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Article

Polynitrobenzene Derivatives, Containing -CF₃, -OCF₃, and -O(CF₂)_nO- Functional Groups, as Candidates for Perspective Fluorinated High-Energy Materials: Theoretical Study

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Abstract: The study of the morphology, thermal, and chemical stability of the fluorinated compounds was performed using Becke's three-parameter hybrid functional approach with the correlation provided by Lee, Yang, and Parr and the cc-pVTZ basis set aiming to design low sensitivity, toxicity, instability, and proneness to decomposition or degradation over a short time high-energy materials. The most stable conformers of the compounds under study were selected based on their total energy. Their thermal and chemical stability was evaluated based on the binding energy per atom, chemical hardness, and softness. The oxygen-fluorine balance is assessed to evaluate the sensitivity of these new materials. The density, detonation pressure, and velocity of the selected conformers were theoretically obtained to reveal the influence of -CF₃, -OCF₃, and cyclic -O(CF₂)_nO- fragments on the energetic properties of nitroaromatics as well as their stability and resistance to shock stimuli. The results allow us to predict new multipurpose energetic materials with a good balance between power and stability. Referring to the results obtained, we recommend CF₃N₂, OCF₃N₂, C₂F₆N₂, 1CF₂N₂/O₂CF₂N₂, and 2CF₄N₂/O₂C₂F₄N₂ for practical usage because these compounds possess greater stability compared to tetryl and better explosive properties than TNT.

Keywords: nitro compounds; polynitrobenzenes; fluorinated high-energy materials (F-HEMs); energetic properties; density; detonation pressure; detonation velocity; oxygen balance; stability; sensitivity

1. Introduction

The seeking of new high-energy materials (HEMs) which, from one side, correspond to safety and environment-friendly requirements and, on the opposite side, should be powerful, stable, insensitive to mechanical stimuli, and provide large quantities of energy release during intentional detonation [1-3] is a long-lasting process. There are various ways to reach the above goal: incorporating nitro, nitramine, or azido groups into the molecular structure; developing completely new compounds; forming salts, etc. Since the 1960s some fluorinated polymers (Viton-A, Teflon, Kel-F) were widely applied in producing of various polymer-bonded explosives (PBX). These polymers were selected as optimal binders, substantially improving the physicochemical and energetic properties of explosive charges [4].

The first fluorine-containing group, which was introduced in energetic materials (HEMs) during structural design, was -C(NO₂)₂F [5-11]. Notably, -C(NO₂)₃ changing in HEMs with -C(NO₂)₂F or -C(NO₂)F₂ groups leads to the development of the energetic materials, possessing markedly higher stability and decreased sensitivity to mechanical impact [12, 13].

Currently, known perspective energetic fluorinated groups used in the new energetic structures are $-\text{C}(\text{NO}_2)_2\text{F}$ and $-\text{C}(\text{NO}_2)_2\text{F}_2$ [14-21], $-\text{NF}_2$ and $-\text{C}(\text{NO}_2)_2\text{NF}_2$ [22-31], and $-\text{SF}_5$ [32-36]. It was obtained that introducing even the simplest fluorine “C-F” group instead of “C-H” sometimes substantially improves practical HEMs properties, i.e. it lowers sensitivity and increases the density of traditional explosives leading to upgrading energetic properties. For example, the sensitivity to shock stimuli of the 3,5-difluoro-2,4,6-trinitroaniline [37] or 3,5-difluoro-2,4,6-trinitrophenol [38], 3,5-difluoro-2,4,6-trinitrotoluene [39], 3,5-difluoro-2,4,6-trinitroanisole [40-42] and 1, 2-difluoro-4, 5-dinitrobenzene [43], are lower than that of trinitroaniline, trinitrophenol, trinitrotoluene, trinitro anisole, and dinitrobenzene compound without F. It is because the fluorine introduction improves the oxygen balance of the corresponding energetic material due to their ability to generate HF (from H) and CF_4 (from C) [38, 43]. The introduction of fluorine promotes an increase in the density and detonation velocity. Chinese authors, Guo et al. [44], exhibit that the energy of the C-F bond (485 kJ/mol) is higher than that of the C-H bond (413 kJ/mol), which means that fluorine-containing energetic materials possess in general higher energy. Moreover, C-F bond can stabilize the corresponding energetic material due to halogen and hydrogen bonds. It implies that fluorine-containing materials could be thermally and chemically stable and possess a high amount of energy to be released during detonation.

The fluorinated high-energy materials also have been reported to have a good potential as perspective melt-castable explosives, and energetic plasticizers since fluorination is beneficial for lowering the melting point and increasing the interval between the melting point and thermal decomposition temperature of the oxidative properties of energetic materials [39, 43, 45].

It is also reported that typical CHNO-containing explosives deliberate mostly carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), and water (H_2O) after the explosion, while gaseous products of the explosion of fluorine-containing HEMs (F-HEMs) can include hydrogen fluoride (HF), carbon tetrafluoride (CF_4), and minor product, carbon oxodifluoride (COF_2) [44, 46].

The fluorinated HEMs can be divided into separate classes such as $-\text{NF}_2$, $-\text{C}(\text{NO}_2)_2\text{NF}_2$, SF_5 , etc. based on the type of fluorine-containing functional groups HEM molecule [44]. Previously widely investigated F-HEMs possessed mostly $-\text{NF}_2$ [47, 48] or $\text{C}(\text{NO}_2)_2\text{F}$ [49]. However, other F-groups (such as $-\text{CF}_3$, etc.) could also improve the energetic properties and stability of HEMs [50-55].

Thus, for this reason, we performed an investigation of polynitrobenzene derivatives containing more rare $-\text{CF}_3$, $-\text{OCF}_3$, and $-\text{O}(\text{CF}_2)_n\text{O}-$ functional groups aiming to observe their potential to be used as multifunctional energetic materials possessing better energetic properties than that of currently expended, i.e. we proposed and investigated a low sensitivity, toxicity, instability, and proneness to decomposition or degradation over a short time high-energy materials. On the other hand, the results of this study allow us to propose ways to increase the explosion properties of high-energy materials along with high resistance to various environmental impacts.

2. Materials and Methods

Let us remind you that the study was performed aiming to develop new energetic materials and predict which of them could be used practically. We do not change our research methodology provided in [56]:

- Design of the compounds and their conformers for the study. The difference between conformers lies in both: i). the position of NO_2 and fluorine containing groups; ii). The cis/trans position of $-\text{OCF}_3$ group where it is possible.
- Performance of the Berny optimization without any symmetry constraints (all bond lengths, angles, and dihedral angles are changed) to find an equilibrium point. The vibration frequencies analysis was performed to verify that the energy minima were reached. The total energy of the conformers was compared to selecting the most abundant conformers. The stability and energetic properties of the designated conformers were only investigated.
- Evaluation of the binding energy per atom to compare the thermal stability of the compounds under study. This energy indicates the amount of energy required to separate an atom from a system of particles and its larger value shows higher thermal stability.

- Determination of the stability related to the chemical properties and aging of the compounds. HOMO-LUMO gap, chemical hardness, and softness are calculated for this purpose. It is known that compounds with larger HOMO-LUMO gap and chemical hardness are more resistant to undergoing a chemical reaction or to being transformed by an external perturbation, such as an applied electric field. On the other hand, a low chemical softness value denotes a high tendency of the molecule to degrade [57,58].
- Calculation of hardness index to evaluate the stability of the compounds.

To obtain data necessary to evaluate the above-listed parameters, Becke's three-parameter hybrid functional approach with non-local correlation provided by Lee, Yang, and Parr (B3LYP), and the cc-pVTZ basis set implemented in a GAUSSIAN package was applied [59-62]. This approach accurately described the geometric and electronic structure of various molecules and their derivatives [63-75].

The energetic properties, such as detonation velocity and pressure of the compounds under study, were obtained by approaching a low computational demand-required approach created for the $C_6H_5N_3O_6F_3$ compound. The reliability of the approach used was checked by comparison of the results of simulations of TNT, APATO (3-amino-5-[(2, 4, 6-trinitrophenyl) amino]-1H-1, 2, 4-triazole), and the known fluorinated compounds with experimental ones. We also checked if the conclusions following the results of the investigations coincided with the common properties of the energetic materials such as the relationship of the number of nitro groups and energetic properties [1].

The oxygen/fluorine balance [57] was calculated to evaluate the resistance to impact. We used oxygen-fluorine balance because of the introduction of another oxidant fluorine element [76].

The main obstacle in this research was the calculation of the density. This is due to several issues. First, the density evaluated as the division of molecular weight from the molar volume calculated by the division of molar from additive increments is, in some cases, significantly larger than that obtained experimentally [77]. Second, the experimental data on the density of the $C_6H_5N_3O_6F_3$ are scarce, i.e. there is no possibility of evaluating the deviations of the simulations. So, the density of the compounds was calculated by using three approaches: one implemented in ACD/ChemSketch based on the Van der Waals volumes molecular modeling program [78], second one, suggested in [79], i.e., the calculated density is corrected by the obtained dependence; iii) the division of molecular weight from the molar volume without any corrections. In the last cases, the molar volume was calculated by B3LYP/cc-pVTZ approach implemented in the Gaussian program. A comparison of the calculated densities revealed that in many cases, the densities obtained by using ACD/ChemSketch approach are significantly larger than those obtained from the approach including density correction, while in another case, the above density is lower. Nevertheless, the density of CF₃N₃ following experimental measurement is reported as 1.716 - 1.816 g/cm³, while that calculated by ACD/ChemSketch is equal to 1.77 g/m³ [80]. So, considering the dependence of the energetic parameters on the density of the compound as well as the goal of our investigations, below we presented the energetic parameters obtained with the values of ACD/ChemSketch density of the compounds to avoid unreliable conclusions. However, the possibility to exhibit the dependence of energetic properties on the conformation of compounds is lost. Thus, the density obtained from one of the rest mentioned methods is presented to show that the density of the conformers is different and leads to a variety of energetic properties and difficulties in producing certain materials.

We obtained detonation velocity and pressure to predict the energetic properties of the compound investigated to evaluate the energetic properties of the compounds under study. The detonation velocity was calculated by approaching the equation and pressure presented in [81] and [82].

