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Polynitrobenzene Derivatives, Containing -CF$_3$, -OCF$_3$, and -O(CF$_2$)$_n$O- Functional Groups, as Candidates for Perspective Fluorinated High-Energy Materials: Theoretical Study

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Abstract: We performed a theoretical investigation of the fluorinated compounds' morphology and stability. The research was conducted using the widely adopted DFT approach, specifically the B3LYP method and the cc-pVTZ basis set, aiming to design high-energy materials that exhibit low sensitivity, toxicity, instability, and reduced proneness to decomposition or degradation over a short period. In the paper, we presented the investigation results for the compounds whose total energy is the lowest. Their thermal and chemical stability was evaluated based on stability indicators such as cohesion, chemical hardness, and softness. The oxygen–fluorine balance is assessed to determine the sensitivity of these advanced materials. The density, detonation pressure, and velocity of the selected conformers were theoretically obtained to reveal the influence of -CF$_3$, -OCF$_3$, and cyclic -O(CF$_2$)nO- fragments on the energetic properties of nitroaromatics as well as their stability and resistance to shock stimuli. The results enable the prediction of advanced energetic materials that achieve a favorable balance between power and stability. Based on the results achieved, we put forward 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 pursuit of advanced high-energy materials (HEMs) which, on one hand, correspond to safety and environment-friendly requirements and, on the other hand, do not lose their power, display resistance to mechanical stimuli, and have the capability of providing large quantities of energy when it is necessary [1–3] is an enduring process. There are various ways to achieve the above goal: incorporating nitro, nitramine, or azido groups into molecular structures; developing completely new compounds; forming salts; etc. Since the 1960s, some fluorinated polymers (Viton-A, Teflon, Kel-F) have been widely applied in producing 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(NO$_2$)$_2$F [5–11]. Notably, -C(NO$_2$)$_3$ changing in HEMs with -C(NO$_2$)$_2$F or -C(NO$_2$)F$_2$ groups has led to the development of energetic materials, possessing markedly higher stability and decreased sensitivity to mechanical impact [12,13].

Currently, the known perspective energetic fluorinated groups used in the new energetic structures are -$C(NO_2)_2F$ and -$C(NO_2)_2F_2$ [14–21], -NF_2 and -$C(NO_2)_2NF_2$ [22–31], and -SF_5 [32–36]. It was learned that introducing even the simplest fluorine "C-F" group instead of "C-H" sometimes substantially improves practical HEM 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. This is because the fluorine introduction boosts the oxygen balance of the relevant HEMs due to their ability to generate HF (from H) and CF_4 (from C) [38,43]. Fluorination promotes a growth in the density and detonation velocity. 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. Moreover, the presence of C-F bonds could lead to the formation of halogen and hydrogen bonds which stabilize relevant energetic materials. This implies that fluorine-containing materials could be highly stable and possess a high energy output to be released during detonation.

The fluorinated high-energy materials also have been reported to have good potential as prospective melt-castable explosives, along with energetic plasticizers, since fluorination is favorable for reducing the melting point and expanding interval between the melting point and thermal decomposition temperature of the oxidative properties of energetic materials [39,43,45].

It has also been reported that typical CHNO-containing explosives primarily release 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, as a minor product, carbon oxodifluoride (COF_2) [44,46].

The fluorinated HEMs can be divided into separate classes such as -NF_2, -$C(NO_2)_2NF_2$, SF_5, etc. following fluorine-containing functional groups HEM molecule [44]. Previously widely investigated F-HEMs possessed mostly -NF_2 [47,48] or $C(NO_2)_2F$ [49]. However, other F-groups (such as -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 -CF_3, -OCF_3, and -$O(CF_2)_nO$- functional groups, aiming to observe their potential to be used as multifunctional energetic materials possessing better energetic properties than that which is currently expended; i.e., we proposed and investigated a low sensitivity, toxicity, instability, and high-energy materials, with low proneness to decomposition or degradation over a short time. 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

This research was undertaken to develop new energetic materials and predict which of them could be used practically. We do not change our research methodology, as 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 the -OCF_3 group where it is possible.
- Execution of Berny Optimization Without Symmetry Constraints: This process allowed for changes in all bond lengths, angles, and dihedral angles to locate an equilibrium point. A vibrational frequency analysis was conducted to confirm the achievement of energy minima. The total energy of the conformers was compared to select the most prevalent conformers, focusing on investigating their stability and energetic properties.

- Cohesion Evaluation for Thermal Stability Comparison: Cohesion energy was assessed to determine the thermal stability of the compounds. This energy represents the amount required to detach an atom from a system of particles, with higher values indicating greater thermal stability.
- Assessment of Stability Linked to Chemical Properties and Aging: The HOMO-LUMO gap, chemical hardness, and softness were estimated to evaluate stability. Compounds with a larger HOMO-LUMO gap and higher chemical hardness demonstrate increased resistance to chemical reactions and transformations induced by external perturbations, such as electric fields. Conversely, a low chemical softness value indicates a higher susceptibility of the molecule to degradation [57,58].
- Calculation of hardness index to evaluate the stability of the compounds.

To obtain data necessary to evaluate the above-listed parameters, a B3LYP/cc-pVTZ approach executed in a GAUSSIAN 09 package was employed [59–62]. The parameters obtained using this approach to describe geometric and electronic structures of numerous compounds are comparable to experimental data [63–75].

