Research article

Design of new energetic materials based on derivatives of 1,3,5-trinitrobenzenes: A theoretical and computational prediction of detonation properties, blast impulse and combustion parameters

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ABSTRACT

This paper reports the design of some of the new ionic based high energy materials derived from the anion of picric acid (2,4,6-trinitrobenzene-1-ol), styphnic acid (2,4,6-trinitrobenzene-1,3-diol) and 2,4,6-trinitrophloroglucinol (2,4,6-trinitrobenzene-1,3,5-triol) and cation derived from the key synthons molecules such as 5-trifluoromethyl-1H-tetrazole, 5-dinitromethyl-1H-tetrazole and 5-azido-1H-tetrazole-1-carbonitrile. The detonation properties of these newly proposed compounds are predicted by using software such as EXPLO-5, EXTEC and LOTUSES and Keshvarz method. Moreover, other explosive parameters such as density, gurney velocity, and oxygen balance and decomposition products of the newly designed molecules have also been predicted and reported for the first time in this manuscript. The predicted detonation parameters of some of the newly designed compounds exhibit higher velocity of detonation (VOD) and detonation pressure in comparison to other well-known benchmark explosives such as 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazinane (RDX). Further, the peak over pressure (POP) and the blast impulse parameters of the newly designed compounds are predicted by using Shock physics explicit eulerian dynamics (SPEED) software, and the same is reported for the first time in this work. The work also reports the theoretical prediction of impact and electrostatic spark sensitivity parameters for the newly designed molecules. The ballistic performance parameters of the newly designed ionic energetic materials are also predicted by incorporating them into model composite rocket propellant formulations. The predicted ballistic parameters indicate that the proposed materials may find an application in the propellant formulation as an energetic additive.

1. Introduction

Research and development programmes are on all over the world to develop energetic materials based on ionic compounds. The latest trend in the area of energetic materials is to develop insensitive energetic materials with higher performance and longer shelf life. There have been several research publications on ionic solid based explosives (which can be easily synthesised) reported in the literature [1, 2, 3, 4, 5, 6]. The advantages of ionic solid based energetic materials are that they are insensitive in nature with higher thermal stability and possess low vapour pressure coupled with higher performance. It has been reported [7, 8] that TKX-50 (ionic compound) has higher performance properties than the benchmark explosive viz., 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). Ionic liquids [9] also have drawn considerable attention due to their unique properties such as high stability, shelf life, high ionic conductivity, low toxicity and structural diversity.

In view of these inherent advantages associated with the ionic based explosives, this work reports the design of some of the ionic explosives based on the picric acid (PA), styphnic acid (SA) and 2,4,6-trinitrophloroglucinol (TNPG). The proposed ionic solids may be synthesised by the reaction of PA/SA/TNPG with key synthons such as 5-trifluoromethyl-1H-tetrazole 1, 5-dinitromethyl-1H-tetrazole 5 and 5-azido-1H-tetrazole-1-carbonitrile 9 (Figure 1). It is reported that the introduction of picryl functional moiety in the compound, while designing the energetic materials, decreases the sensitivity of the material and also increases the stability of overall compound [10, 11].

Picric acid is a known explosive which is acidic in nature. Picric acid contains three powerful oxidizing groups and therefore it can be used to produce sensitive compounds which can decompose and explode at
and miscellaneous expenses including those on raw materials required.

Styphnic acid is more expensive and more powerful than picric acid. It is a strong dibasic acid and forms notably more violent explosives than picrates. Salts of styphnic acid have been reported as potential explosives

2,4,6-Trinitrophloroglucinol possesses stronger acidity than phenol as it has three nitro groups and three phenolic hydroxyl groups. It can serve as an explosive, as an important intermediary in the synthesis of several other high performance explosives and also as an ingredient for explosive composition. The aromatic compounds formed using TNPG are said to be more stable and less sensitive to impact than the parent compounds. The products of TNPG are ecologically clean as they don’t contain any toxic-heavy metals [2, 14, 15]. The following key synthons

Tetrazoles are nitrogen rich five-membered azoles with numerous contiguous N-N bonds, which give rise to higher heat of formation and powerful energy release on explosion. The higher nitrogen content in the tetrazoles meet the green chemistry concept as they release nitrogen gas as the main decomposition product. The tetrazole derivative 5-trifluoromethyl-1H-tetrazole 1 was reported by Norris in the year 1962 at the Naval Ordinance test station, California, 5-dinitromethyl-1H-tetrazole 5 by Einberg in the year 1963 at Pittman-Dunn institute, USA and 5-azido-1H-tetrazole-1-carbonitrile 9 by Marsh in the year 1972 by E I du Pont Nemours and Company [16, 17].

The introduction of picric acid, styphnic acid and 2,4,6-trinitrophloroglucinol functional moiety to the tetrazoles decreases the strong electron withdrawing power of the picryl group. Insertion of picryl group into an organic compound leads to the increase in density. Intramolecular hydrogen bonding and π-π stacking are established in the designed compounds. The formation of hydrogen bond between the two groups increases the stability of the molecule. Hence, the compounds formed from TNPG are expected to possess high density and melting point [18].

Fluorine containing energetic salts such as 3-N-(2-pentafluorosulfanylacetamide)-4-(1H-tetrazo-5-yl)-1,2,5-oxadiazole and 5-N-(2-pentafluorosulfanylacetamide)1H-tetrazole were synthesized and their energetic properties were studied. Fluorine is electron withdrawing like other fluorinated compounds. The higher electron withdrawing ability of CF$_3$ (r (CF$_3$ = 0.54)) gives larger dipole moment to organic molecules resulting in higher chemical and thermal stability [40, 41].

Generally, the measurement of peak over pressures and blast impulse measurements involve the use of expensive gauges, skilled manpower and miscellaneous expenses including those on raw materials required for the preparation of explosive compositions. In order to save all these costs, it is essential to carry out the performance prediction of energetic materials prior to their synthesis and their compositions for the predicted blast and peak over pressure and TNT equivalence data.