These approaches are suitable for compounds consisting of F and as exhibited below, give reliable results.

3. Results

The views of the selected compounds are depicted in Appendix 1. The thermal and chemical stability of the compounds under study were evaluated based on the binding energy per atom,

HOMO -LUMO gap, chemical hardness, electronegativity, and hardness index calculation. These parameters are presented in Table 1.

Table 1. The binding energy per atom (BEA), HOMO -LUMO gap (G), chemical hardness (H), chemical softness (S)), and hardness index (Y) evaluated by B3LYP/cc-pVTZ approach.

Compound	BDE, eV	G, eV	H,eV	S, eV	Y
CF ₃ N ₂	6.00	4.94	2.47	0.20	0.92
CF ₃ N ₃	5.43	4.73	2.36	0.21	0.91
C ₂ F ₆ N ₂	5.42	5.24	2.62	0.19	0.93
C ₂ F ₆ N ₃	5.38	5.02	2.51	0.20	0.92
C ₃ F ₉ N ₂ a	5.39	5.16	-2.58	0.19	0.92
C ₃ F ₉ N ₂ b	5.39	5.46	2.73	0.18	0.93
C ₃ F ₉ N ₃	5.35	5.01	2.50	0.20	0.92
OCF ₃ N ₂ /CF ₃ ON ₂	5.41	5.10	2.55	0.20	0.92
OCF ₃ N ₃ /CF ₃ ON ₃	5.37	4.94	2.47	0.20	0.92
¹ O ₂ C ₂ F ₆ N ₂ a	5.33	4.65	2.33	0.21	0.91
¹ O ₂ C ₂ F ₆ N ₂ b	5.33	4.95	2.47	0.20	0.92
¹ O ₃ C ₃ F ₉ N ₂ b	5.27	5.14	2.57	0.19	0.92
¹ O ₂ C ₂ F ₆ N ₃ a	5.30	4.96	2.48	0.20	0.92
¹ O ₂ C ₂ F ₆ N ₃ b	5.30	4.95	2.47	0.20	0.92
¹ O ₂ C ₂ F ₆ N ₄ a	5.27	4.85	2.43	0.21	0.92
¹ O ₂ C ₂ F ₆ N ₄ b	5.27	4.85	2.43	0.21	0.92
¹ O ₃ C ₃ F ₉ N ₃ a	5.24	5.22	2.61	0.19	0.93
¹ O ₃ C ₃ F ₉ N ₃ b	5.24	5.23	2.62	0.19	0.93
1CF ₂ N ₂ / ¹ O ₂ CF ₂ N ₂	5.61	4.65	2.33	0.22	0.91
1CF ₂ N ₃ / ¹ O ₂ CF ₂ N ₃	5.68	4.00	2.00	0.25	0.87
1CF ₂ N ₄ / ¹ O ₂ CF ₂ N ₄	5.48	4.48	2.24	0.22	0.90
2CF ₄ N ₂ / ¹ O ₂ C ₂ F ₄ N ₂	5.66	4.73	2.37	0.21	0.91
¹ 2CF ₄ N ₃	5.47	4.77	2.39	0.21	0.91
2CF ₄ N ₄ //O ₂ C ₂ F ₄ N ₄	5.42	4.89	2.44	0.20	0.92
3CF ₆ N ₂ /O ₂ C ₃ F ₆ N ₂	5.43	4.93	2.46	0.20	0.92
3CF ₆ N ₃	5.53	4.46	2.23	0.22	0.90
3CF ₆ N ₄ / ¹ O ₂ C ₃ F ₆ N ₄	5.36	4.99	2.50	0.20	0.92
TNT	5.52	4.15	2.07	0.24	0.88
APATO*	5.70	3.21	1.60	0.31	0.81

¹ There and below a and b letters mark the conformers of the compounds under study. The difference between conformers relies on *cis*- and *trans*-position F containing groups or their different positions.

We would like to pay attention to the fact that APATO is not used as a standard to evaluate the energetic properties of new materials. It is included to show the validity of the approach for the simulations, i.e. the parameters of this compound obtained by well-known and widely used equations and that presented here coincide well.

The calculated densities are presented in Table 2. As mentioned above, the density was calculated by approaching the ChemSkech program and as the division of molecular weight from the molar volume obtained by B3LYP/cc-pVTZ approach implemented in the Gaussian09 program package.

Table 2. The densities obtained by the approach implemented in the ChemSkech program (ACD, ρ_{ACD}) and as the division of molecular weight from the molar volume obtained (Gaussian ρ).

Compounds	ACD ρ_{ACD} , g/cm ³	Gaussian ρ , g/cm ³
CF ₃ N ₃	1.77	2.07
C ₂ F ₆ N ₂	1.69	2.07
C ₂ F ₆ N ₃	1.82	2.34
C ₃ F ₉ N _{2a}	1.74	2.09
C ₃ F ₉ N _{2b}	1.74	1.96
C ₃ F ₉ N ₃	1.85	2.01
OCF ₃ N ₂ /CF ₃ ON ₂	1.64	1.93
OCF ₃ N ₃ /CF ₃ ON ₃	1.80	2.11
O ₂ C ₂ F ₆ N _{2a}	1.74	2.42
O ₂ C ₂ F ₆ N _{2b}	1.73	1.99
O ₃ C ₃ F ₉ N _{2b}	1.79	2.11
O ₂ C ₂ F ₆ N _{3a}	1.85	1.98
O ₂ C ₂ F ₆ N _{3b}	1.85	2.01
O ₂ C ₂ F ₆ N _{4a}	1.96	2.14
O ₂ C ₂ F ₆ N _{4b}	1.96	2.14
O ₃ C ₃ F ₉ N _{3b}	1.89	2.13
O ₃ C ₃ F ₉ N _{3a}	1.89	2.05
1CF ₂ N ₂ /O ₂ CF ₂ N ₂	1.84	1.83
1CF ₂ N ₃ /O ₂ CF ₂ N ₃	1.95	1.80
1CF ₂ N ₄ /O ₂ CF ₂ N ₄	2.05	2.23
2CF ₄ N ₂ /O ₂ C ₂ F ₄ N ₂	1.85	2.09
2CF ₄ N ₃ /O ₂ C ₂ F ₄ N ₃	1.98	1.81
2CF ₄ N ₄ /O ₂ C ₂ F ₄ N ₄	2.01	1.89
3CF ₆ N ₂ /O ₂ C ₃ F ₆ N ₂	1.85	2.19
3CF ₆ N ₃ /O ₂ C ₃ F ₆ N ₃	1.97	2.42
3*O ₂ CF ₆ N ₄ /O ₂ C ₃ F ₆ N ₄	1.98	2.34

Indeed, in many cases, the densities of the compounds under study obtained by the approaches applied are higher than 1.8 g/cm³, coinciding with the results obtained by L. Wen et al [80]. However, in many cases, the density ρ is significantly higher than that ρ_{ACD} , although ρ exhibits the influence of compound morphology on the density. Considering good agreement between the density of CF₃N₃ obtained theoretically (1.77 g/cm³) and experimentally (1.716 - 1.816 g/cm³), the energetic parameters are calculated with smaller values of ρ_{ACD} aiming not to overestimate the energetic properties of the compounds under study. On the other hand, it is very well known that the density could vary depending on its morphology (variety of conformers) and physical forms. Thus, the densities presented in Table 2 could represent the highest and lowest densities of the compounds. We would like to point out, that we do not evaluate precise values of detonation pressure and velocity but exhibit the case of usage of the same approach, one can ensure that the statistical errors in the densities, detonation velocities, and pressure for each molecule will be similar. This allows us to compare the detonation velocities of the compounds studied here, subsequently rank those molecules, and make qualitative conclusions concerning the influence of substitutions on the

energetic properties of the compounds under study. Going ahead, we would like to mention that the values of detonation pressure and velocity of the TNT and APATO obtained from the methodology described in this paper coincide well with experimental measures which indicate its reliability.

The oxygen/fluorine balance is calculated to evaluate the resistance to shock stimuli. The results of this simulation along with the dependence of the sensitivity on the number of nitro groups are presented in Fig 1. It is seen that increasing the nitro group in the compounds with F leads to lower resistance to shock stimuli. These results coincide with the previously obtained tendencies for the development of safe energetic materials [1,12,14,19,44] and indicate that some proposed materials could be addressed to high-safety HEMs.

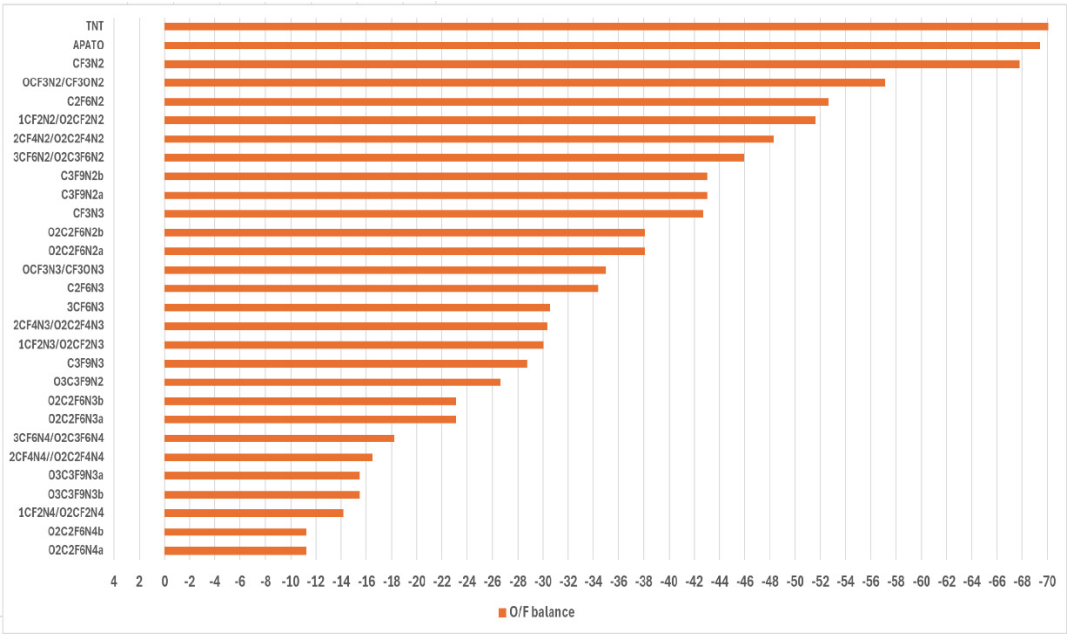


Figure 2. The oxygen balance and its dependence on the number of nitro groups in the compounds.