The energetic properties, such as detonation velocity and pressure of the analyzed compounds, were obtained by approaching a minimal-computational-resources-required approach, created for the $C_aH_bN_cO_dF_e$ compound. The accuracy of the method was assessed by the similarity of the results to those of TNT, APATO (3-amino-5-[(2, 4, 6-trinitrophenyl) amino]-1*H*-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 HEMs, such as the relationship between the quantity of nitro groups and energetic properties [1].

The oxygen/fluorine balance [57] was estimated to assess the resistance to mechanical stimuli. This balance was chosen due to the inclusion of fluorine as an additional oxidizing 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 estimated by the division of molar from additive increments is, in some cases, significantly larger than that obtained experimentally [77]. Second, experimental data on the density of the $C_aH_bN_cO_dF_e$ are scarce; i.e., there is no possibility of evaluating the deviations of the simulations. So, the density of the compounds was estimated by using three approaches: one was implemented in ACD/ChemSketch based on the Van der Walls volumes molecular modeling program [78]; the second one, as suggested in [79]; i.e., the estimated density is corrected by the obtained dependence; and (iii), with the division of molecular weight from the molar volume without any corrections. In the latter cases, the molar volume was estimated by a B3LYP/cc-pVTZ approach implemented in the Gaussian program. A comparison of the estimated densities revealed that in many cases, the densities obtained by using the 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/cm^3, while that estimated by ACD/ChemSketch is equal to 1.77 g/m^3 [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 present the energetic parameters obtained with the ACD/ChemSketch values for the 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 remaining 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 their energetic properties. The detonation velocity was estimated by approaching the equation and pressure presented in [81,82].

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

3. Results

The profiles of the selected compounds are depicted in Appendix A. The thermal and chemical stability of the analyzed compounds were evaluated based on the cohesion, HOMO-LUMO gap, chemical hardness, electronegativity, and hardness index calculation. Table 1 presents these parameters.

Table 1. The cohesion (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
CF3N2	6.00	4.94	2.47	0.20	0.92
CF3N3	5.43	4.73	2.36	0.21	0.91
C2F6N2	5.42	5.24	2.62	0.19	0.93
C2F6N3	5.38	5.02	2.51	0.20	0.92
C3F9N2 a	5.39	5.16	−2.58	0.19	0.92
C3F9N2 b	5.39	5.46	2.73	0.18	0.93
C3F9N3	5.35	5.01	2.50	0.20	0.92
OCF3N2/CF3ON2	5.41	5.10	2.55	0.20	0.92
OCF3N3/CF3ON3	5.37	4.94	2.47	0.20	0.92
[1] O2C2F6N2 a	5.33	4.65	2.33	0.21	0.91
[1] O2C2F6N2 b	5.33	4.95	2.47	0.20	0.92
[1] O3C3F9N2 b	5.27	5.14	2.57	0.19	0.92
[1] O2C2F6N3 a	5.30	4.96	2.48	0.20	0.92
[1] O2C2F6N3 b	5.30	4.95	2.47	0.20	0.92
[1] O2C2F6N4 a	5.27	4.85	2.43	0.21	0.92
[1] O2C2F6N4 b	5.27	4.85	2.43	0.21	0.92
[1] O3C3F9N3 a	5.24	5.22	2.61	0.19	0.93
[1] O3C3F9N3 b	5.24	5.23	2.62	0.19	0.93
1CF2N2/[1] O2CF2N2	5.61	4.65	2.33	0.22	0.91
1CF2N3/[1] O2CF2N3	5.68	4.00	2.00	0.25	0.87
1CF2N4/[1] O2CF2N4	5.48	4.48	2.24	0.22	0.90
2CF4N2/[1] O2C2F4N2	5.66	4.73	2.37	0.21	0.91
[1] 2CF4N3	5.47	4.77	2.39	0.21	0.91
2CF4N4/O2C2F4N4	5.42	4.89	2.44	0.20	0.92
3CF6N2/O2C3F6N2	5.43	4.93	2.46	0.20	0.92
3CF6N3	5.53	4.46	2.23	0.22	0.90
3CF6N4/[1] O2C3F6N4	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 a and b letters mark the conformers of the analyzed compounds. The difference between conformers relies on *cis-* and *trans-*position F-containing groups or their different positions. * The explanation of the choosing APATO for the result comparison is given below.

We would like to draw attention to the fact that APATO is not used as a standard to evaluate the energetic properties of advanced 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, as presented here, coincide well.