In view of the above observations and in continuation of our work in the area of energetic materials [19], a systematic theoretical performance study was undertaken to design some of the new ionic molecules derived from picric acid, styphnic acid and TNPG (The structures of the newly proposed ionic explosive compounds are given in Figure 2). The main reason for choosing key synthons such as 5-trifluoromethyl-1H-tetrazole, 5-dinitromethyl-1H-tetrazole and 5-azido-1H–tetrazole-1-carbonitrile is the expected high positive heat of formation of the tetrazole ring/azide functional group. The presence of functional groups such as –CF$_3$ and gem dinitro group is expected to increase the density of the compounds. The authors also chose these key synthons due to their predicted positive heat of formation and higher density.

The codes such as Linear Output Thermodynamic User Friendly Software for Energetic Systems (LOTUSES) [20], EXPLO-5 [21] and EXTEC [22] and Keshavarz method [23] were used in the present study to predict theoretically the performance parameters of the newly designed energetic materials 1-12. The software used were validated using the reported experimental performance parameters of conventional energetic materials such as TNT, RDX, HMX and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). In this study, various parameters such as density, heat of formation, oxygen balance, detonation velocity, detonation pressure, impact sensitivity, gurney velocity, power index and decomposed detonation products were also computed, and the comparative analysis of the predicted data was also carried out.

This paper presents the theoretical blast impulse and peak over pressure (POP) of the newly designed molecules using SPEED software [22]. The paper also presents the performance prediction of ballistic parameters of the newly designed molecules for the first time. The newly designed ionic compounds were theoretically incorporated in the composite propellant formulation model and the specific impulse, characteristic velocity and density impulse were also computed [24] and are reported in this research paper.

2. Methods

The density of the proposed compounds was calculated on the basis of volume additivity method [25]. The velocity of detonation, detonation pressure were computed using advanced software such as LOTUSES [20], EXPLO-5 [21] and EXTEC [22] and Keshavarz method [23]. The heat of detonation was simulated using EXPLO-5 [22] and the explosive power was calculated using a standard method. The gurney velocity, heat of explosion and power index were computed using EXPLO-5 software [21]. The correlation propounded by Zohari et al. [26] was taken for calculating the values of impact sensitivity. Zeman method was used for predicting the electric spark sensitivity for the designed compounds [27].

Figure 1. Simple molecular structures of 1, 5, 9, picric acid, styphnic acid and 2,4,6-trinitrophloroglucinol.
The peak over pressure and blast impulse of the newly designed molecules were computed using SPEED software [22]. The method of Keshvarz and Zamani [23] was used to calculate VOD for fluorine-containing compounds. The ballistic performance parameters were theoretically computed by incorporating the proposed new compounds in model composite propellant formulation (Ammonium perchlorate (AP): Hydroxy terminated polybutadiene (HTPB) and newly designed molecule) using PRO PEP-3 [24] software programme.

3. Results and discussion

3.1. Estimation of density

The theoretical approach follows the detailed information of the crystal structure on the basis of inter and intra molecular forces while calculating density. It is very much advantageous because it considers bonding patterns such as hydrogen bonding or conjugation [28, 29].

Table 1. Explosive performance parameters predicted using EXPLO-5 software.

| Comp. | Molecular Formula | Molecular Weight | Density (g/cm³) | Heat of Formation (kcal/mol) | VOD (m/s) (EXPLO-5) | Detonation Pressure (kbar) | Heat of Detonation (kJ/kg) | Volume of Gases (dm³/kg) | Explosive Power (kJ/g.cm³/g × 10⁴) | Power Index (%) | TNT Equivalence | Gurney Velocity (m/s) |
|-------|------------------|------------------|----------------|--------------------------|----------------------|-----------------|------------------------|------------------------|-----------------------------|----------------|----------------|-------------------|
| TNT | C₆H₃N₃O₇ | 229 | 1.76 | -51.86 | 7426 | 234 | 5470 | 638 | 349 | 122 | 1.25 | 2712 |
| C₂H₂N₆O₄ | 174.09 | 1.97 | 123.95 | 8670 | 309 | 4677 | 752 | 352 | 123 | 1.26 | 3061 |
| 1 | C₂H₅N₉O₁₁ | 403.21 | 1.85 | 220.52 | 8518 | 352 | 5652 | 628 | 355 | 124 | 1.27 | 2824 |
| 2 | C₂H₅N₉O₁₂ | 419.21 | 1.86 | -156.55 | 8569 | 437 | 5947 | 591 | 351 | 122 | 1.25 | 3222 |
| 3 | C₂H₅N₉O₁₃ | 435.21 | 1.87 | 114.72 | 8918 | 360 | 5471 | 677 | 370 | 129 | 1.32 | 2974 |
| 4 | C₂N₈ | 136.10 | 1.94 | 251.10 | 8549 | 103 | 843 | 719 | 61 | 21 | 0.22 | 1969 |
| 5 | C₂H₃N₁₁O₇ | 365.22 | 1.82 | 328.52 | 8081 | 279 | 3663 | 662 | 242 | 84 | 0.87 | 2559 |
| 6 | C₂H₃N₁₁O₈ | 381.22 | 1.83 | 302.79 | 8247 | 297 | 3922 | 662 | 260 | 90 | 0.93 | 2688 |
| 7 | C₂H₃N₁₁O₉ | 397.22 | 1.84 | 241.58 | 8586 | 324 | 4305 | 661 | 285 | 99 | 1.02 | 2832 |