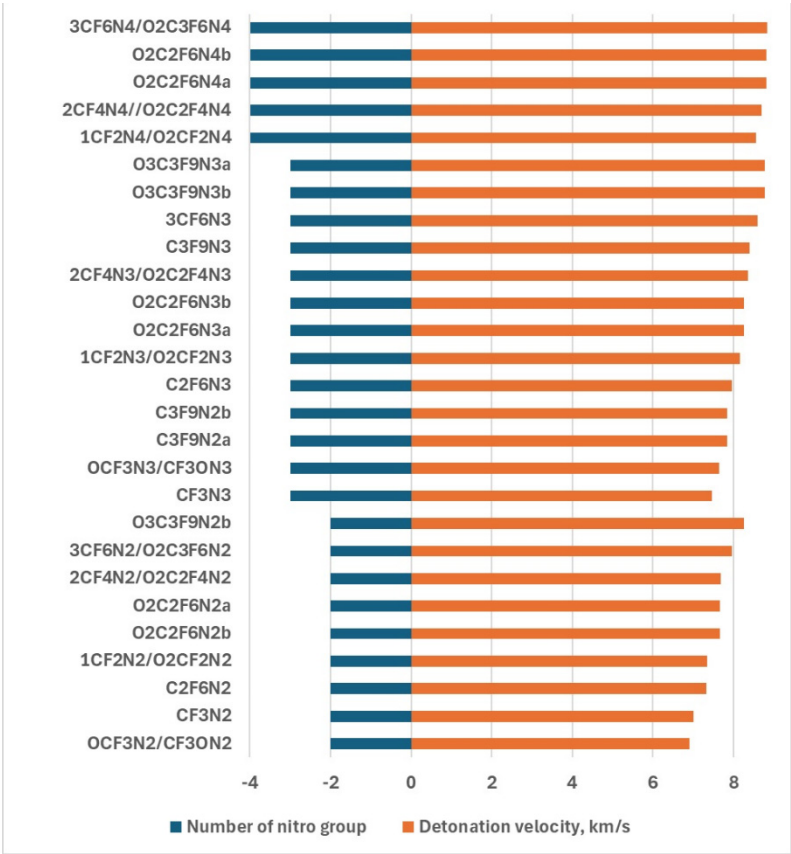
Table 2. The detonation velocity (v) and detonation pressure (p) calculated by using equations presented by M. H. Keshavarz [82, 83].

Compounds	v,km/s	p,kba
CF3N2	7.01	189.13
CF3N3	7.46	308.45
C2F6N2	7.31	348.83
C2F6N3	7.96	385.51
C3F9N2a	7.83	432.39
C3F9N2b	7.84	432.63
C3F9N3	8.40	459.75
OCF3N2/CF3ON2	6.91	276.32
OCF3N3/CF3ON3	7.63	322.50
O2C2F6N2a	7.66	383.27
O2C2F6N2b	7.66	371.38
O3C3F9N2b	8.27	458.16
O2C2F6N3a	8.26	452.77
O2C2F6N3b	8.26	408.54

O2C2F6N4a	8.82	483.42
O2C2F6N4b	8.82	447.03
O3C3F9N3b	8.78	448.03
O3C3F9N3a	8.78	449.03
1CF2N2/O2CF2N2	7.34	329.08
1CF2N3/O2CF2N3	8.16	363.76
1CF2N4/O2CF2N4	8.55	400.03
2CF4N2/O2C2F4N2	7.69	386.62
2CF4N3/O2C2F4N3	8.36	430.63
2CF4N4//O2C2F4N4	8.70	436.06
3CF6N2/O2C3F6N2	7.97	437.87
3CF6N3	8.60	478.82
3CF6N4/O2C3F6N4	8.84	471.75
TNT	6.74	172.02
APATO	7.67	253.06

We pointed out the coincidence between the experimentally obtained detonation velocity of 6.9 km/s TNT and the 6.8 km/s obtained by us [83]. The calculated value of detonation pressure of 217.15 kbar of this compound fits the reported 210 kbar at 1.63 g/cm³ density in a solid which is used as a standard [85]. Moreover, the detonation velocity of CF₃N₃ obtained experimentally varies from 6.919 km/s to 8.029 km/s, while that of 7.46 km/s obtained by us coincides with these results. This coincidence proves that the approaches and methodology used give trustworthy results.

The detonation velocity and detonation process are depicted in Figs. 3 and 4 to exhibit the parameter dependence on the number of nitro, -CF₃, and -OCF₃ groups as well as cycling O₂(CF₂)_n.



a

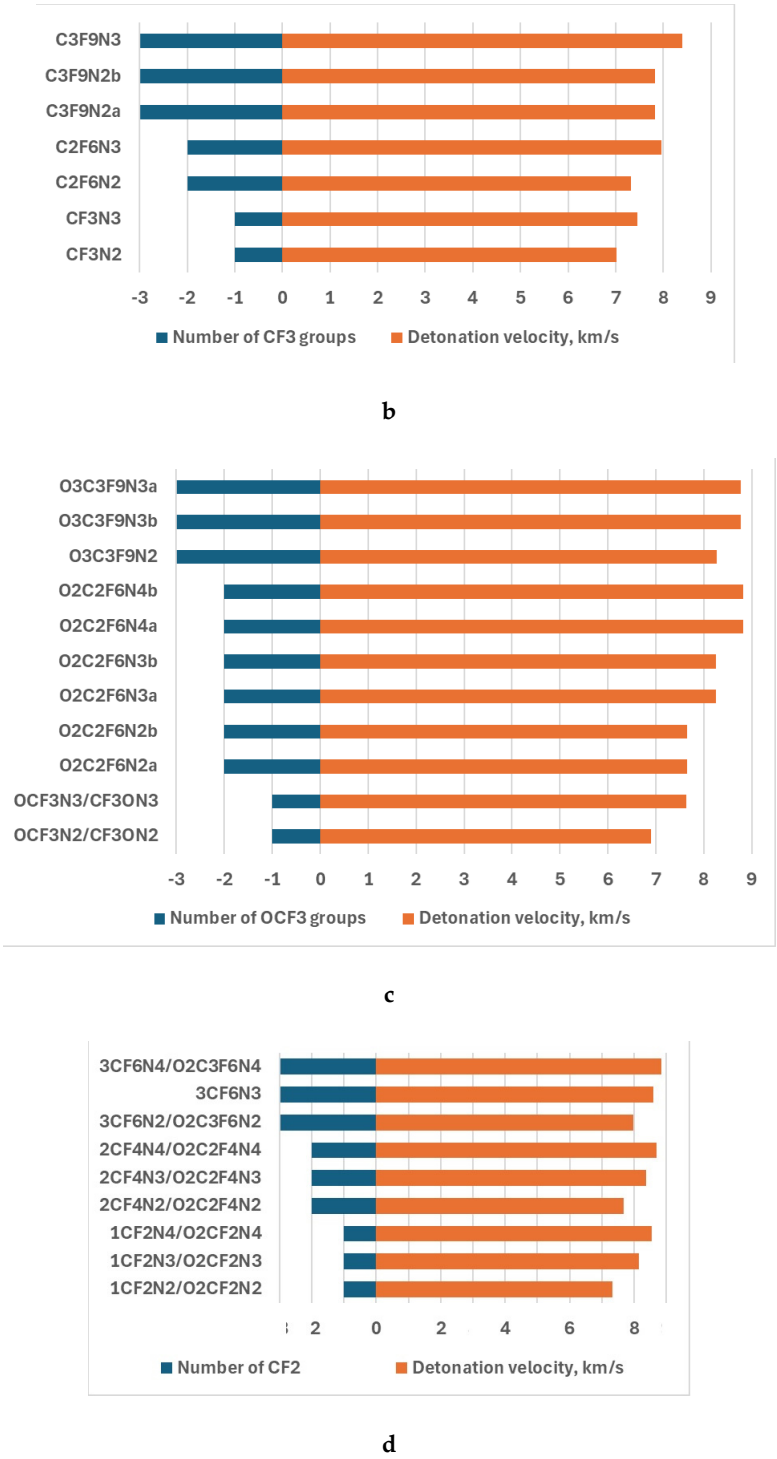
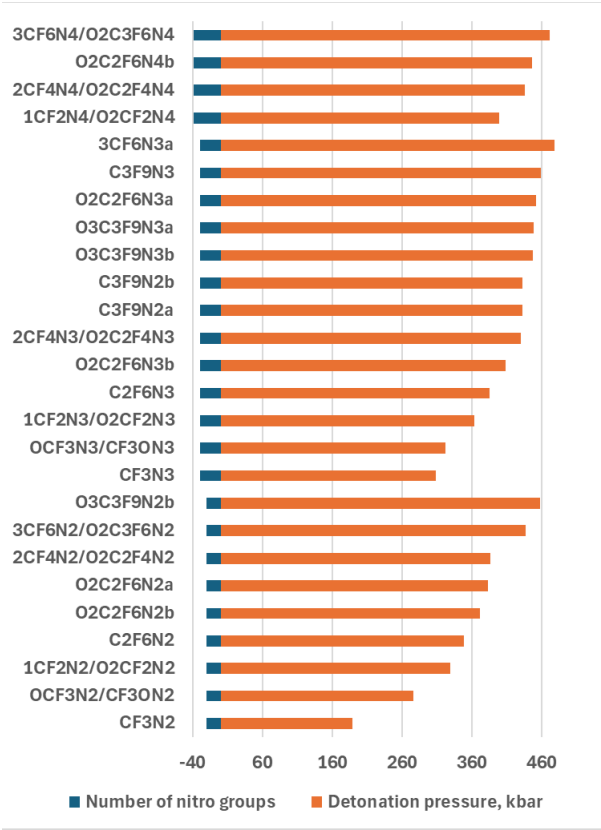
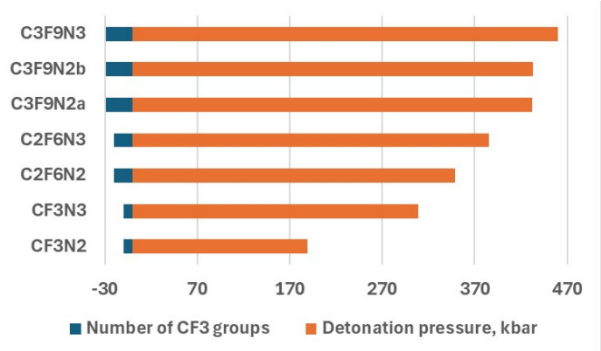