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

Table 2. The densities found by the method suggested 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
CF3N3	1.77	2.07
C2F6N2	1.69	2.07
C2F6N3	1.82	2.34
C3F9N2 a	1.74	2.09
C3F9N2 b	1.74	1.96
C3F9N3	1.85	2.01
OCF3N2/CF3ON2	1.64	1.93
OCF3N3/CF3ON3	1.80	2.11
O2C2F6N2 a	1.74	2.42
O2C2F6N2 b	1.73	1.99
O3C3F9N2 b	1.79	2.11
O2C2F6N3 a	1.85	1.98
O2C2F6N3 b	1.85	2.01
O2C2F6N4 a	1.96	2.14
O2C2F6N4 b	1.96	2.14
O3C3F9N3 b	1.89	2.13
O3C3F9N3 a	1.89	2.05
1CF2N2/O2CF2N2	1.84	1.83
1CF2N3/O2CF2N3	1.95	1.80
1CF2N4/O2CF2N4	2.05	2.23
2CF4N2/O2C2F4N2	1.85	2.09
2CF4N3/O2C2F4N3	1.98	1.81
2CF4N4//O2C2F4N4	2.01	1.89
3CF6N2/O2C3F6N2	1.85	2.19
3CF6N3/O2C3F6N3	1.97	2.42
3CF6N4/O2C3F6N4	1.98	2.34

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

Indeed, in many cases, the densities of the analyzed compounds obtained by the approaches applied are higher than 1.8 g/cm^3, coinciding with the results obtained by L. Wen et al. [80]. However, in many cases, the density ρ is significantly higher than ρ_{ACD}, although ρ exhibits the influence of compound morphology on the density. Considering the good agreement between the density of CF3N3 obtained theoretically (1.77 g/cm^3) and experimentally (1.716–1.816 g/cm^3), the energetic parameters are estimated with smaller values of ρ_{ACD}, aiming not to overestimate the energetic properties of the analyzed compounds. 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 for detonation pressure and velocity, but show the case of usage of the same methods. This ensures that the statistical errors in the densities, detonation velocities, and pressures for each molecule remain consistent. As a result, the detonation velocities of the analyzed compounds can be compared, allowing for their ranking and enabling qualitative conclusions about the impact of substitutions on the energetic properties of the analyzed compounds. Going ahead, we would like to mention that the measurements for 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 estimated 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 provided in Table 3. An increase shows that 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.

Table 3. The oxygen balance and its dependence on the number of nitro groups in the compounds.

| Compounds	O/F Balance	Number of Nitro Groups
TNT	−73.97	3.00
APATO	−69.41	3.00
CF3N2	−67.77	2.00
OCF3N2/CF3ON2	−57.12	2.00
C2F6N2	−52.61	2.00
1CF2N2m/O2CF2N2	−51.59	2.00
2CF4N2m/O2C2F4N2	−48.31	2.00
3CF6N2m/O2C3F6N2	−45.96	2.00
C3F9N2 a	−43.00	2.00
C3F9N2 b	−43.00	2.00
CF3N3	−42.69	3.00
O2C2F6N2 a	−38.08	2.00
O2C2F6N2 b	−38.08	2.00
OCF3N3/CF3ON3	−35.00	3.00
C2F6N3	−34.37	3.00
3CF6N3mp	−30.53	3.00
2CF4N3/O2C2F4N3	−30.31	3.00
1CF2N3mp/O2CF2N3	−30.02	3.00
C3F9N3	−28.77	3.00
O3C3F9N2 b	−26.66	2.00
O2C2F6N3 a	−23.09	3.00
O2C2F6N3 b	−23.09	3.00
3CF6N4/O2C3F6N4	−18.26	4.00
2CF4N4//O2C2F4N4	−16.49	4.00
O3C3F9N3 b	−15.48	3.00
O3C3F9N3 a	−15.48	3.00
1CF2N4/O2CF2N4	−14.20	4.00
O2C2F6N4 a	−11.27	4.00
O2C2F6N4 b	−11.27	4.00