TNT: 2,4,6-Trinitrotoluene; RDX: 1,3,5-Trinitrohydroxy-1,3,5-triazine, HMX: 1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane, PA: Picric acid, SA: Styphnic acid, TNPG: 2,4,6-Trinitrophloroglucinol.
estimation of density can be achieved by several means such as (a) Group additivity method where the volume parameters of different kinds of groups or atoms are considered, (b) Average atom volume method and (c) High-level ab initio calculations [30]. Methods (a) and (b) render satisfactory results for estimation of density for neutral molecules and while method (c) can compute density theoretically for any large molecule but it is expensive and time consuming. The accurate prediction of the density for energetic ionic salts is more challenging and intriguing. However, the volume parameter method provides an accurate way to predict the density of complex ionic salts. Chavez et al. reported the density of tetrathonium based high energetic salts [25, 31, 32]. Accordingly, the density of the designed compounds is calculated and enumerated in Table 1. The calculated density of the designed compounds is found to be lesser than that of parent compounds. But the density of the compounds containing trinitrophloroglucinol is very close to the parent compounds. The predicted density of most of the compounds is above the benchmark compounds such as TNT and RDX (Table 1). The title compounds containing trinitrophloroglucinol is very close to the parent compounds. The predicted density of most of the compounds is above the benchmark compounds such as TNT and RDX (Table 1). The title compounds containing trinitrophloroglucinol is very close to the parent compounds. The predicted density of most of the compounds is above the benchmark compounds such as TNT and RDX (Table 1).

3.2. Heat of formation

Heat of formation is an essential factor to assess the energetic properties of explosives because the heat released on combustion or decomposition is essential to determine deflagration or detonation. Heat of formation is important for the prediction of detonation velocity and pressure [33]. The predicted heat of formation of the title compounds indicates that except compound 4 all others show positive heat of formation (0.20–328.52 kcal/mol). The predicted heat of formation of the key synths 5 and 9 are also found to be positive except compound 1. This is the main reason for the selection of these synths for designing the new ionic based energetic materials. The derived heat of formation is high for the parent compounds, and compound 10 has the highest heat of formation. The designed compounds containing trifluoromethyl groups possess negative values. All the carbonitrile based compounds possess a high positive heat of formation. The picrate salts have a high positive heat of formation than that of styphnic acid or trinitrophloroglucinol salts. The presence of tetroazole group may be responsible for the positive heat of formation [34]. The predicted heat of formation data is presented in Table 1.

3.3. Velocity of detonation and detonation pressure

Detonation velocity is one of the most important parameters in determining the explosives performance parameters. The rate of velocity at which the shock waves travel upon the initiation of explosive charge is considered the most critical parameter during the detonation phenomenon.

The predicted velocity of detonation (VOD) of most of the proposed compounds is higher than those of the VOD of TNT. A similar trend is seen or followed in case of the predicted detonation pressure for the proposed compounds. Most of the proposed compounds have shown a lower velocity of detonation compared to well-known benchmark explosives such as RDX and HMX (Table 1). The velocity of detonation of the order 8918 m/s was observed for title compound 8, which exceed the VOD of benchmark explosive compound such as RDX. Similarly, the title compound 8 exhibited higher detonation pressure (360 kbar) compared to the compounds proposed in this study. The higher detonation pressure of the title compound 8 indicates its ability to do work and determines that it possesses higher brisance. The velocity of detonation of the newly proposed compounds was predicted independently using EXPLO-5, EXTEC and LOTUSES and Keshavarz method, and the data were compared. In order to validate the predicted data, some of the well-known benchmark compounds such as TNT, RDX and HMX were also predicted in parallel, and the predicted data were compared with the experimentally reported velocity of detonation. Among all the four methods EXPLO-5 (Table 2) gave better theoretically predicted VOD than Keshavarz and LOTUSES software. The ionic salts derived through the introduction of picric acid moiety into 5-trifluoromethyl-1H-tetrazole, 5-dinitromethyl-1H-tetrazole and 5-azido-1H-tetrazole-1-carbonitrile showed a higher velocity of detonation in the range 8081–8587 m/s from EXPLO-5 data. A similar increasing trend in the velocity of detonation was observed in case of Keshavarz and LOTUSES methods. All the three methods (LOTUSES, EXTEC & EXPLO-5) used in the present study for the computer simulation of detonation properties have 5–10% uncertainty. The EXTEC method is reasonably well established and the software...
package is sold from Germany. It is globally accepted to be one of the best software to determine the detonation properties of theoretically designed and synthesized explosives. Explo-5, the computer program for the calculation of detonation parameters of an explosive is based on the chemical equilibrium and steady-state model of detonation. It is well established and internationally accepted methodology for the theoretical performance prediction of the detonation parameters. The LOTUSES programme originates from India and is not available for the international community as on date. The LOTUSES programme also considers the logic similar to that of the BKW programme which is internationally available. The key requirement in the design of the new energetic materials based on ionic solids emerges from the fact that, the designed ionic solid energetic compounds are anticipated to possess higher thermal stability and higher shelf life. The predicted detonation parameters using LOTUSES and Keshvarj method appears to give higher detonation parameters in comparison to EXPLO-5.

### 3.4. Heat of detonation

The heat of detonation is a quantity used to assess a newly designed candidate’s velocity of detonation. It determines the energy content of the proposed ionic explosives. The heat of detonation indicates the energy available within the compound to do mechanical work and has been used to estimate potential damage to the target. It can be defined as the negative of the enthalpy change of the detonation reaction. The calculated heat of detonation of most of the newly designed compounds is on par with that of TNT, or in some cases, marginally better. The title compound 4 shows the heat of detonation in the order of 5858 kJ/kg (Table 1) which is on par with the bench mark explosives such as RDX and HMX. The ionic compounds derived from key synthon viz., 5-azido-1H-tetrazole-1-carbonitrile give the lowest predicted heats of detonation of the order 3663–4305 kJ/kg (Table 1).

### 3.5. Volume of gases

The volume of gases produced during the detonation of the newly designed compounds provides information on the amount of work done by the energetic material. The calculated volume of gases of most of the newly designed compounds indicates that the volume of gases liberated (628–681 dm³/kg) after the decomposition is on par with the benchmark explosive TNT (633 dm³/kg). The liberation of higher volume of gases was predicted for the title compound 5 (Table 1).

