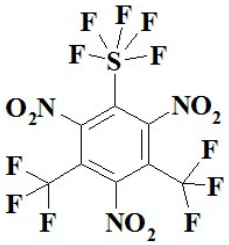
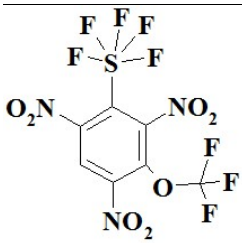
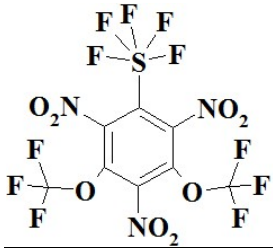


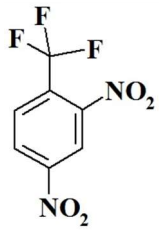
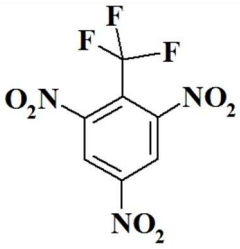
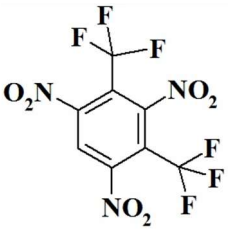
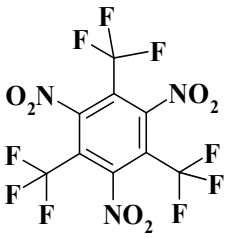
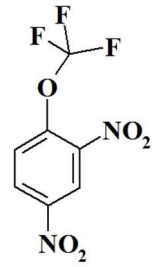
Code (Assignation) and Chemical Name:
OCF3N2—2,4-dinitro-1-(trifluoromethoxy)benzene
OCF3N3—1,3,5-trinitro-2-(trifluoromethoxy)benzene
O2C2F6N3—1,3,5-trinitro-2,4-bis(trifluoromethoxy)benzene
O3C3F9N3—1,3,5-trinitro-2,4,6-tris(trifluoromethoxy)benzene

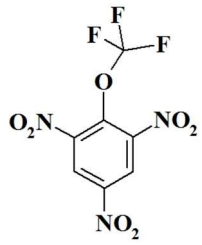
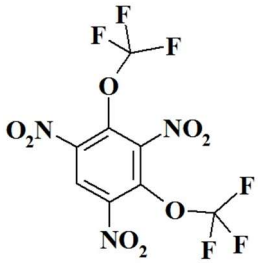
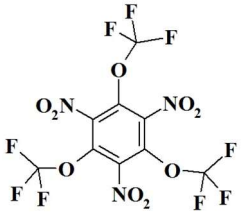
Appendix B

The chemical composition of the compounds under study.

No.	Structural Formula	Mol. Formula	MW	Elemental Analysis Data (Calculated)					
				C, %	H, %	N, %	O, %	S, %	F, %
1.		$C_6H_3F_5N_2O_4S$	294.16	24.50	1.03	9.52	21.76	10.90	32.29
2.		$C_6H_2F_5N_3O_6S$	339.16	21.25	0.59	12.39	28.30	9.45	28.01
3.		$C_6HF_{10}N_3O_6S_2$	465.20	15.49	0.22	40.84	9.03	13.78	40.84

No.	Structural Formula	Mol. Formula	MW	Elemental Analysis Data (Calculated)					
				C, %	H, %	N, %	O, %	S, %	F, %
4.		$C_6F_{15}N_3O_6S_3$	591.25	12.19	0	7.11	16.24	16.27	48.20
5.		$C_7HF_8N_3O_6S$	407.15	20.65	0.25	10.32	23.58	7.88	37.33
6.		$C_8F_{11}N_3O_6S$	475.15	20.22	0	8.84	20.20	6.75	43.98
7.		$C_7HF_8N_3O_7S$	423.15	19.87	0.24	9.93	26.47	7.58	35.92
8.		$C_8F_{11}N_3O_8S$	507.15	18.95	0	8.29	25.24	6.32	41.21