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

We pointed out the coincidence between the measured detonation velocity of 6.9 km/s TNT and the 6.8 km/s obtained by us [83]. The estimated value of detonation pressure of 217.15 kbar of this compound fits the reported 210 kbar at 1.63 g/cm^3 density in a solid which is used as a standard [84]. 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.
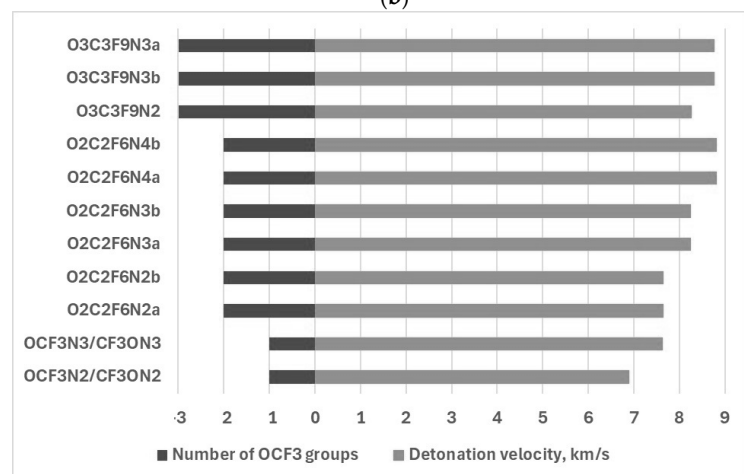
The detonation velocity and detonation pressure are depicted in Figures 1 and 2 to exhibit the parameter dependence on the number of nitro, -CF$_3$, and -OCF$_3$ groups, as well as cycling O$_2$(CF$_2$)$_n$.
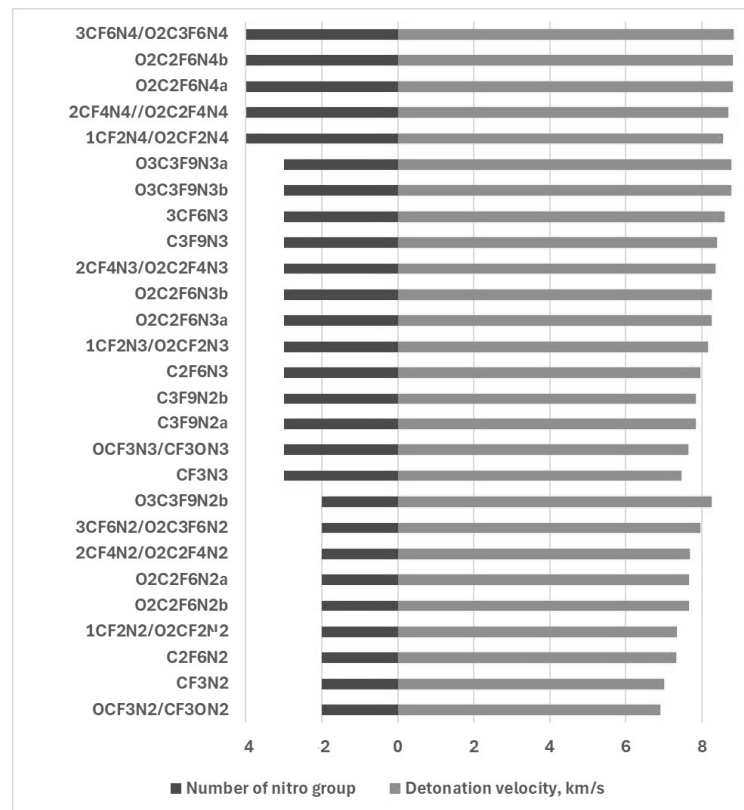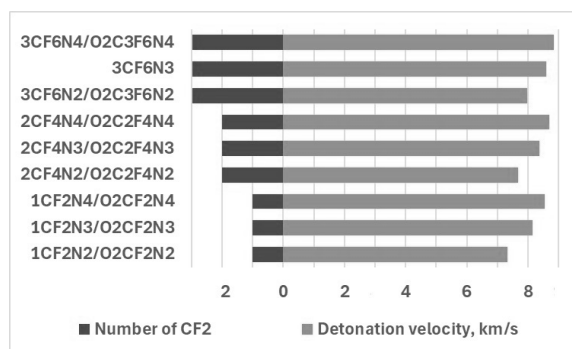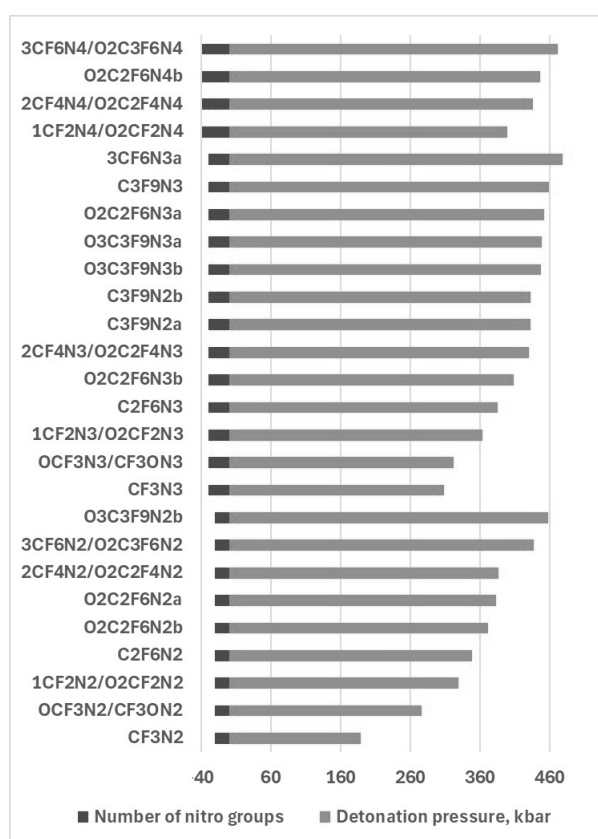
(**a**)
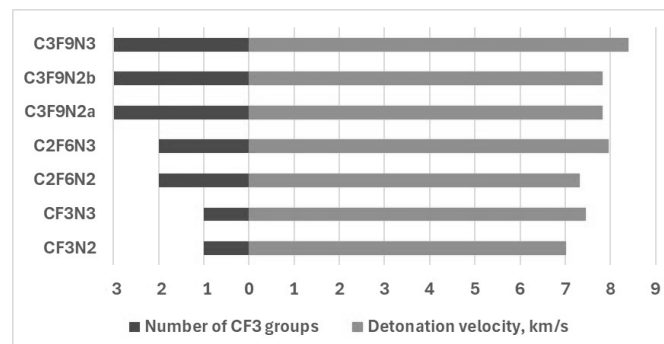
(**b**)

(**c**)

Figure 1. *Cont.*

(**d**)

Figure 1. The detonation velocity dependence on the number of -NO_2 group (**a**), -CF_3 (**b**), -OCF_3 (**c**), and that of CF_2 in the -O-$(CF_2)_n$-O- (**d**).