### 3.6. Explosive power

The predicted explosive power for the proposed new compounds indicates that the title compound 4 exhibits the highest explosive power among the newly designed compounds (371 kJ/g,cm³/g). The explosive power of title compound 4 is much higher than that of TNT. However, the explosive power of the newly designed compounds is lower than that of the bench mark explosive compounds such as RDX and HMX (Table 1). The compounds derived from key synthon viz., 5-azido-1H-tetrazole-1-carbonitrile show the lowest explosive power of the order 242–285 kJ/g,cm³/g. This may be attributed to the presence of azide group and the liberation of cooler gases upon detonation.

### 3.7. Power index

Explosive power is the product of heat of explosion Q, and the volume of gases liberated V. Power index is the value of explosive power of the energetic material divided by the value of explosive power of picric acid, multiplied by 100 [20,26]. From the values of power index listed in Table 1, the power index of most of the designed compounds is better than that of the standard compound viz., picric acid and also conventional benchmark energetic material TNT. The title compounds 9-12 showed a lower power index than standard compound (picric acid).

### 3.8. TNT equivalence

The terminology “TNT Equivalence” is used by the energetic materials’ community and also related industries to compare the effects of the output of a given explosive (in this case designed compounds) to that of TNT. This is done for reasons related to technical design related reasons in scaling calculations pertaining to the prediction of blast waves, craters and structural response. It is also used as a basis for STEC pamphlet regulations for controlling the shipping, handling and storage of explosive materials as well as for siting and design of explosive facilities within the country. In this work, the calculated TNT equivalence of the title compounds shows that compounds 1-8 are more powerful than the benchmark compound viz., TNT. However, the title compounds 9-12 show a lower explosive performance than benchmark TNT (Table 1).

### 3.9. Gurney velocity

Gurney velocity is calculated using the values of heat of formation and density [35]. The calculated values of gurney velocity for the designed compounds are produced in Table 1. The calculated Gurney velocity of the proposed compounds is much higher than that of the benchmark explosives such as TNT (2.29 km/s). The title compounds 5 (3.06 km/s) and 8 (2.97 km/s) show that, the predicted gurney velocity is on par with that of benchmark explosives such as HMX (3.09 km/s) and RDX (2.96 km/s) respectively.

### 3.10. Balancing explosion reaction process

To predict the detonation products on explosion, a set of rules was developed by Kistiakowsky and Wilson (K-W rules), which was modified later. Springall-Roberts’ further modified K-W rules and introduced two more conditions. Mohammed Keshavarz also gave a set of rules for balancing explosion reaction process [36]. The determined and simulated balanced explosive reaction is the same and given in the Table 3. From Table 3, it is inferred that the designed compounds are environmentally eco-friendly since they release a higher amount of nitrogen.

### 3.11. Oxygen balance (OB% or Ω)

The oxygen balance of the explosive material containing fluorine is calculated using the formula propounded by Muthurajan and Ghee [36].

The calculated and LOTUSES simulated oxygen balance for the designed compounds are nearly the same, and the simulated values are shown in Table 3. All the designed and parent compounds possess negative oxygen balance. Compounds 1 and 2, which are devoid of oxygen, possess the highest negative oxygen balance. Compound 5, which has only two carbons and four oxygen’s, possesses the highest oxygen balance [19] (Table 3). In view of this observation these compounds, when they are used in composition and oxygen rich compounds such as ammonium perchlorate or ammonium dinitramide, need to be used in order to improve the oxygen balance.

### 3.12. Explosive reaction, and volume of gases

From Table 3, it is inferred that the percentage composition of nitrogen and oxygen is greater than that of carbon for all the designed compounds. The title compounds 1-4 contain fluorine in its elemental composition. These compounds may find application as an energetic additive for propellant formulations. The title compound 9 might find application in the field of gas generator.

### 3.13. Prediction of the volume of explosion products

The volume of gas generated immediately after detonation was calculated using the software EXPLO-5 [21]. The volume of gas products for the newly designed compounds is enumerated in Table 3. From that it
is inferred that the cyano compounds release the largest volume of gases in litres for one kg of the energetic materials at 15 °C.

### 3.14. Physical stability and sensitivity

Explosive sensitiveness is the measure of an explosive's ability to propagate detonation across an air gap, and it depends upon the condition of heating and the mode of propagation of reaction [36]. Here, the impact sensitivity and electric spark sensitivity were taken into consideration to evaluate the physical stability and sensitivity of the designed compounds. The hydrogen bonds are very effective in lowering the impact and friction sensitivities of energetic salts. Tetrazole rings and benzene rings form π-π stacking interaction, and they have a positive influence on sensitivity. Impact sensitivity is the phenomenon in which the hot spots in energetic materials contribute to initiation by external stimuli [27]. If the impact sensitivity value is less than 25, it is said to be highly sensitive. If the value is between 25 to 40, it is sensitive. If the value is greater than 40 it is insensitive. The presence of nitro groups in tetryzole rings in compounds 5-8 has a higher predicted impact sensitivity. Electric spark (ES) sensitivity plays a vital role in the safety of the designed molecules. Generally, if the predicted or experimental value of ES sensitivity is more, then the sensitivity is low. Compounds 5-8 possess high values of electric spark sensitivity, and therefore they have low sensitivity. The sensitivity of compound 9 is high whereas, incorporation of picric acid, styphnic acid and 2,4,6-trinitrophloroglucinol reduces the sensitivity (Table 3). It is to be noted that most of the available predictive methods are based on the RDAD instrument. It is reported the electric spark sensitivity of some cyclic and acyclic nitramines based on ESZ KTTV method gave more reliable results than RDAD instruments [37, 38].

### 3.15. Calculated percentage composition of elements

The percentage composition of elements is very much important to determine the explosive nature of a compound. If a compound contains less percentage of carbon and hydrogen than that of nitrogen and oxygen, the compound would possess high detonation parameters, as it would have high oxygen for oxidation in the form of nitro group. The explosive materials undergo decomposition to produce energy by the process of oxidation [17]. The computed elemental composition of the designed molecules is given in Table 4.