No.	Structural Formula	Mol. Formula	MW	Elemental Analysis Data (Calculated)					
				C, %	H, %	N, %	O, %	S, %	F, %
9.		$C_6H_3F_3N_2O_4$	236.11	35.61	1.28	11.86	27.11	0	24.14
10.		$C_7H_2F_3N_3O_6$	281.11	29.91	0.72	14.95	34.15	0	20.28
11.		$C_8HF_6N_3O_6$	349.10	27.52	0.29	12.04	27.50	0	32.65
12.		$C_9F_9N_3O_6$	417.10	25.92	0	10.07	23.02	0	40.99
13.		$C_7H_3F_3N_2O_5$	252.11	33.35	1.20	11.11	31.73	0	22.61

No.	Structural Formula	Mol. Formula	MW	Elemental Analysis Data (Calculated)					
				C, %	H, %	N, %	O, %	S, %	F, %
14.		$C_7H_2F_3N_3O_7$	297.11	28.30	0.68	14.14	37.70	0	19.18
15.		$C_8HF_6N_3O_8$	381.11	25.21	0.26	11.03	33.59	0	29.91
16.		$C_9F_9N_3O_9$	465.10	23.24	0	9.03	30.96	0	36.76

References

1. Lin, H.; Zhu, Q.; Huang, C.; Yang, D.D.; Lou, N.; Zhu, S.G.; Li, H.Z. Dinitromethyl, fluorodinitromethyl derivatives of RDX and HMX as high energy density materials: A computational study. *Struct. Chem.* **2019**, *30*, 2401–2408. [CrossRef]
2. Yang, J.; Bai, T.; Guan, J.; Li, M.; Zhen, Z.; Dong, X.; Wang, Y.; Wang, Y. Novel fluorine-containing energetic materials: How potential are they? A computational study of detonation performance. *J. Mol. Model.* **2023**, *29*, 228. [CrossRef] [PubMed]
3. Wang, Y.; Song, X.L.; Yu, Z.H.; Song, D.; An, C.W.; Li, F.S. A high density and low sensitivity carrier explosive promising to replace TNT: 3-Bromo-5-fluoro-2,4,6-trinitroanisole. *Energetic Mater. Front.* **2024**, *5*, 131–140. [CrossRef]
4. Gao, H.; Ye, C.; Winter, R.W.; Gard, G.L.; Sitzmann, M.E.; Shreeve, J.N.M. Pentafluorosulfanyl (SF5) containing energetic salts. *Eur. J. Inorg. Chem.* **2006**, *16*, 3221–3226. [CrossRef]
5. Martinez, H.; Zheng, Z.; Dolbier, W.R., Jr. Energetic materials containing fluorine. Design, synthesis and testing of furazan-containing energetic materials bearing a pentafluorosulfanyl group. *J. Fluor. Chem. Y* **2012**, *143*, 112–122. [CrossRef]
6. Das, J.; Shem-Tov, D.; Zhang, S.; Gao, C.Z.; Zhang, L.; Yao, C.; Flaxer, E.; Stierstorfer, J.; Wurzenberger, M.; Rahinov, I.; et al. Power of sulfur–Chemistry, properties, laser ignition and theoretical studies of energetic perchlorate-free 1, 3, 4–thiadiazole nitramines. *J. Chem. Eng.* **2022**, *443*, 136246. [CrossRef]
7. Kumar, P.; Ghule, V.D.; Dharavath, S. Advancing energetic chemistry: The first synthesis of sulfur-based C–C bonded thiadiazole-pyrazine compounds with a nitrimino moiety. *Dalton Trans.* **2024**, *53*, 19112–19115. [CrossRef]
8. Tamuliene, J.; Sarlauskas, J. Polynitrobenzene derivatives, containing -CF3, -OCF3, and -O(CF2)nO- functional groups, as candidates for perspective fluorinated high-energy materials: Theoretical study. *Energies* **2024**, *17*, 6126. [CrossRef]