(**a**)

(**b**)

Figure 2. *Cont.*

(c)

(d)
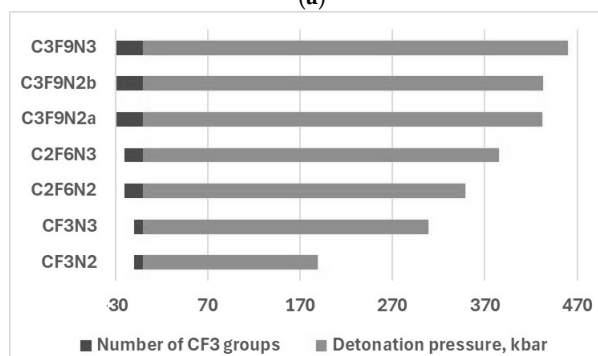
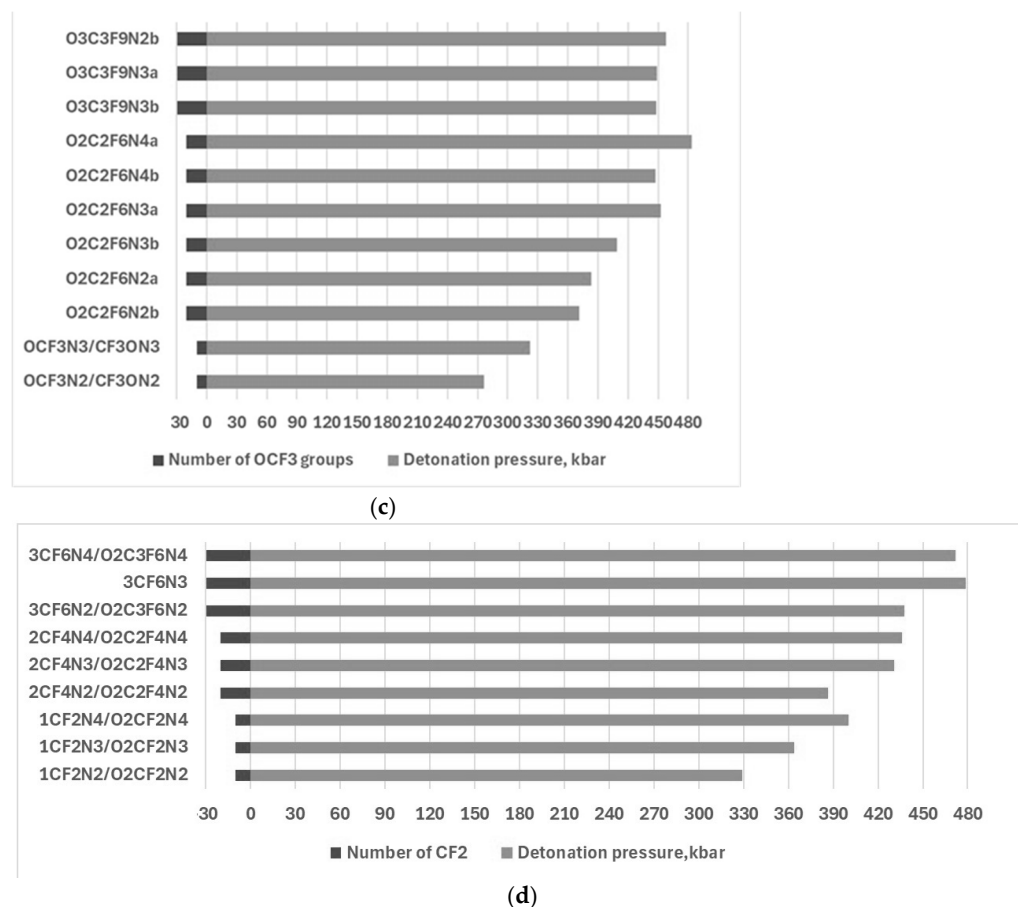**Figure 2.** The detonation pressure dependence on the $-NO_2$ group (**a**), $-CF_3$ (**b**), $-OCF_3$ (**c**), and that of CF_2 in the $-O-(CF_2)_n-O-$ (**d**). The numbers of the groups and cycle sizes are enlarged by 10 for better viewing.

4. Discussion

The stability of the energetic materials is handled using different methodologies. The investigation of thermal stability could be based on the comparison of the total energy of the conformers or cohesion (BDE) when the stability of compounds with distinct chemical compositions 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 evaluated the cohesion (BDE), HOMO–LUMO gap, chemical hardness, and softness. It is well established that compounds with a larger HOMO–LUMO gap and higher chemical hardness are more stable and less likely to undergo chemical reactions or transformations when exposed to external influences, such as an applied electric field. Conversely, a low value of chemical softness indicates a greater susceptibility of the molecule to degradation [76,77]. The BDA values shed some light on the thermal stability of the compounds.

We would like to draw 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, estimated by the same approach, are equal to 0.88 and 0.81, exhibiting their slightly lower stabilities than those of the analyzed compounds (Table 1). The higher chemical stability of the analyzed compounds than those of TNT and APATO is also confirmed by other param-

eters 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 and/or chemically than the above-mentioned known ones.

Referring to BDE, we may state that compounds consisting of 1CF2N3/O2CF2N3 and 1CF2N2/O2CF2N2 are slightly thermally more stable than TNT, but less stable than APATO. The thermal resistance of CF3N2 is higher than that of APATO.