### 3.16. Prediction of peak over pressure and blast impulse

A numerical simulation of the newly designed molecules was carried out using SPEED software [22]. In this modelling study, an explosive charge quantity of 2 kg was considered for the prediction of blast peak over pressure and blast impulse. Some of the selected compounds such as 1, 2, 3, 5, 6, 8, 9, 10 and 12 were considered for modelling. It is clear from the Table 5 that the blast peak over pressure and blast impulse increase with a decrease in the distance. Compounds derived from key synthons 5-trifluoromethyl-1H-tetrazole showed the blast peak over pressure and blast impulse on par with benchmark explosive viz., HMX. However, the compounds derived from synthons viz., 5-dinitromethyl-1H-tetrazole and 5-azido-1H–tetrazole-1-carbonitrile showed blast peak over pressure and blast impulse on par with benchmark compound TNT. The peak over pressure and blast impulse computed using SPEED software are depicted in Table 5. The predicted data have also been depicted in the form of Figures 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, and 22 to by drawing graphs on peak over pressure Vs time and blast impulse Vs time. The predicted blast POP Vs

### Table 3. Explosive reaction, Volume of gases, Oxygen balance and Sensitivity parameters.

| Comp. | Empirical Formula | Balanced explosive reaction | Volume of gas products (dm³/kg) | Oxygen Balance (%) | Impact Sensitivity (cm) | Electrostatic Spark Sensitivity (J) |
|-------|------------------|-----------------------------|---------------------------------|--------------------|--------------------------|-----------------------------------|
| 1     | C₂H₅N₅O₄F₃      | HF + 2N₂ + 2C + 1F₂         | 568                             | -52.14             | 24.91                    | 12.29                             |
| 2     | C₂H₅N₅O₆F₃      | 7CO + 3HF + 0.5H₂ + 3.5N₂ + 1C | 636                             | -47.93             | 45.71                    | 9.038                             |
| 3     | C₂H₅N₅O₆F₃      | 8CO + 3HF + 0.5H₂ + 3.5N₂   | 628                             | -41.75             | 41.75                    | 9.108                             |
| 4     | C₂H₅N₉O₆F₃      | 1CO₂ + 7CO + 3HF + 0.5H₂ + 3.5N₂ | 634                             | -36.07             | 38.41                    | 9.322                             |
| 5     | C₂H₅N₉O₆F₃      | 1CO₂ + 1CO + 1H₂O + 3N₂    | 752                             | -99.19             | 108.2                    | 10.61                             |
| 6     | C₂H₅N₉O₁₁       | 1CO₂ + 7CO + 2H₂O + 0.5H₂ + 4.5N₂ | 681                             | -29.76             | 81.66                    | 10.86                             |
| 7     | C₂H₅N₉O₁₂       | 2CO₂ + 6CO + 2H₂O + 0.5H₂ + 4.5N₂ | 678                             | -24.80             | 73.52                    | 11.24                             |
| 8     | C₂H₅N₉O₁₃       | 3CO₂ + 6CO + 2H₂O + 0.5H₂ + 4.5N₂ | 677                             | -20.21             | 66.71                    | 11.67                             |
| 9     | C₈N₈         | 4N₂ + 2C                  | 719                             | -47.92             | 56.67                    | 3.134                             |
| 10    | C₂H₅N₉O₁₂     | 7CO + 0.5H₂ + 5.5N₂ + 1C  | 662                             | -45.99             | 62.30                    | 7.729                             |
| 11    | C₂H₅N₉O₁₃     | 8CO + 1.5H₂ + 5.5N₂       | 662                             | -39.87             | 56.14                    | 7.963                             |
| 12    | C₂H₅N₉O₁₃     | 8CO + 1H₂O + 0.5H₂ + 5.5N₂ | 661                             | -34.23             | 51.01                    | 8.305                             |

### Table 4. Percentage composition of elements.

| Compound | Empirical Formula | Molecular Weight | % of H | % of C | % of N | % of O | % of F |
|----------|------------------|------------------|--------|--------|--------|--------|--------|
| 1        | C₂H₅N₅O₄F₃      | 138.07           | 0.73   | 17.39  | 40.58  | -      | 41.28  |
| 2        | C₂H₅N₅O₆F₃      | 367.18           | 1.09   | 26.16  | 26.70  | 30.50  | 15.52  |
| 3        | C₂H₅N₅O₆F₃      | 383.18           | 1.05   | 25.07  | 25.59  | 33.40  | 14.87  |
| 4        | C₂H₅N₅O₆F₃      | 399.18           | 1.01   | 24.07  | 24.56  | 36.07  | 14.27  |
| 5        | C₂H₅N₅O₄        | 174.09           | 1.15   | 13.79  | 48.28  | 36.76  | -      |
| 6        | C₂H₅N₉O₆        | 403.21           | 1.24   | 23.83  | 31.27  | 43.64  | -      |
| 7        | C₂H₅N₉O₆        | 419.21           | 1.20   | 22.92  | 30.07  | 45.79  | -      |
| 8        | C₂H₅N₉O₆        | 435.21           | 1.15   | 22.07  | 28.97  | 47.79  | -      |
| 9        | C₂N₂            | 136.10           | -      | 17.65  | 82.35  | -      | -      |
| 10       | C₂H₅N₉O₂        | 365.22           | 0.82   | 26.30  | 42.19  | 30.66  | -      |
| 11       | C₂H₅N₉O₂        | 381.22           | 0.79   | 25.20  | 40.42  | 33.57  | -      |
| 12       | C₂H₅N₉O₂        | 397.22           | 0.76   | 24.19  | 38.79  | 36.25  | -      |
distance and blast impulse Vs distance are also depicted in Figures 23 and 24.