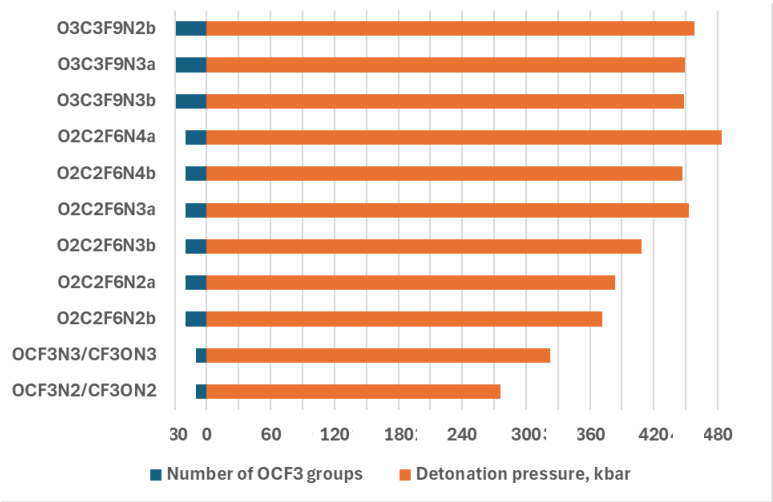
Figure 3. The detonation velocity dependence on the number of -NO₂ group (a), -CF₃ (b), -OCF₃ (c), and that of CF₂ in the -O-(CF₂)_n-O- (d).



a



b



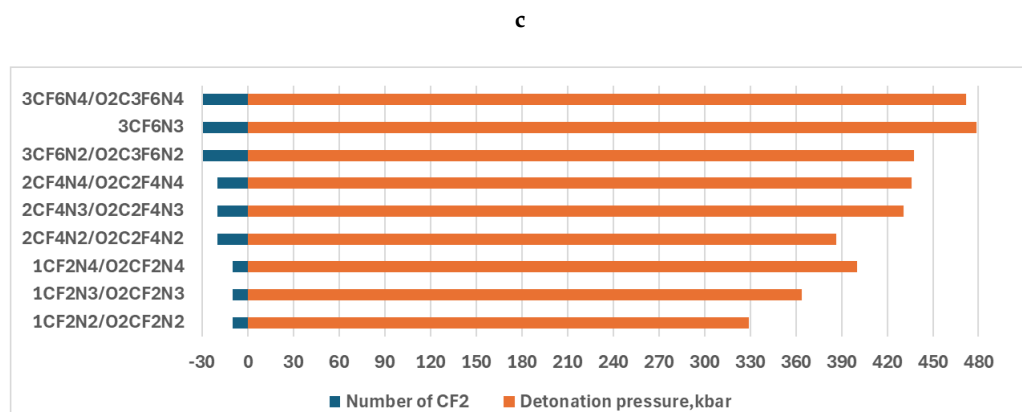


Figure 4. The detonation pressure dependence on $-\text{NO}_2$ group (a), $-\text{CF}_3$ (b), $-\text{OCF}_3$ (c), and that of CF_2 in the $-\text{O}-(\text{CF}_2)_n-\text{O}-$ (d). The numbers of the groups and cycle size are enlarged by 10 for better viewing.

4. Discussion

The evaluation of the stability of the energetic materials is performed by using different methodologies. The investigation of thermal stability could be based on the comparison of the total energy of the conformers or binding energy per atom (BDE) when the stability of different chemical composition compounds is investigated. The chemical stability could be predicted based on the electronic structure, i.e. the HOMO-LUMO gap, and the parameters, such as chemical softness and hardness, etc. The study of the compound behavior under different conditions also gives insight into thermal stability, while calculations of Gibbs Free energy, enthalpy, and entropy are essential to predict different decomposition reactions. We emphasize that at this stage of the research, there is no aim to predict the products of the decomposition of the energetic materials, thus we limit ourselves to the studies of total energies and electronic structure. So, we calculated the Binding energy per atom (BDE), HOMO-LUMO gap, chemical hardness, and softness. 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 low chemical softness value denotes a high tendency of the molecule to degrade [76, 77]. The values BDA shed some light on the thermal stability of the compounds.

We would like to pay attention to the values of the hardness indexes that are larger than 0.9 indicating high thermal and chemical stability. These indexes of TNT and APATO calculated by the same approach are equal to 0.88 and 0.81 exhibiting their slightly lower stability than that of the compounds under study (Table 1). The higher chemical stability of the compounds under study than that of TNT and APATO is also confirmed by other parameters presented in Table 1, although the thermal stability and resistance to degradation of APATO could be higher and comparable with that of TNT. Overall, we may predict that the new high-energy materials could be more stable thermally or/and chemically than the above-mentioned known ones.

Referring to BDE, we may state that compounds consisting of $1\text{CF}_2\text{N}_3/\text{O}_2\text{CF}_2\text{N}_3$ and $1\text{CF}_2\text{N}_2/\text{O}_2\text{CF}_2\text{N}_2$ are slightly more thermally stable than TNT, but less stable than APATO. The thermal resistance of CF_3N_2 is higher than that of APATO.

The high chemical stability of the compounds under study represents values of HOMO-LUMO gaps as well as chemical hardness (Table 1). The chemical stability of $1\text{CF}_2\text{N}_4/\text{O}_2\text{CF}_2\text{N}_4$ is higher than that of APATO and lower than TNT, while the rest compounds considering our results are more chemically stable than TNT. The analysis of chemical hardness and softness confirms these findings. Additionally, our study reveals, that increasing nitro groups in the compounds does not significantly influence the thermal stability, or the resistance to degradation, and that undergoing chemical reactions to being transformed by an external perturbation of the compound consisting of fluorine.

The increase of the -CF₃ or -OCF₃ groups as well as the inclusion of -CF₂ in the -O-(CF₂)_n- cycle does not significantly influence the chemical and thermal stability of the compound of the study – the parameters presented in Table 1 are comparable to the results presented [84-89].

The investigation of the energetic properties exhibited significant effects of the nitro groups on the energetic properties of the compounds under study. The -CF₃, or -OCF₃ groups as well as -O-(CF₂)_n-O cycle also change the energetic properties of the compounds under study, but their influence is nitro group number dependent. For example, the enlargement of the above cycle due to the inclusion of CF₂ leads to an increase in the sensitivity to the shock stimuli of this group materials under study when the nitro group in the compound is two (Fig. 5). The opposite effect is obtained for the compounds with four nitro groups. In this case, the inclusion of -CF₂ leads to a decrease in this sensitivity. When this type of compound consists of three nitro groups, the above enlargement does not change the sensitivity to shock stimuli (Fig. 5).

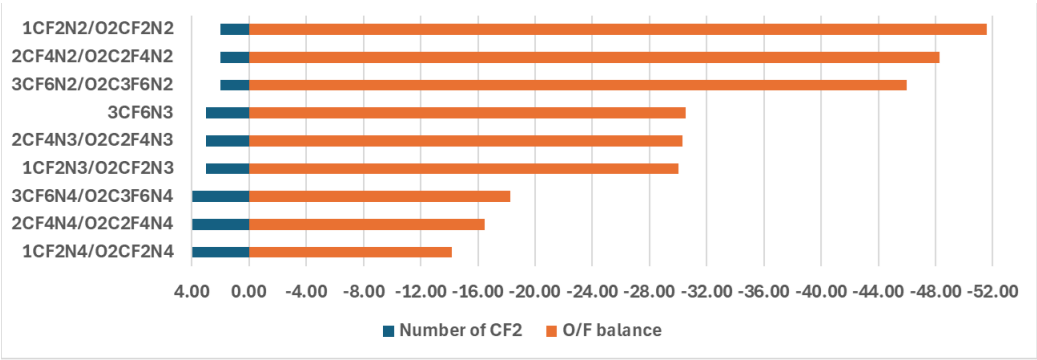


Figure 5. The O/F balance dependence on the CF₂ in the -O-(CF₂)_n-O- cycle.

The increase in -CF₃ or -OCF₃ number in the compounds with the same nitro group number also leads to a decrease in the resistance to shock stimuli (Fig. 2). Moreover, the compounds with -OCF₃ are more sensitive to shock than those with CF₃ when the nitro group number in the compound is the same. To exhibit this conclusion evidently, we present O/F balance separately in Table 3.

Table 3. The O/F balance dependence on OCF₃ and CF₃ and nitro group number.

N	m	O _n C _n F _{3n} N _m	C _n F _{3n} N _m
1		-57.12	-67.77
2	2	-38.08	-52.61
3		-26.66	-43.00
1		-35.00	-42.69
2	3	-23.09	-34.37
3		-15.48	-28.77

Hence, we obtain that increasing the nitro group leads to lower resistance to shock stimuli which indicates the results of the analysis of the O/F balance (OB) (Fig.1). The increase of CF₃ or -OCF₃ number also leads to an increase of the sensitivity to stimuli. However, there is no clear influence of the -O-(CF₂)_n-O- cycle on the sensitivity of shock stimuli.