The high chemical stability of the analyzed compounds represents values of HOMO-LUMO gaps as well as chemical hardness (Table 1). The chemical stability of 1CF2N4/O2CF2N4 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 the ability to participate in chemical reactions due to effects of external perturbations of the compound consisting of fluorine.

The increase in the $-CF_3$ or $-OCF_3$ groups as well as the inclusion of $-CF_2$ in the $-O-(CF2)_n-$ cycle does not significantly influence the chemical and thermal stability of the analyzed compounds. These parameters (Table 1) are comparable to the results presented [85–89].

The investigation of the energetic properties revealed significant effects of the nitro groups on the energetic properties of the analyzed compounds (Table 4). The $-CF_3$, or $-OCF_3$ groups, as well as the $-O-(CF2)_n-O$ cycle, also change the energetic properties of the analyzed compounds, but their influence is nitro-group-number dependent. For example, the enlargement of the above cycle due to the inclusion of CF_2 leads to an increase in sensitivity to the shock stimuli of this group materials under study when the nitro group in the compound is a two nitro group (Figure 3). The opposite effect is obtained for the compounds with four nitro groups. In this case, the inclusion of $-CF_2$ 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 (Figure 3).
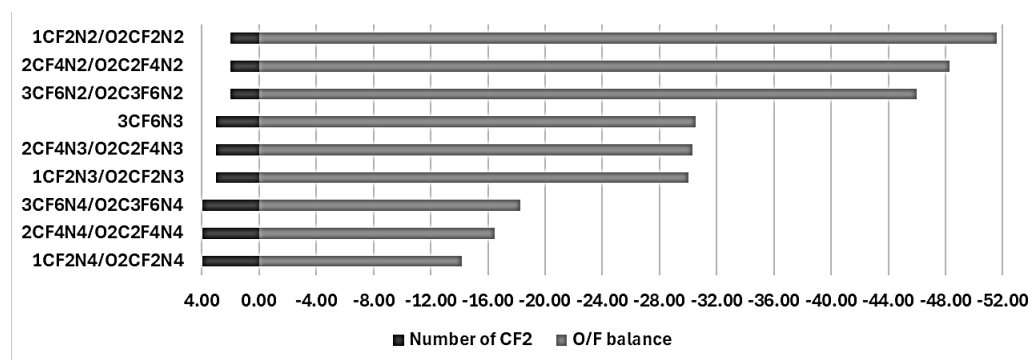

Figure 3. The O/F balance dependence on the CF_2 in the $-O-(CF2)_n-O-$ cycle.

The increase in $-CF_3$ or $-OCF_3$ numbers in the compounds with the same nitro group number also leads to a decrease in the resistance to shock stimuli (Table 2). Moreover, the compounds with $-OCF_3$ are more sensitive to shock than those with CF_3 when the nitro group number in the compound is the same. To exhibit this conclusion evidently, we present the O/F balance separately in Table 5.

Hence, we obtain that increasing the nitro group results in lower shock resistance to stimuli which indicates the results of the analysis of the O/F balance (OB) (Table 3). The increase of CF_3 or $-OCF_3$ number also leads to an increase in the sensitivity to stimuli. However, there is no clear influence of the $-O-(CF2)_n-O-$ cycle on the sensitivity of shock stimuli.

Table 4. The detonation velocity (v) and detonation pressure (p) estimated 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
C3F9N2 a	7.83	432.39
C3F9N2 b	7.84	432.63
C3F9N3	8.40	459.75
OCF3N2/CF3ON2	6.91	276.32
OCF3N3/CF3ON3	7.63	322.50
O2C2F6N2 a	7.66	383.27
O2C2F6N2 b	7.66	371.38
O3C3F9N2 b	8.27	458.16
O2C2F6N3 a	8.26	452.77
O2C2F6N3 b	8.26	408.54
O2C2F6N4 a	8.82	483.42
O2C2F6N4 b	8.82	447.03
O3C3F9N3 b	8.78	448.03
O3C3F9N3 a	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

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

Table 5. The O/F balance dependence on OCF_3 and CF_3 and nitro group number.

N	M	$O_nC_nF_{3n}N_m$	$C_nF_{3n}N_m$
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

The oxygen balance of TNT, commonly used as a reference, is −74%, while 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%. This 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 considering increased resistance to stimuli as follows:

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

The detonation velocity of the analyzed compounds varies from 6.67 to 8.84 km/s; thus, they could be addressed to the high explosives whose detonation velocities lie in the range 1.01 km/s to 9.89 km/s. The detonation velocity of OCF3N2/CF3ON2 is lower

than the measured 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, the detonation velocities 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 their better energetic properties.

The investigation of the dependence of the detonation velocity on the number of the -NO_2, -CF_3,-OCF_3, and -O-$(CF_2)_n$-O-cycle revealed some interesting features (Figure 1). 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 -OCF_3 and -CF_3 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 -CF_3 number is the same. So, the improvement in the energetic properties is related to the nitro group inclusion. In the case that 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 -CF_3. The detonation velocity of C3F9N3 formed due to C2F6N3 joining -CF_3 also increased to 8.40 km/s. This value for the detonation velocity is the largest for this type of compound, and allows us to speculate that the nitro group/-CF_3 rate could be properly chosen to improve energetic properties.