The availability of the blast and peak over pressure data obtained from high speed computational thermochemical codes enable the explosive engineers/technologists and scientists to optimize building layouts and blast walls surrounding the storage facility. This will further help in protecting the civilian and military infrastructure surrounding the storage sites in case of accidental or unintended initiation of the weapon system. The proposed constructed buildings must have sufficient ductility and redundancy to withstand or prevent the progressive collapse of the blast wave in accordance with the safety distance proposed in the storage & transport of explosives committee (STEC) pamphlet guidelines. The suitable internal lay out structure of the building must be such that it should allow the escape of hot gases generated after internal explosion prevents the channelling effect due to successive shock wave generation and reflection. The explosion of the designed molecules may result in the sudden and rapid release of a high amount of energy, whereas metallized explosives of the designed explosive molecules and their composition may undergo a violent explosion resulting in the formation of hot gases and create a multilayer of

| Compound | Density (g/cm³) | VOD (m/s) | Distance from Charge | Blast POP (bar) | Blast Impulse (bar. ms) |
|----------|----------------|-----------|---------------------|-----------------|------------------------|
|          |                |           | 2                   | 3               | 4                      | 5                      |
|          |                |           | 2                   | 3               | 4                      | 5                      |
| TNT      | 1.65           | 6700      | 3.51                | 1.37            | 0.72                   | 0.45                   | 0.95                  | 0.67                  | 0.5                   | 0.38                   |
| HMX      | 1.91           | 9150      | 4.03                | 1.52            | 0.82                   | 0.53                   | 1.24                  | 0.95                  | 0.75                  | 0.62                   |
| 1        | 2.07           | 9426      | 4.8                 | 1.76            | 0.94                   | 0.6                    | 1.4                   | 1.06                  | 0.84                  | 0.69                   |
| 2        | 1.88           | 7820      | 4.05                | 1.52            | 0.82                   | 0.53                   | 1.24                  | 0.94                  | 0.74                  | 0.61                   |
| 3        | 1.93           | 8070      | 4.06                | 1.53            | 0.82                   | 0.53                   | 1.24                  | 0.94                  | 0.75                  | 0.61                   |
| 5        | 1.97           | 9576      | 3.63                | 1.4             | 0.76                   | 0.49                   | 1.16                  | 0.88                  | 0.7                   | 0.57                   |
| 6        | 1.85           | 8289      | 3.55                | 1.35            | 0.74                   | 0.48                   | 1.15                  | 0.87                  | 0.68                  | 0.56                   |
| 8        | 1.87           | 8748      | 3.67                | 1.43            | 0.76                   | 0.5                    | 1.17                  | 0.89                  | 0.7                   | 0.58                   |
| 9        | 1.94           | 8714      | 3.66                | 1.41            | 0.76                   | 0.5                    | 1.17                  | 0.89                  | 0.7                   | 0.58                   |
| 10       | 1.82           | 8079      | 3.53                | 1.65            | 0.74                   | 0.48                   | 1.15                  | 0.86                  | 0.68                  | 0.55                   |
| 12       | 1.85           | 8632      | 3.58                | 1.38            | 0.75                   | 0.41                   | 1.16                  | 0.88                  | 0.69                  | 0.57                   |

Table 5. Predicted blast impulse and peak over pressure for some of the selected newly designed compounds.

Figure 3. The graph of peak over pressure Vs time for compound 1.

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Figure 4. The graph of blast impulse Vs time for compound 1.

Figure 5. The graph of peak over pressure Vs time for compound 2.
Figure 6. The graph of blast impulse Vs time for compound 2.

Figure 7. The graph of peak over pressure Vs time for compound 3.
compressed air and shock wave expansion of the hot gases from the epicentre, creating a layer of compressed air and shock wave. The influence of the shock wave reflections on the pressure was also analysed. The quantity of the explosives detonated is directly related to the magnitude of the explosion. The energy equivalence of the newly designed molecules is compared with the conventional energetic material 2,4,6-trinitrotoluene (TNT). The TNT equivalence (Table 1) of the newly designed molecules can be used to evaluate the explosive strength.

The shape of the explosives charge plays a pivotal role in defining the shock front, which is very important in the analysis of close-range explosion processes. The most commonly used explosive charge by most of
the researchers are that of spherical charge [39]. In the current study also, the spherical charge of two kilograms was used for an analysis of the blast impulse and peak over pressure of the designed molecules.

In case of spherical charges, generally, the shock waves generated after the explosion expand radially in the air from the detonation point. It is also very much essential to have previous knowledge about the shock wave behaviour to evaluate blast loading on the surrounding civilian/military infrastructure. During the speed analysis of the shock waves the important properties considered are the arrival time of the shock wave, the incidental pressure and the duration time of the positive phase.

Figure 10. The graph of blast impulse Vs time for compound 5.

Figure 11. The graph of peak over pressure Vs time for compound 6.
Figure 12. The graph of blast impulse Vs time for compound 6.

Figure 13. The graph of peak over pressure Vs time for compound 8.
3.17. Prediction of ballistic performance parameters of the proposed compounds

The predicted ballistic performance data are presented in Table 6. It is clear from the Table 6 that most of the compounds show the ballistic performance parameters on par with RDX and HMX, and better than TNT. Surprisingly, the identified key synthon viz., 5-trifluoromethyl-1H-tetrazole gives better specific impulse (268.5 s) compared to other compounds and controls propellant formulation studied in this work. The predicted characteristic velocity also indicates that the title compound 1 performs better than the other compounds studied.
Figure 16. The graph of blast impulse Vs time for compound 9.

Figure 17. The graph of peak overpressure Vs time for compound 10.
Figure 18. The graph of blast impulse Vs time for compound 10.

Figure 19. The graph of peak over pressure Vs time for compound 12.
Figure 20. The graph of blast impulse Vs time for compound 12.