The oxygen balance of TNT, a standard reference for many purposes, is equal to -74%, and that of tetryl is -47.36%. Referring to our results of simulations, the O balance of TNT is -72.05% and that of APATO is -68.30%. The O/F balance of many of the compounds is higher than -47%. It means that their resistance to stimuli is lower than that of tetryl. Nevertheless, the above parameters of 1CF₂N₂/O₂CF₂N₂, 2CF₄N₂/O₂C₂F₄N₂, C₂F₆N₂, OCF₃N₂, and CF₃N₂ are lower than tetryl, but higher APATO. They can be ranged considered increased resistance to stimuli followingly

TNT<APATO<CF₃N₂<OCF₃N₂<C₂F₆N₂<1CF₂N₂<2CF₄N₂<Tetryl

The detonation velocity of the compounds under study varies from 6.67 to 8.84 km/s thus they could be addressed to the high explosives whose detonation velocity lies in the range 1,01 km/s to 9.89 km/s. The detonation velocity of OCF₃N₂/CF₃ON₂ is lower than the experimentally obtained detonation velocity of 6.9 km/s of TNT [83]. So, only this compound's energetic properties are worse than TNT. On the other hand detonation velocity of the C₃F₉N₂, C₂F₆N₃, 1CF₂N₃mp/O₂CF₂N₃, O₂C₂F₆N₃, 2CF₄N₃/O₂C₂F₄N₃, C₃F₉N₃, 3CF₆N, O₃C₃F₉N₃, 1CF₂N₄/O₂CF₂N₄, 2CF₄N₄/O₂C₂F₄N₄, O₂C₂F₆N₄, and 3CF₆N₄/O₂C₃F₆N₄ are larger than that of APATO indicating better energetic properties of them.

The investigation of the dependence of the detonation velocity on the number of the -NO₂, -CF₃, -OCF₃, and -O-(CF₂)_n-O-cycle revealed some interesting features (Fig. 3). The enlargement of the above cycle leads to increasing the detonation velocity of this type compounds under study with the same number of nitro groups. Similar results are obtained in the case of the increase of -OCF₃ and -CF₃ numbers. Comparison of the detonation velocity of the same type of compounds with different nitro and fluorine-containing groups allows us to predict that the influence of the nitro group competes with that of the F number, i.e. only a certain proportion of various components leads to significantly improving energetic properties. For example, the detonation velocity of CF₃N₂ and CF₃N₃ is equal to 7.01 km/s and 7.46 km/s respectively. These compounds consist of different numbers of nitro groups, while the -CF₃ number is the same. So, the improvement in the energetic properties is related to the nitro group inclusion. In the case when the nitro group number is the same, the detonation velocity of 7.96 km/s of C₂F₆N₃ is larger than that of CF₃N₃, which exhibited improving energetic properties due to the bonding of -CF₃. The detonation velocity of C₃F₉N₃ formed due to C₂F₆N₃ joining of -CF₃, also increased to 8.40 km/s. This value of the detonation velocity is the largest for this type of compound and allows us to speculate that the nitro group/-CF₃ rate could be properly chosen to improve energetic properties.

A similar tendency takes place in the case of -OCF₃ and -O-(CF₂)_n-O- cycle. The largest values of detonation velocity are 8.82 and 8.84 of O₂C₂F₆N₄ and 3CF₆N₄/O₂C₃F₆N₄ respectively when the nitro/fluorine group rate is the largest. The results of the study of the detonation pressure exhibited the worse energetic properties of CF₃N₂ than APATO, and better than TNT. That of the rest compounds is better even than the properties of APATO (Fig.4). The results followed from the analysis of the detonation pressure confirm that.

The importance of the rate of nitro/fluorine groups for the energetic properties of the fluorine-containing compounds was followed by the results of the investigation of detonation velocity. The study of the detonation pressure supports this finding. For example, the largest detonation pressure of 483.42 is O₂C₂F₆N₄a, consisting of four nitro and two -OCF₃ groups. Adding -OCF₃ and -CF₂ in the -O-(CF₂)_n-O- ring is more effective than -CF₃ for energetic properties improvement. For example, the detonation pressure of 348.83 km/s, 383.27 km/s or 371.38 km/s, and 386.62 km/s possesses C₂F₆N₂, O₂C₂F₆N₂a/b, and 2CF₄N₂/O₂C₂F₄N₂, respectively.

We also considered that the steric hindrance leads to density increase and improvement of energetic performances (Fig. 6).

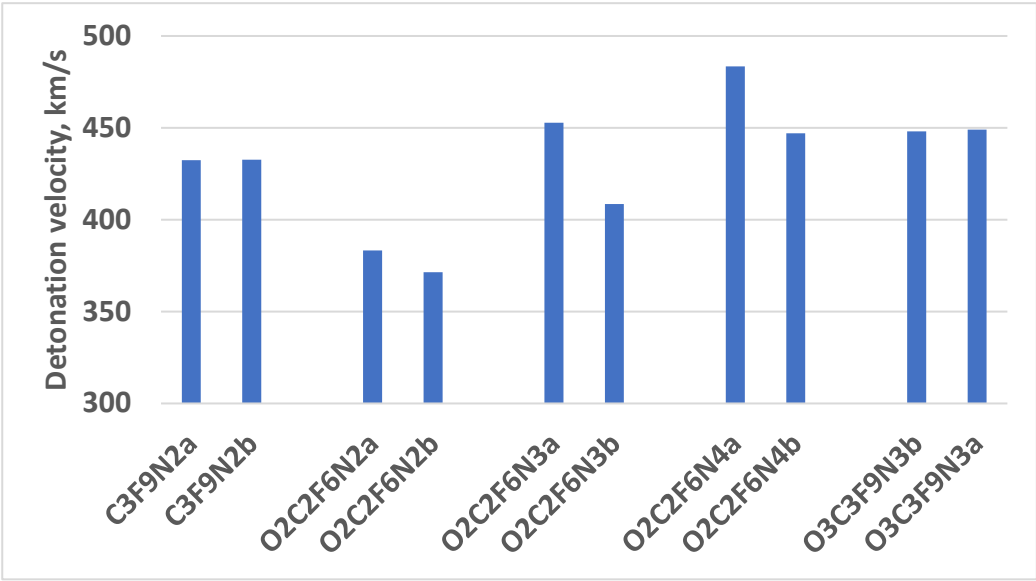


Figure 6. The detonation pressure of the selected conformers to exhibit the importance of the steric hindrance.

The last statement is based on the comparison of the detonation pressure of compounds which is conformer morphology dependent. The detonation pressure of the conformers, whose morphology is different only due to the position of the -CF₃ group in the core of the molecule, is unlike by 0.1 % (Appendix B). The parameters of the *cis* and *trans* conformers (O2C2F6N2, O2C2F6N3, and O2C2F6N4) are distinct 3.2 %-10.8 %. The *cis* and *trans* conformers of O3C3F9N3 are also mentioned as the most stable compounds, but their detonation pressure is dissimilar only by 0.2%. It is because this compound consists of three -OCF₃ that are out of the plane of the core molecule, thus the *trans* or *cis* position of one of them does not significantly influence the volume of this molecule, i.e. the density of the compound as well as the detonation pressure. To prove the above statements, we present the molar volume of the above-mentioned conformers (Table 4). It is also reflected by the different densities of the conformers presented in Table 2.

Table 4. The molar volume of the conformers to point out the reason for discrimination of their energetic properties.

Compounds	Conformer a	Conformer, b
	cm ³ /mol	cm ³ /mol
C3F9N2	177.79	190.26
O2C2F6N2	167.02	174.62
O2C2F6N3	203.04	189.67
O2C2F6N4	166.04	198.60
O3C3F9N3	217.75	226.03

As mentioned above the detonation pressure of the compounds under study is better than that of TNT and, in many cases, APATO. Considering resistance to shock stimuli and the energetic properties of the compound under study, we concluded that CF₃N₂, OCF₃N₂, C₂F₆N₂, 1CF₂N₂m/O2CF₂N₂, and 2CF₄N₂m/O2C₂F₄N₂ could be practically used. These findings indicate the indirect advantage of -OCF₃ and adding of -CF₂ in the -O-(CF₂)_n-O- cycle* for -CF₃.

5. Conclusions

Our research provides a theoretical foundation for developing advanced, highly energetic, and stable fluorine-containing materials. We focused on the $-\text{O}(\text{CF}_2)_n\text{O}-$ cycle, $-\text{OCF}_3$, and $-\text{CF}_3$ as scarce groups investigated whose presence in the compounds indicates a way to improve the energetic properties of the known materials.

Our study has demonstrated that the incorporation of cyclic $-\text{O}(\text{CF}_2)_n\text{O}-$, $-\text{OCF}_3$, and $-\text{CF}_3$ groups in fluorine-containing compounds significantly enhances their energetic properties. The investigation revealed that the positioning and morphology of these groups play a crucial role in determining the compounds' thermal and chemical stability as well as energetic properties.

Our findings indicate that compounds under study are overall stabler than TNT, although only $1\text{CF}_2\text{N}_3/\text{O}_2\text{CF}_2\text{N}_3$ and $1\text{CF}_2\text{N}_2/\text{O}_2\text{CF}_2\text{N}_2$ exhibit slightly higher thermal stability compared to TNT. However, only $1\text{CF}_2\text{N}_4/\text{O}_2\text{CF}_2\text{N}_4$ compounds demonstrate lower chemical stability than TNT, while other compounds surpass TNT in that. Interestingly, increasing the number of nitro groups along with the enlargement of $-\text{CF}_3$ or $-\text{OCF}_3$ groups, and with the inclusion of $-\text{CF}_2$ in the $-\text{O}(\text{CF}_2)_n\text{O}-$ cycle in the compounds does not markedly affect their thermal stability or resistance to degradation. Nonetheless, the nitro group number substantially impacts the energetic properties, with $-\text{CF}_3$, $-\text{OCF}_3$, and the $-\text{O}(\text{CF}_2)_n\text{O}-$ cycle contributing variably depending on their quantity.