A similar tendency takes place in the case of the -OCF_3 and -O-$(CF_2)_n$-O- cycle. The largest values for 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 worse energetic properties for CF3N2 than APATO, but better than TNT. Those of the rest of the compounds are better even than the properties of APATO (Figure 1). The results following the analysis of the detonation pressure confirm that (Figure 2).

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 presser supports this finding. For example, the largest detonation pressure of 483,42 is O2C2F6N4a, consisting of four nitro and two -OCF_3 groups. Adding -OCF_3 and -CF_2 in the -O-$(CF_2)_n$-O- ring is more effective than -CF_3 for energetic property improvements. For example, the detonation pressure of 348.83 km/s, 383.27 km/s or 371.38 km/s, and 386.62 km/s account for C2F6N2, O2C2F6N2a/b, and 2CF4N2/O2C2F4N2, respectively.

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

Table 6. The detonation pressure of the selected conformers shows the importance of the steric hindrance.

Compounds	Detonation Pressure, kbar
C3F9N2 a	432.39
C3F9N2 b	432.63
O2C2F6N2 a	383.27
O2C2F6N2 b	371.38
O2C2F6N3 a	452.77
O2C2F6N3 b	408.54
O2C2F6N4 a	483.42
O2C2F6N4 b	447.03
O3C3F9N3 b	448.03
O3C3F9N3 a	449.03

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

The last statement is based on comparing the detonation pressure of compounds which are conformer morphology-dependent. The detonation pressure of the conformers, whose morphology is different only due to the position of the -CF$_3$ group in the core of the molecule, is different 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 -OCF$_3$ 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 7). This is also reflected by the different densities of the conformers presented in Table 2.

Table 7. 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 analyzed compounds are better than those 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 -OCF$_3$ and the addition of -CF$_2$ in the -O-(CF$_2$)$_n$-O- cycle for -CF$_3$.

5. Conclusions

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

Our study has demonstrated that the incorporation of cyclic -O(CF$_2$)$_n$O-, -OCF$_3$, and -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 1CF2N3/O2CF2N3 and 1CF2N2/O2CF2N2 exhibit slightly higher thermal stability compared to TNT. However, only 1CF2N4/O2CF2N4 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 -CF$_3$ or -OCF$_3$ groups, and with the inclusion of -CF$_2$ in the -O(CF$_2$)$_n$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 -CF$_3$, -OCF$_3$, and the -O(CF$_2$)$_n$O- cycle contributing variably depending on their quantity.

Referring to the results of the O/F balance investigation, we found compounds with -OCF$_3$ groups more shock-sensitive than those with CF$_3$ when the nitro group count is identical. An increase in CF$_3$ or -OCF$_3$ groups also heightens sensitivity to stimuli, although the -O(CF$_2$)$_n$O- cycle's influence on shock sensitivity remains inconclusive. However,

1CF2N2/O2CF2N2, 2CF4N2/O2C2F4N2, C2F6N2, OCF3N2, and CF3N2 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 -OCF$_3$ and -CF$_2$ in the -O(CF$_2$)$_n$O- ring proved more effective in enhancing energetic performance than -CF$_3$. This improvement is attributed to steric hindrance, which increases density and, consequently, energetic efficiency.

In summary, the compounds CF3N2, OCF3N2, C2F6N2, 1CF2N2/O2CF2N2, and 2CF4N2/O2C2F4N2 demonstrate potential for practical application, highlighting the advantages of -OCF$_3$ and the incorporation of -CF$_2$ in the -O(CF$_2$)$_n$O- cycle over -CF$_3$. A brief exploration of the potential synthetic accessibility of proposed structures is presented in Appendix C.

Appendix A

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

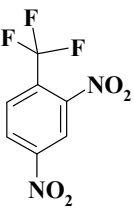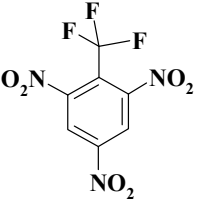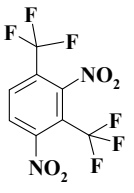| No.	Structural Formula	Compound Abbreviation
1.		CF3N2
2.		CF3N3
3.		C2F6N2

Table A1. *Cont.*

No.	Structural Formula	Compound Abbreviation
4.		C2F6N3
5.		C3F9N2
6.		C3F9N3
7.		CF3ON2/OCF3N2
8.		CF3ON3/OCF3N3
9.		O2C2F6N2
10.		O2C2F6N2b/m

Table A1. *Cont.*

No.	Structural Formula	Compound Abbreviation
11.		O3C3F9N2 a
12.		O3C3F9N2 b
13.		O3C3F9N3 a
14.		O3C3F9N3 b
15.		O2C2F6N2 a
16.		O2C2F6N2 b
17.		O2C2F6N3

Table A1. *Cont.*

No.	Structural Formula	Compound Abbreviation
18.		O2C2F6N4
19.		1CF2N2/O2CF2N2
20.		1CF2N3/O2CF2N3
21.		1CF2N4/O2CF2N4
22.		2CF4N2/O2C2F4N2
23.		2CF4N3/O2C2F4N3
24.		2CF4N4/O2C2F4N4

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

Appendix B

The views of the conformers. Orange color denotes carbon; yellow—fluorine; red—oxygen; blue—nitrogen; and gray—hydrogen.