Figure 21. The graph of peak over pressure Vs time for HMX.
4. Proposed synthesis routes for the newly designed ionic explosives

To illustrate the rationality of the designed molecules, their possible paths of synthesis are suggested in Scheme 1. The proposed compounds can be easily synthesized by the reaction of picric acid, styphnic acid and 2,4,6-trinitrophloroglucinol with key synthons such as 5-trifluoromethyl-1H-tetrazole, 5-dinitromethyl-1H-tetrazole and 5-azido-1H-tetrazole-1-carbonitrile in a suitable solvent such as methanol or acetonitrile. The reaction should be stirred using a mechanical stirrer for 5–6 h, and the solvent and vacuum should be removed. Ultimately, one may obtain the desired newly designed energetic materials.
The major requirement of Navies all over the world is that of insensitive munitions since the storage space in the dockyards and onboard of ships is limited. The new energetic materials designed must meet the criteria of insensitive munitions aspects. The anticipated cost of the newly designed compounds is expected to be slightly higher than that of the conventionally available or currently used energetic materials in services. As a part of the search towards newer energetic materials, the cost of the material should not matter much in the initial level. If once the potential of the candidate energetic molecule is ascertained then the cost issues also needs attention.

Current explosive research is also focused on developing enhanced blast warheads using explosive formulations tailored to create sustained blast and thermal effects. Enhanced blast explosives are fuel rich compositions capable of producing high impulse blast and thermal outputs. These explosives, generally classified as ‘Non-ideal explosives’, are optimized not for high blast pressure or fragmentation.

![Blast Impulse (bar.ms) Vs Distance (m)](image)

**Figure 24.** Blast impulse Vs distance for compounds 1, 2, 3, 5, 6, 8, 9, 10 and 12.

### Table 6. Ballistic performance parameters of the newly designed compounds into model composite propellant formulations.

| S. No. | Molecular formula | Density composition (g/cm³) | Heat of Formation (cal/g) | Molecular Weight (g/mol) | Flame Temperature | Impulse specific (s) | C* (m/s) | Density Impulse |
|--------|-------------------|------------------------------|---------------------------|--------------------------|------------------|----------------------|-----------|----------------|
| TNT    | C₂H₅N₃O₆         | 1.737                        | -366                      | 24.448                   | 3168             | 261.6               | 1566      | 454            |
| RDX    | C₃H₆N₆O₆         | 1.754                        | -368                      | 24.775                   | 3300             | 264.7               | 1586      | 464            |
| HMX    | C₄H₈N₈O₈         | 1.761                        | -368                      | 24.775                   | 3300             | 264.7               | 1586      | 466            |
| CL-20  | C₅N₁₂H₁₀O₁₂      | 1.773                        | -354                      | 25.13                    | 3342             | 264.7               | 1586      | 469            |
| PA     | C₂H₅N₉O₉         | 1.748                        | -397                      | 24.94                    | 3231             | 261.4               | 1565      | 457            |
| SA     | C₃H₃N₉O₉         | 1.754                        | -420                      | 23.85                    | 2410             | 239.9               | 1415      | 421            |
| TNPG   | C₂H₅N₉O₈         | 1.784                        | -434                      | 23.851                   | 2404             | 239.1               | 1410      | 427            |
| 1      | C₂H₃N₆F₃         | 1.775                        | -314                      | 24.943                   | 3333             | 268.5               | 1690      | 477            |
| 2      | C₈H₄N₇O₇F₃      | 1.759                        | -369                      | 24.931                   | 3258             | 264                  | 1581      | 464            |
| 3      | C₈H₄N₇O₈F₃      | 1.764                        | -375                      | 25.008                   | 3275             | 264.2               | 1582      | 466            |
| 4      | C₈H₄N₉O₉F₃      | 1.764                        | -380                      | 25.081                   | 3290             | 264.3               | 1583      | 466            |
| 5      | C₈H₄N₉O₆         | 1.764                        | -360                      | 25.155                   | 3309             | 263.2               | 1576      | 464            |
| 6      | C₈H₄N₉O₁₁        | 1.757                        | -384                      | 25.036                   | 3262             | 262                  | 1569      | 460            |
| 7      | C₂H₅N₈O₆         | 1.761                        | -388                      | 25.108                   | 3277             | 262.2               | 1570      | 462            |
| 8      | C₂H₅N₈O₁₃        | 1.764                        | -393                      | 25.175                   | 3290             | 262.3               | 1571      | 463            |
| 9      | C₂N₈           | 1.749                        | -256                      | 24.752                   | 3158             | 259.1               | 1555      | 453            |
| 10     | C₈H₄N₁₂O₇       | 1.754                        | -348                      | 24.868                   | 3205             | 261                  | 1563      | 458            |
| 11     | C₈H₄N₁₂O₈       | 1.759                        | -362                      | 24.959                   | 3217             | 261                  | 1562      | 459            |
| 12     | C₂H₅N₉O₉        | 1.764                        | -360                      | 25.027                   | 3247             | 261.8               | 1567      | 462            |
| Reference | 1.765                   | -434                      | 25.599                   | 3388             | 263.8               | 1579      | 466            |

Control sample: Ammonium perchlorate 68%, Al 18% Dioctyl adipate 3%, Hydroxy terminated polybutadiene 11%.

Test sample compound 1 to 12 (10%) + Ammonium perchlorate 58%, Al 18% Dioctyl adipate 3%, Hydroxy terminated polybutadiene 11%.
The sustained effects are achieved due to the post detonation combustion of excess metal fuel with the detonation products and oxygen in air. The shock waves generated from the explosion of energetic materials have both defense and civilian applications. The unintended explosion of energetic materials may cause severe risk to the civil infrastructure and pose grave threats to the users of weapon systems filled with energetic materials. The blast generated upon the explosion of the explosive compositions is a nonlinear phenomenon and warrants several theoretical and experimental studies. With the advancements in the science and technology of information science, several researchers and scientists all over the world are making use of the high speed computational facilities to predict the blast phenomenon of weapon systems filled with energetic materials in order to save the time, energy and resources involved in carrying out the blast experiments.

Research and development work is also on in many laboratories all over the world to develop potential energetic materials that can be used as an energetic additive for the rocket propellant formulations. The essential requirements of these ingredients are that they should be insensitive in nature with high specific impulse and also exhibit lower vapor pressure, since the shelf life of the propellant formulation increases tremendously.