Referring to the results of the O/F balance investigation, we found compounds with $-\text{OCF}_3$ groups more shock-sensitive than those with CF_3 when the nitro group count is identical. An increase in CF_3 or $-\text{OCF}_3$ groups also heightens sensitivity to stimuli, although the $-\text{O}(\text{CF}_2)_n\text{O}-$ cycle's influence on shock sensitivity remains inconclusive. However, $1\text{CF}_2\text{N}_2/\text{O}_2\text{CF}_2\text{N}_2$, $2\text{CF}_4\text{N}_2/\text{O}_2\text{C}_2\text{F}_4\text{N}_2$, $\text{C}_2\text{F}_6\text{N}_2$, OCF_3N_2 , and CF_3N_2 exhibit resistance to stimuli lower than TNT, but higher than that tetryl,

Furthermore, comparing the detonation velocity of compounds with varying nitro and fluorine-containing groups revealed that the energetic properties improve significantly with the optimal proportion of these components. Notably, the addition of $-\text{OCF}_3$ and $-\text{CF}_2$ in the $-\text{O}(\text{CF}_2)_n\text{O}-$ ring proved more effective in enhancing energetic performance than $-\text{CF}_3$. This improvement is attributed to steric hindrance, which increases density and, consequently, energetic efficiency.

In summary, the compounds CF_3N_2 , OCF_3N_2 , $\text{C}_2\text{F}_6\text{N}_2$, $1\text{CF}_2\text{N}_2/\text{O}_2\text{CF}_2\text{N}_2$, and $2\text{CF}_4\text{N}_2/\text{O}_2\text{C}_2\text{F}_4\text{N}_2$ demonstrate potential for practical application, highlighting the advantages of $-\text{OCF}_3$ and the incorporation of $-\text{CF}_2$ in the $-\text{O}(\text{CF}_2)_n\text{O}-$ cycle over $-\text{CF}_3$.

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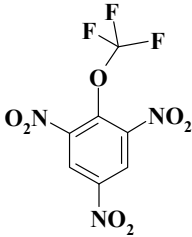
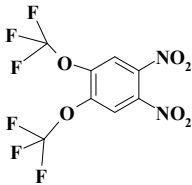
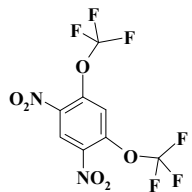
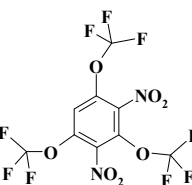
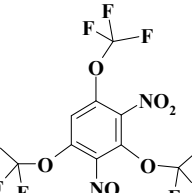
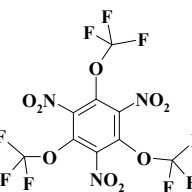
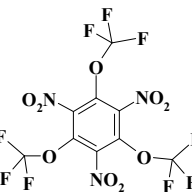
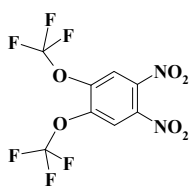
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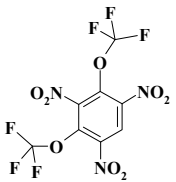
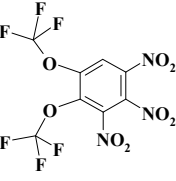
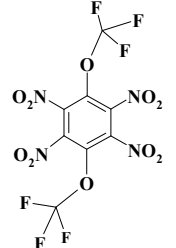
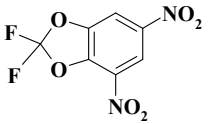
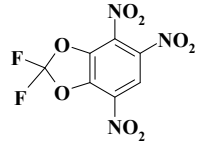
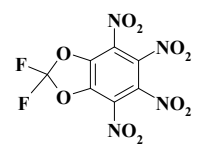
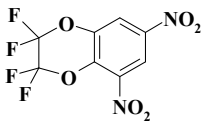
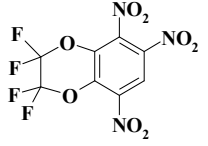
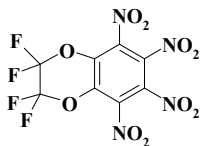
Conflicts of Interest: The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Appendix A

Table A1. The views of the compounds are defined as the most stable between developed and investigated.

No.	Structural formula	Compound Abbreviation
1.		CF3N2
2.		CF3N3
3.		C2F6N2
4.		C2F6N3
5.		C3F9N2
6.		C3F9N3
7.		CF3ON2/OCF3N2

8.		CF3ON3/OCF3N3
9.		O2C2F6N2
10.		O2C2F6N2b/m
11.		O3C3F9N2a
12.		O3C3F9N2b
13.		O3C3F9N3a
14.		O3C3F9N3b
15.		O2C2F6N2a

16.		O2C2F6N2b
17.		O2C2F6N3
18.		O2C2F6N4
19.		1CF2N2/O2CF2N2
20.		1CF2N3/O2CF2N3
21.		1CF2N4/O2CF2N4
22.		2CF4N2/O2C2F4N2
23.		2CF4N3/O2C2F4N3
24.		2CF4N4/O2C2F4N4

Appendix B

The views of the conformers. Borrow color denotes carbon, yellow – fluorine, red – oxygen, blue – nitrogen, and grey – hydrogen.

Compound	Conformer	
	a	B
C3F6N2		
O2C2F6N2		
O2C2F6N3		
O2C2F6N4		
O3C3F9N3		

References

1. Koch, E.C. High Explosives, Propellants, Pyrotechnics; Walter de Gruyter GmbH: Berlin, Germany; Boston, MA, USA, 2021; pp. 1-759. ISBN: 978-3-11-066052-4.
2. Agrawal, J.P. High Energy Materials: Propellants, Explosives and Pyrotechnics. Wiley-VCH: Weinheim, Germany, 2010; pp.1-498. ISBN: 978-3-527-32610-5.
3. Olah, G.A.; Squire, D.R. (Eds.). Chemistry of Energetic Materials; Academic Press: Cambridge, MA, US, 2012; pp. 1-212. ISBN: 978-0-1239-5897-6.
4. Kominia, A.; Smith, J.L.; Sheehan, P.; Oxley, J.C. Thermal decomposition of fluorinated polymers used in plasticized explosives and munitions. Propellants, Explos. Pyrotech. 2024, 49, e202300207. DOI: 10.1002/prop.202300207.
5. Grakauskas, V.; Baum, K. Aqueous fluorination of nitronate salts. J. Org. Chem. 1968, 33, 3080-3082. DOI: 10.1021/jo01272a013.
6. Grakauskas, V. Direct liquid-phase fluorination of methyl trichloroacetate and acetic anhydride. J. Org. Chem. 1969, 34, 963-965. DOI: 10.1021/jo01256a040.
7. Kamlet, M.J.; Adolph, H.G. Fluoronitro aliphatics. II. Fluorodinitromethyl compounds. Synthetic approaches and general properties. J. Org. Chem. 1968, 33, 3073-3080. DOI: 10.1021/jo01272a012.