Compound	Conformer	
	a	b
C3F6N2		
O2C2F6N2		
O2C2F6N3		
O2C2F6N4		
O3C3F9N3		
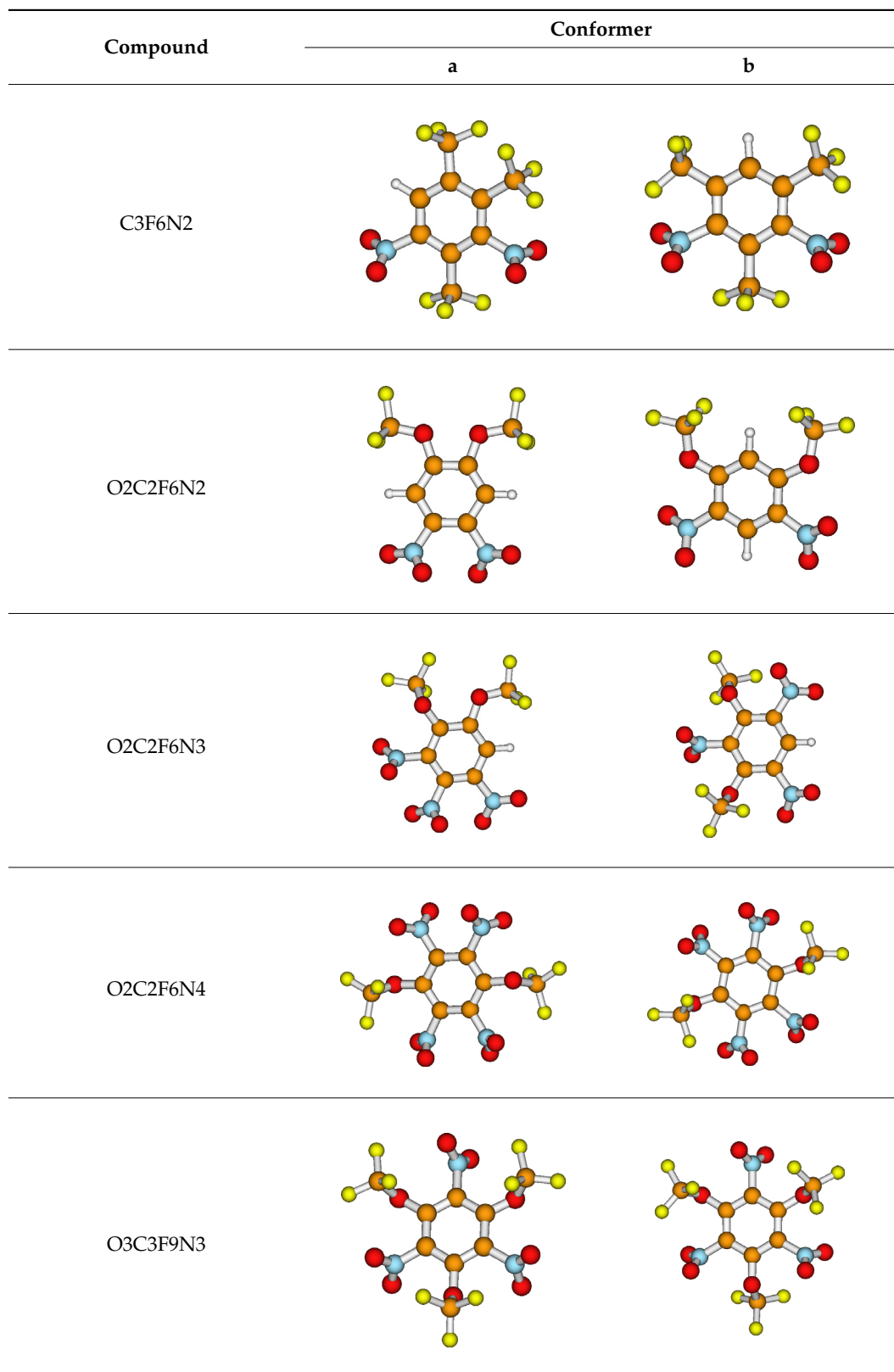
Appendix C

A brief exploration of the potential synthetic accessibility of proposed structures.

A typical approach for constructing the CF$_3$ group is to turn the carboxylic acid COOH itself into the trifluoromethyl group. Currently, various well-explored methods exist for introducing CF$_3$ functionality. Carboxylic acids can be converted to trifluoromethyl

groups by treatment with sulfur tetrafluoride SF_4. Another effective synthetic pathway to trifluoromethyl aromatics involves the reaction of aryl iodides with trifluoromethyl copper ($CuCF_3$). The starting aryl carboxylic acids typically could be accessed from an appropriate CH_3 functionality by oxidation (for example, by using CrO_3/H_2SO_4). Fluoro-substituted alkoxy derivatives or their cyclic analogs could be accessed by standard nitration methods.

Another synthetic possibility could be the alkylation of the aryl-OH functional group by using an ICF3/basic agent or, analogously, by di-iodo derivatives for cyclic analogs: $I(CF_2)nI$. A reagent such as the Ruppert–Prakash reagent (trifluoromethyl)trimethylsilane, CF_3TMS) represents an alternative to trifluoromethylation of an appropriate phenol or catechol to OCF_3 functionalities. More details you will find in [90,91].

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