9. Sitzmann, M.E.; Ornellas, D.L. The Effect of the Pentafluorothio (SF_5S) Group on the Properties of Explosive Nitro Compounds: New SF_5 Explosives. In Proceedings of the Ninth Symposium (International) on Detonation, Red Lion Inn, Columbia River Portland, OR, USA, 28 August–1 September 1989; Volume 2, pp. 1162–1169. Available online: https://archive.org/details/DTIC_ADA247996#:~:text=DTIC%20ADA247996:%20Proceedings%20of%20the%20International%20Symposium%20on,Free%20Download,%20Borrow,%20and%20Streaming%20:%20Internet%20Archive (accessed on 8 February 2025).
10. Becke, A.D. Density functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* **1993**, *98*, 5648. [CrossRef]
11. Dunning, T.H., Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007. [CrossRef]
12. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Petersson, G.A.; Nakatsuji, H.; et al. *Gaussian 09 W Reference*; Gaussian, Inc.: Wallingford, CT, USA, 2016; p. 139. Available online: https://gaussian.com/citation/ (accessed on 8 February 2025).
13. Cardia, R.; Malloci, G.; Mattoni, A.; Cappellini, G. Effects of TIPS-Functionalization and Perhalogenation on the Electronic, Optical, and Transport Properties of Angular and Compact Dibenzochrysene. *J. Phys. Chem. A* **2014**, *118*, 5170–5177. [CrossRef] [PubMed]
14. Cardia, R.; Malloci, G.; Rignanese, G.M.; Blasé, X.; Molteni, E.; Cappellini, G. Electronic and optical properties of hexathiapentacene in the gas and crystal phases. *Phys. Rev. B* **2016**, *93*, 235132. [CrossRef]
15. Dardenne, N.; Cardia, R.; Li, J.; Malloci, G.; Cappellini, G.; Blasé, X.; Charlier, J.C.; Rignanese, G. Tuning Optical Properties of Dibenzochrysenes by Functionalization: A Many-Body Perturbation Theory Study. *Phys. Chem. C* **2017**, *121*, 24480–24488. [CrossRef]
16. Antidormi, A.; Aprile, G.; Cappellini, G.; Cara, E.; Cardia, R.; Colombo, L.; Farris, R.; d'Ischia, M.; Mehrabanian, M.; Melis, C.; et al. Physical and Chemical Control of Interface Stability in Porous Si–Eumelanin Hybrids. *J. Phys. Chem. C* **2018**, *122*, 28405–28415. [CrossRef]
17. Mocci, P.; Cardia, R.; Cappellini, G. Inclusions of Si-atoms in Graphene nanostructures: A computational study on the ground-state electronic properties of Coronene and Ovalene. *J. Phys. Conf. Ser.* **2018**, *956*, 012020. [CrossRef]
18. Mocci, P.; Cardia, R.; Cappellini, G. Si-atoms substitutions effects on the electronic and optical properties of coronene and ovalene. *New J. Phys.* **2018**, *20*, 113008. [CrossRef]
19. Kumar, A.; Cardia, R.; Cappellini, G. Electronic and optical properties of chromophores from bacterial cellulose. *Cellulose* **2018**, *25*, 2191–2203. [CrossRef]
20. Szafran, M.; Koput, J. Ab initio and DFT calculations of structure and vibrational spectra of pyridine and its isotopomers. *J. Mol. Struct.* **2001**, *565*, 439–448. [CrossRef]
21. Begue, D.; Carbonniere, P.; Pouchan, C. Calculations of Vibrational Energy Levels by Using a Hybrid ab Initio and DFT Quartic Force Field: Application to Acetonitrile. *J. Phys. Chem. A.* **2005**, *109*, 4611–4616. [CrossRef]
22. Rajakumar, B.; Arathala, P.; Muthiah, B. Thermal Decomposition of 2-Methyltetrahydrofuran behind Reflected Shock Waves over the Temperature Range of 1179–1361 K. *Phys. Chem. A.* **2021**, *125*, 5406–5422. [CrossRef]
23. Arathala, P.; Musah, R.A. Oxidation of Dipropyl Thiosulfinate Initiated by Cl Radicals in the Gas Phase: Implications for Atmospheric Chemistry. *ACS Earth Space Chem.* **2021**, *5*, 2878–2890. [CrossRef]
24. Free Chemical Drawing Software. ChemSketch. Version 10.0. ACD/Labs. Available online: https://www.acdlabs.com/resources/free-chemistry-software-apps/chemsketch-freeware/ (accessed on 30 January 2023).
25. Wen, L.; Wang, B.; Yu, T.; Lai, W.; Shi, J.; Liu, M.; Liu, Y. Accelerating the search of CHONF-containing highly energetic materials by combinatorial library design and high-throughput screening. *Fuel* **2022**, *310*, 122241. [CrossRef]
26. Politzer, P.; Martinez, J.; Murray, J.S.; Concha, M.C.; Toro-Labbé, A. An electrostatic interaction correction for improved crystal density prediction. *Mol. Phys.* **2009**, *107*, 2095–2101. [CrossRef]
27. Keshavarz, M.H.; Zamani, A. A simple and reliable method for predicting the detonation velocity of CHNOFCl and aluminized explosives. *Cent. Eur. J. Energ. Mater.* **2015**, *12*, 13–33.
28. Keshavarz, M.H.; Pouretedal, H.R. An empirical method for predicting detonation pressure of CHNOFCl explosives. *Thermochim. Acta* **2004**, *414*, 203–208. [CrossRef]
29. Singh, R.P.; Winter, R.W.; Gard, G.L.; Gao, Y.; Shreeve, J.N.M. Quaternary salts containing the pentafluorosulfanyl (SF5) group. *Inorg. Chem.* **2003**, *42*, 6142–6146.
30. Ye, C.; Gard, G.L.; Winter, R.W.; Syvret, R.G.; Twamley, B.; Shreeve, J.M. Synthesis of pentafluorosulfanylpyrazole and pentafluorosulfanyl-1,2,3-triazole and their derivatives as energetic materials by click chemistry. *Org. Lett.* **2007**, *9*, 3841–3844. [CrossRef]
31. Džingalašević, V.; Antić, G.; Mlađenović, D. Ratio of detonation pressure and critical pressure of high explosives with different compounds. *Sci. Tech. Rev.* **2004**, *5*, 72–76. Available online: http://www.vti.mod.gov.rs/ntp/rad2004/34-04/dzin/dzin.pdf (accessed on 8 February 2025).