8. Adolph, H.G.; Kamlet, M.J. Fluoronitroaliphatics. IV. Reactions of 2-fluoro-2, 2-dinitroethanol. *J. Org. Chem.* 1969, 34, 45-50. DOI: 10.1021/jo00838a012.
9. Grakauskas, V.; Albert, A.H. Polynitroalkyltetrazoles. *J. Het. Chem.* 1981, 18, 1477-1479. DOI: 10.1002/jhet.5570180741.
10. Pepekin, V.I.; Matyushin, Y.N.; Rozantsev, G.G.; Shevelev, S.A.; Apin, A.Y. Enthalpies of formation of dinitrophenylmethane, trinitrophenylethane, and fluorodinitrophenylmethane. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1972, 21, 2634-2636.
11. Pepekin, V.I.; Natsibullin, F.Y.; Eremenko, L.T.; Lebedev, Y.A. Enthalpy of formation of fluoronitromethyl radical and dissociation energy of CH and CF bonds in fluorodinitromethane. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* 1974, 23, 892-893.
12. Hurwitz, H. Computation of detonation properties of fluoroexplosives. Technical Report DTIC NOLTR 65-217, Naval Ordnance Laboratory, White Oak, ML, USA. 1966, pp. 1-54. URL: <https://apps.dtic.mil/sti/citations/AD0374171>, accessed at 30-05-2024.
13. Bogdanova, Yu.A.; Gubin, S.A.; Korsunskii, B.L.; Pepekin, V.I. Detonation Characteristics of Powerful Insensitive Explosives. *Combust. Explos. Shock Waves.* 2009, 45, 738-743.
14. Politzer, P.; Lane, P. Structures and Properties of Energetic Difluoramines. In: Hargittai, M.; Hargittai, I. *Advances in Molecular Structure Research*, Vol.3, 1997, pp.269-285. ISBN: 978-0-7623-0208-6
15. Dalinger, I.L.; Kormanov, A. V.; Suponitsky, K.Y.; Muravyev, N.V.; Sheremetev, A.B. Pyrazole-tetrazole hybrid with trinitromethyl, fluorodinitromethyl, or (difluoroamino) dinitromethyl groups: High-performance energetic materials. *Chem. Asian J.* 2018, 13, 1165-1172. DOI:10.1002/asia.201800214
16. Palsyaeva, N.V.; Gladyshekin, A.G.; Vatsadze, I.A.; Suponitsky, K.Y.; Dmitriev, D.E.; Sheremetev, A.B. N-(2-Fluoro-2, 2-dinitroethyl) azoles: a novel assembly of diverse explosophoric building blocks for energetic compound design. *Org. Chem. Front.* 2019, 6, 249-255. DOI:10.1039/C8QO01173G
17. Kettner, M.A.; Klapötke, T.M.. New energetic polynitrotetrazoles. *Chem. Eur. J.* 2015, 21, 3755-3765. DOI: 10.1002/chem.201405659.
18. Klapötke, T.M.; Krumm, B.; Moll, R.; Rest, S.F.; Schnick, W.; Seibald, M. Asymmetric fluorodinitromethyl derivatives of 2, 2, 2-trinitroethyl N-(2, 2, 2-trinitroethyl) carbamate. *J. Fluor. Chem.* 2013, 156, 253-261. DOI: 10.1016/j.jfluchem.2013.06.019.
19. Zhai, L.; Zhang, J.; Wu, M.; Huo, H.; Bi, F.; Wang, B. Balancing good oxygen balance and high heat of formation by incorporating of-C (NO₂) 2F Moiety and Tetrazole into Furoxan block. *J. Mol. Struct.* 2020, 1222, 128934. DOI: 10.1016/j.molstruc.2020.128934.
20. Zhai, L.; Wang, B.; Xu, K.; Huo, H.; Liu, N.; Li, Y.; Li, H.; Lian, P.; Fan, X. A new synthetic route for 3, 3'-bis (fluorodinitromethyl) difurazanyl ether (FOF-13) and its energetic properties. *J. Energ. Mater.* 2016, 34, 92-102. DOI: 10.1080/07370652.2014.1001917.
21. Sheremetev, A.B. 3, 3-Bis(1-fluoro-1, 1-dinitromethyl)difurazanyl ether. In *Proc. 29th Int. Ann. Conf. ICT*, Karlsruhe, Germany. June 30-July 3. 1998, 58, 1-6.
22. Dalinger, I.L.; Vinogradov, V.M.; Shevelev, S.Y.A.; Kuz'min, V.S.; Arnautova, E.A.; Pivina, T.Y.S. Synthesis and Calculation of Properties of N-Difluoroaminoazoles, the Novel Type of Energetic Materials. *Propellants Explos. Pyrotech.* 1998, 23, 212-217. DOI: 10.1002/(SICI)1521-4087(199808)23:4<212::AID-PRP212>3.0.CO;2-Y.
23. Chapman, R.D. Organic difluoramines derivatives. In: Klapötke, T. M. (Ed.). *High energy density materials*. Springer Verlag, Berlin Heidelberg. Struct. Bond., Vol. 125. 2007, pp.123-151. DOI:10.1007/430_2007_058.
24. Reddy, V.P. Synthetic methods for high-energy Organofluorine Compounds. In: *Energetic Materials. Advanced Processing Technologies for Next-Generation Materials*. Eds. Mezger, M.J.; Tindle, K.J.; Pantoya, M.; Groven, L.J.; Kalyon, D.M. Boca Raton, FL., Taylor&Francis, CRC Press, 2017, pp. 1-19. ISBN 978-1-3516-8125-4.
25. Wu, Q.; Li, Q.; Yan, G.; Zhang, Z.; Zhu, W. Molecular design of novel super high energy compounds by incorporating the difluoroamino group, N-oxide and different bridge groups into the 1H-tetrazole. *J. Fluor. Chem.* 2019, 218, 21-26. DOI: 10.1016/j.jfluchem.2018.11.014.
26. Oxley, J.C.; Smith, J.L.; Zhang, J.; Bedford, C. A comparison of the thermal decomposition of nitramines and difluoramines. *J. Phys. Chem. A.* 2001, 105, 579-590. DOI: 10.1021/jp002516a.
27. Ye, C.; Gao, H.; Shreeve, J.M. Synthesis and thermochemical properties of NF₂-containing energetic salts. *J. Fluor. Chem.* 2007, 128, 1410-1415. DOI: 10.1016/j.jfluchem.2007.07.006.
28. Dalinger, I.L.; Shkineva, T.K.; Sheremetev, A.B. Ethyl butyrate bearing nitro and difluoroamino groups. *Mendeleev Commun.* 2023, 33, 841-843. DOI:10.1016/j.mencom.2023.10.034.
29. Ugrak, B.I.; Shkineva, T.K.; Sheremetev, A.B.; Dalinger, I.L. (Difluoroamino) furazans. *Russ. Chem. Bull.* 2023, 72, 2706-2716.
30. Muravyev, N.V.; Fershtat, L.; Zhang, Q. Synthesis, design and development of energetic materials: Quo Vadis?. *J. Chem. Eng.* 2024, 150410. DOI: 10.1016/j.cej.2024.150410.

31. Muravyev, N.V.; Meerov, D.B.; Monogarov, K.A.; Melnikov, I.N.; Kosareva, E.K.; Fershtat, L.L.; Sheremetev A.B.; Dalinger I.L.; Fomenkov I.V.; Pivkina, A.N. Sensitivity of energetic materials: Evidence of thermodynamic factor on a large array of CHNOFCl compounds. *J. Chem. Eng.* 2021, 421, 129804. DOI: 10.1016/j.ccej.2021.129804.
32. Sitzmann, M.E.; Gilligan, W.H.; Ornellas, D.L.; Thrasher, J.S. Polynitroaliphatic explosives containing the pentafluorosulfanyl (SF₅) group: The selection and study of a model compound. *J. Energ. Mater.* 1990, 8, 352-374. DOI: 10.1080/07370659008012580.
33. Martinez, H.; Zheng, Z.; Dolbier Jr, W.R. Energetic materials containing fluorine. Design, synthesis and testing of furazan-containing energetic materials bearing a pentafluorosulfanyl group. *J. Fluor. Chem.* 2012, 143, 112-122. DOI: 10.1016/j.jfluchem.2012.03.010.
34. 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. DOI: 10.1002/ejic.200600098.
35. Xiao-Hong, L.; Hong-Ling, C.; Wei-Wei, J.; Tong-Wei, L.; Rui-Zhou, Z.; Yong-Liang, Y. Theoretical studies on energetic materials bearing pentafluorosulphyl (SF₅) groups. *J. Chem. Sci.* 2014, 126, 1163-1172.
36. Sitzmann, M.E.; Gilardi, R.D. Polynitroalkyl derivatives of SF₅N CCl₂: nitrations of SF₅ imines. *J. Fluor. Chem.* 1993, 63, 203-215. DOI: 10.1016/S0022-1139(00)80564-3.
37. Li, C.; Liu, M.; Li, T.; Wang, L.; Zhang, R.; Jing, S. Fluorine Added to Lead the Way to Future Energetic Materials: 3, 5-difluoro-2, 4, 6-trinitroaniline. *J. Energ. Mater.* 2022, 1-10. DOI: 10.1080/07370652.2022.2155729.
38. Zhu, J.; Li, C.; Jing, S.; Yang, L.; Liu, Y.; Zhang, W.; Zhang, J. 3,5-difluoro-2,4,6-trinitrophenol: A high-energy compound born under the “NO₂FNO₂” construction strategy. *Propellants Explos. Pyrotech.* 2024, 49(2), e202300184. DOI:10.1002/prep.202300184.
39. Zhang, J.; Liu, Y.; Zhou, J.; Bi, F.; Wang, B. Effect of fluoro substituents on polynitroarylenes: design, synthesis and theoretical studies of fluorinated nitrotoluenes. *ChemPlusChem*, 2019, 84, 92-97. DOI: 10.1002/cplu.201800523.
40. Hu, F.; Wang, L.J.; Zhao, W.; Liu, Y.C.; Jing, S.M.; Liu, P.; He, J.X. Thermal Decomposition Kinetics and Compatibility of 3, 5-difluoro-2, 4, 6-trinitroanisole (DFTNAN). *Materials*, 2021, 14, 4186. DOI: 10.3390/ma14154186.
41. Jing, S.; Jiang, Z.; Jiao, Q.; Li, Z.; Liu, Y.; Yang, L. 3, 5-difluoro-2, 4, 6-trinitroanisole: Promising melt-cast insensitive explosives instead of TNT. *J. Energ. Mater.* 2022, 40, 206-217. DOI:10.1080/07370652.2020.1859645.
42. Jiao, Q.; Li, T.; Ou, Y.; Jing, S.; Wang, F. Probing the Reaction Mechanisms of 3,5-Difluoro-2,4,6-Trinitroanisole (DFTNAN) through a Comparative Study with Trinitroanisole (TNAN). *Materials*, 2022, 15(7), 2568. DOI: 10.3390/ma15072568.
43. Li, Y.; Xue, M.; Sun, B.; Tu, Z.; Wang, X. Regulating the melting point by non-covalent interaction toward a promising insensitive melt-castable energetic material: 1, 2-Difluoro-4, 5-dinitrobenzene. *Chinese J. Struc. Chem.* 2023, 42(4), 100002. DOI:https://doi.org/10.1016/j.cjsc.2022.100002.
44. Guo, Z.; Yu, Q.; Chen, Y.; Liu, J.; Li, T.; Peng, Y.; Yi, W. Fluorine-Containing Functional Group-Based Energetic Materials. *Chem. Rec.*, 2023, 23(9), e202300108. DOI: 10.1002/tcr.202300108.
45. Fokin, A.V.; Studnev, Y.N.; Rapkin, A.I.; Komarov, V.A.; Verenikin, O.V.; Potarina, T.M. Synthesis and some properties of 5-fluorodinitromethyl- and 5-difluoronitromethyltetrazoles. *Izv. Akad. Nauk SSSR Ser. Khim.* 1981, 7:1592–1595.
46. Chapman, R. D. Halogenated explosives to defeat biological agents. Defense Threat Reduction Agency. Tech. Report DTRA-IR-14-81. 2015 Sept., pp.1-37.
47. Muravyev, N.V.; Suponitsky, K.Y.; Fedyanin, I.V.; Fomenkov, I.V.; Pivkina, A.N.; Dalinger, I.L. Bis-(2-difluoroamino-2, 2-dinitroethyl) nitramine–Energetic oxidizer and high explosive. *Chem. Eng.* 2022, 449, 137816. DOI: 10.1016/j.ccej.2022.137816.
48. Zhai, L.; Zhang, J.; Zhang, J.; Wu, M.; Bi, F.; Wang, B. Progress in Synthesis and Properties of High Energy Density Compounds Regulated by N–F Bond. *Chin. J. Org. Chem.* 2020, 40, 1484. DOI: 10.6023/cjoc202001018.
49. Kamlet, M.J.; Adolph, H.G. Some comments regarding the sensitivities, thermal stabilities, and explosive performance characteristics of fluorodinitromethyl compounds. In *Proc. Seventh Internat. Symp. Detonation*, Annapolis, Maryland, USA, Jun. 16-19, 1981, pp.84-92.
50. Warner D.A. Bulk synthesis of fluoroexplosives. Tech. Report AFATL-TR-67-154/ DTIC AD0501781. Defense Technical Information Center, Eglin AFB, FL, USA, Oct. 1967, pp.1-35. URL: https://archive.org/details/DTIC_AD0501781, accessed at 30-05-2024.
51. Kumar, A.S.; Kommu, N.; Ghule, V.D.; Sahoo, A.K. Synthesis of trifluoromethyl-substituted N-aryl-poly-1, 2, 3-triazole derivatives. *J. Mater. Chem. A*. 2014, 2, 7917-7926. DOI:10.1039/c3ta15184k.
52. Yan, Z.; Lu, T.; Liu, Y.; Liu, W.; Zhao, B.; Wang, Y.; Ge, Z. High thermal stability and insensitive fused triazole-triazine trifluoromethyl-containing explosives (TFX). *ACS Omega*, 2021, 6, 18591-18597. DOI: 10.1021/acsomega.1c01018.

53. Chinnam, A.K.; Staples, R.J.; Shreeve, J.N.M. Selective Synthesis of Bis (3-(3-(trifluoromethyl)-1 H-1, 2, 4-triazol-5-yl)-4, 4'-azo-and-azoxyfuran Derivatives. *J. Org. Chem.*, 2021, 86, 7781-7786. DOI: 10.1021/acs.joc.1c00531.
54. Yang, T.; Xu, Z.; Meng, Z.; Zhai, L. A Novel Synthesis, Characterization and Performances of 1, 3, 5-Trinitro-2, 2-bis (trifluoromethyl)-1, 3, 5-triazinane. *ChemistrySelect*, 2019, 4, 6338-6341. DOI:10.1002/slct.201901065.
55. Liu, Q.; Yuan, M.; He, J.; Yu, P.; Guo, X.; Liu, Y.; Gao, H.; Yin, P. Exchanging of NH₂/NHNH₂/NHOH groups: An effective strategy for balancing the energy and safety of fused-ring energetic materials. *J. Chem. Eng.* 2023, 466, 143333. DOI: 10.1016/j.cej.2023.143333.
56. Tamuliene, J.; Sarlauskas, J. Impact of Incremental Methylene Groups on the Energetic Properties of Aromatic Nitramines. *Energies*, 2023, 16, 3117. DOI: 10.3390/en16073117.
57. Parthasarathi, R.; Padmanabhan, J.; Subramanian, V.; Maiti, B.; Chattaraj, P.K. Toxicity analysis of 3,3',4,4',5-pentachloro biphenyl through chemical reactivity and selectivity profiles. *Curr. Sci.* 2004, 86, 535–542. Available online: <https://www.jstor.org/stable/24107906> (accessed on 10 June 2024).
58. Kaya, S.; Kaya, C. New equation based on ionization energies and electron affinities of atoms for calculating of group electronegativity. *Comput. Theor. Chem.* 2015, 1052, 42–46. DOI: 10.1016/j.comptc.2014.11.017.
59. Becke, A.D. Density functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 1993, 98, 5648. DOI: 10.1063/1.464913.
60. Dunning Jr. T.H. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* 1989, 90, 1007. DOI: 10.1063/1.456153.
61. 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.; Li, X.; Caricato, M.; Marenich, A.; Bloino, J.; Janesko, B.G.; Gomperts, R.; Mennucci, B.; Hratchian, H.P.; Ortiz, J.V.; Izmaylov, A.F.; Sonnenberg, J.L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V.G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J.A.Jr., Peralta, J.E.; Ogliaro, F.; Bearpark, M.; Heyd, J.J.; Brothers, E.; Kudin, K.N.; Staroverov, V.N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J.C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Millam, J.M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J.W.; Martin, R.L.; Morokuma, K.; Farkas, O.; Foresman, J.B., Fox, D.J. *Gaussian, Inc., Wallingford CT.* 2016, pp. 1-139. URL: https://www.cwu.edu/chemistry/sites/cts.cwu.edu/chemistry/files/documents/Gaussian_09_ReferenceManual.pdf (accessed: 26.05.2024).
62. Cardia, R.; Mallocci, 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. DOI: 10.1021/jp502022t.
63. Cardia, R.; Mallocci, 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. DOI: 10.1103/PhysRevB.93.235132.
64. Dardenne, N.; Cardia, R.; Li, J.; Mallocci, 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. DOI: 10.1021/acs.jpcc.7b08601.
65. Antidormi, A.; Aprile, G.; Cappellini, G.; Cara, E.; Cardia, R.; Colombo, L.; Farris, R.; d'Ischia, M.; Mehrabian, M.; Melis, C.; Mula, G.; Pezzella, A.; Pinna, E.; Riva, E.R. Physical and Chemical Control of In-terface Stability in Porous Si–Eumelanin Hybrids. *J. Phys. Chem. C.* 2018, 122, 28405–28415. DOI: 10.1021/acs.jpcc.8b09728.
66. 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. DOI: 10.1088/1742-6596/956/1/012020.
67. 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. DOI: 10.1088/1367-2630/aae7f0.
68. Kumar, A.; Cardia, R.; Cappellini, G. Electronic and optical properties of chromophores from bacterial cellulose. *Cellulose.* 2018, 25, 2191–2203. DOI: 10.1007/s10570-018-1728-0.
69. 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. DOI: 10.1016/S0022-2860(00)00934-0.
70. 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. DOI: 10.1021/jp0406114
71. Cooper, P.W. *Explosives Engineering*; Wiley-VCH: New York, USA. 1996; pp.1-480. ISBN: 0-471-18636-8
72. Shevchenko, A.A.; Dolgoborodov, A.Yu.; Brazhnikov, M.A.; Kirilenko, V.G. Pseudoideal detonation of mechanoactivated mixtures of ammonium perchlorate with nanoaluminum. *J. Phys. Conf. Ser. (IOP Publ.)* 2018, 946, 012055. DOI: 10.1088/1742-6596/946/1/012055.

73. Kozak, G.D. Measurement and calculation of the ideal detonation velocity for liquid nitrocompounds. *Combust. Explos. Shock Waves*. 1998, 34, 581–586. DOI: 10.1007/BF02672682.
74. Bolton, O.; Simke, L.R.; Pagoria, P.F.; Matzger, A.J. High Power Explosive with Good Sensitivity: A 2:1 Cocystal of CL-20:HMX. *Cryst. Growth Des.* 2012, 12, 4311–4314. DOI: 10.1021/cg3010882.
75. Viswanath, D.S.; Ghosh, T.K.; Boddu, V.M. 5-Nitro-2,4-dihydro-3H-1,2,4-Triazole-3-one (NTO). In *Emerging Energetic Materials: Synthesis, Physicochemical, and Detonation Properties*. Springer: Dordrecht, The Netherlands. 2018; pp. 163–211. DOI: 10.1007/978-94-024-1201-7_5.5.
76. Rajakumar, B.; Arathala, P.; Muthiah, B. Thermal Decomposition of 2-Methyltetrahydrofuran behind Reflected Shock Waves over the Temperature Range of 1179–1361 K. *J. Phys. Chem. A*. 2021, 125, 5406–54223. DOI: 10.1021/acs.jpca.0c1149022.5.
77. Šarlauskas, J.; Tamulienė, J. Preparation and Characterization of Cationic Energetic Salts of 5-Amino-3-[(2,4,6-trinitrophenyl)amino]-1H-1,2,4-triazole (APATO). *Central European Journal of Energetic Materials*. 2022, 19(3), 311–325. DOI 10.22211/cejem/154973
78. 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).
79. Kaushik, M. A review of innovative chemical drawing and spectra prediction computer software. *Mediterr. J. Chem.* 2014, 3, 759–766. DOI: 10.13171/mjc.3.1.2014.04.04.16.
80. 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. DOI: 10.1016/j.fuel.2021.122241.
81. Keshavarz, M.H.; Zamani, A. A simple and reliable method for predicting the detonation velocity of CHNOFCl and aluminized explosives. *Cent. Eur. Energ. Mater.* 2015, 12, 13–33.
82. Keshavarz, M.H.; Pouretedal, H.R. An empirical method for predicting detonation pressure of CHNOFCl explosives. *Thermochim. Acta*, 2004, 414, 203–208.
83. Urizar, M.J.; James, E., Jr.; Smith, L.C. Detonation velocity of pressed TNT. *Phys. Fluids*. 1961, 4, 262–274. DOI: 10.1063/1.1724438.
84. Chandler, J.; Ferguson, R.E.; Forbes, J.; Kuhl, A.L.; Oppenheim, A.K.; Spektor, R. Confined combustion of TNT explosion products in air. In *Proc. Conf. 8th international Colloquium on Dust Explosions*, Schaumburg, IL, US. Tech. Rep. UCRL-JC-131748; ON: DE00003648; OSTI ID: 3648, Sept. 21–25, 1998. Accessed at URL: <https://www.osti.gov/biblio/3648> (on 03-07-2024).
85. 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(8), p.228. DOI: 10.21203/rs.3.rs-2873524/v1.
86. Kang, Y.; Dong, Y.; Liu, Y.; Gao, H.; Wang, Y.; Shreeve, J.M. Halogen bonding (CF $\cdots$ X) and its effect on creating ideal insensitive energetic materials. *J. Chem. Eng.* 2022, 440, 135969. DOI:10.1016/j.cej.2022.135969.
87. Wu, W.; You, Y.; Weng, Z. Recent advances in the synthesis of fluoroalkylated compounds using fluoroalkyl anhydrides. *Chin. Chem. Lett.* 2022, 33, 4517–4530. DOI: 10.1016/j.ccl.2022.01.038.
88. Balachandar, K.G.; Thangamani, A. Novel high performance energetic materials of fluorine-containing 2, 6-dinitro-4-(trifluoromethyl) phenol derivatives with substituted azoles. *J. Fluor. Chem.* 2021, 247, 109801. DOI: 10.1016/j.jfluchem.2021.109801.
89. Koch, E.C.; Contini, A. Metal Fluorocarbon Pyrolants, XVI: Theoretical and Experimental Investigation of Poly [bis (2, 2, 2-trifluoroethoxy) phosphazene] (PTFEP) as Oxidizer in Magnesium Based Pyrolants. *Propellants, Explos., Pyrotech.* 2014, 39, 761–767. DOI: 10.1002/prep.201400111.

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