32. Garg, S.; Shreeve, J.M. Trifluoromethyl- or pentafluorosulfanyl- substituted poly-1, 2, 3-triazole compounds as dense stable energetic materials. *J. Mater. Chem.* **2011**, *21*, 4787–4795.
33. Carlowitz, M.V.; Oberhammer, H.; Willner, H.; Boggs, J.E. Structural determination of a recalcitrant molecule (S_2F_4). *J. Mol. Struct.* **1983**, *100*, 161–177. [CrossRef]
34. Chemical and Physical Properties of Sulfur Hexafluoride. Available online: https://www.chemicalbook.com/article/chemical-and-physical-properties-of-sulfur-hexafluoride.htm (accessed on 8 February 2025).
35. Table of Chemical Bond Energies–CALCULLA. Available online: https://calculla.com/bond_energy (accessed on 8 February 2025).
36. Chandler, J.; Ferguson, R.E.; Forbes, J.; Kuhl, A.L.; Oppenheim, A.K.; Spektor, R. Confined combustion of TNT explosion products in air. In Proceedings of the Conference: 8th International Colloquium on Dust Explosions, Schaumburg, IL, USA, 21–25 September 1998; Lawrence Livermore National Lab. (LLNL): Livermore, CA, USA. Available online: https://www.osti.gov/biblio/3648 (accessed on 8 February 2025).