5. Conclusions

The synthesis and production of explosive compounds involve a tedious process with regard to safety aspects for the individuals who deal with it. The work also involves the use of various resources for the experimental work during the synthesis of the proposed molecules. The work reported in the current manuscript establishes that one could go ahead with the synthesis of these salts for their application as an energetic additive in explosives and propellant formulations. The proposed compounds are expected to be insensitive in nature with a higher thermal stability and a lower vapour pressure. Various software codes such as EXPLO-5, EXTEC and LOTUSES and Keshavarz method were used in this study. Among the software codes used, EXPLO-5 gave data with better accuracy than other software did. The manuscript also proposed the possible synthesis method for the synthesis of the newly designed compounds. The predicted peak over pressure and blast impulse for the compounds derived from key synthons viz., 5-trifluoromethyl-1H-tetrazole are on par with benchmark explosives compound viz., HMX. The peak over pressure and the blast impulse increased with the decrease in the distance. The incorporation of newly designed compounds in model composite rocket propellant formulations showed that these materials could find potential application in rocket propellants as energetic additives. The data reported in this work will be useful for researchers, technologists and explosives engineers for developing novel ionic based energetic materials in futuristic applications. The futuristic requirements of most sought after and desired insensitive munition characteristic properties of the explosives compositions may be met through the class of compounds reported in this work. The data reported in this work will be useful to design the energetic materials compositions with higher TNT equivalence and higher specific impulse.

Declarations

Author contribution statement

Arumugam Thangamani: Conceived and designed the experiments. K.G. Balachandar: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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References

[1] J.R. Zhang, J.G. Zhang, 1-Amine-1,2,3-Trazolium salts with oxidizing anions: a new family of energetic materials with good performance, J. Mol. Struct. 1158 (2018) 88–95.

[2] X. Hu, T. Zhang, X. Qiao, L. Yang, Z. Zhang, Crystal structure and thermal decomposition of 5-aminitetrazole trinitrophloroglucinolate, Acta Physico-Chim. Sin. 24 (2006) 576–580.

[3] Z. Zhao, Z. Du, Z. Han, Y. Zhang, C. He, Nitrogen-rich energetic salts: both cations and anions contain tetrazole rings, J. Energetic Mater. 34 (2016) 183–196.

[4] X. Liu, Z. Su, W. Ji, S. Chen, Q. Wei, G. Xie, X. Yang, S. Gao, Structure, physicochemical properties, and density functional theory calculation of high-energy-density materials constructed with intermolecular interaction: nitro group charge determines sensitivity, J. Phys. Chem. C 118 (2014) 23487–23498.

[5] Y.H. Ren, W. Li, F.Q. Zhao, J.H. Yi, B. Yan, H.X. Ma, K.Z. Xu, J.R. Song, R.Z. Hu, Crystal structure and thermal behaviors for 3,5-dinitrobenzoic acid of 3,5-diamino-1,2,4-triazole, J. Anal. Appl. Pyrolysis 102 (2013) 89–96.

[6] P. He, J.G. Zhang, X. Yin, J.T. Wu, L. Wu, Z.N. Zhou, T.L. Zhang, Energetic salts based on tetrazole N-oxide, Chem. Eur. J. 22 (2016) 7670–7685.

[7] N. Fischer, D. Fischer, T.M. Klapotke, D.G. Piercy, J. Stierstorfer, Pushing the limits of energetic materials the synthesis and characterization dihydroxyammonium-5,5′-bistetrazole-1,1′-diolate, J. Mater. Chem. 22 (2012) 20418–20422.

[8] M. Li, H. Chen, X. Xiao, L. Yang, C. Peng, Y. Qin, T. Wang, W. Sun, C. Wang, Computational study of transition states for reaction path of energetic materials TKX-50, J. Energetic Mater. 37 (2019) 240–250.

[9] Q. Zhang, J.M. Shreeve, Energetic ionic liquids as explosives and propellant fuels: a new journey of ionic liquid chemistry, Chem. Rev. 114 (2014) 10527–10574.

[10] J. Akhavan, The Chemistry of Explosives, The Royal Society of Chemistry, United Kingdom, 2011.

[11] T.M. Klapotke, High Energy Density Materials, Springer-Verlag Berlin, Heidelberg, 2007.

[12] T.M. Klapotke, C.M. Sabate, 1,2,4-triazolium and tetrazolium picrate Salts. T.M. Klapotke, High Energy Density Materials, Springer-Verlag Berlin, Heidelberg, 2001, p. 116.

[13] J. Akhavan, The Chemistry of Explosives, The Royal Society of Chemistry, United Kingdom, 2011.

[14] T.L. Davis, Chemistry of Powder and Explosives, Angriff Press, Las Vegas, NV, USA, 1941.

[15] I. Wang, H. Chen, T. Zhang, J. Zhang, L. Yang, Synthesis, characterization, thermal and explosive properties of potassium salts of trinitrophloroglucinol, J. Hazard Mater. 147 (2007) 576–586.

[16] H. Chen, T. Zhang, Z. Zhang, Synthesis, characterization and properties of nitrogen-rich salts of trinitrophloroglucinol, J. Hazard Mater. 161 (2009) 1473–1477.

[17] P. Yin, J.M. Shreeve, Nitrogen rich azoles as high density energy materials: reviewing the energetic footprints of heterocycles, Adv. Heterocycl. Chem. 121 (2016) 89–131.

[18] G. Sphalinger, Recent Advances in High Nitrogen Energetic Materials, CEM 958 – Organic Chemistry Seminar, Michigan State University, USA, February 9 2011, p. 22.

[19] Q. Ma, G. Fan, L. Liao, J.L. Huang, Theoretical modeling of novel 5-cycliperylino-1,2,3,4-tetrazole (PAT) and 5,5′-stilphenylmino-1,2,3,4-tetrazole (SAT) derivatives: a new molecular design strategy of multi-nitrogen energetic materials by introducing intermolecular hydrogen bonds and π-π stacking interactions, Polycycl. Aromat. Compd. 37 (2017) 327–344.

[20] K.G. Balachandar, A. Thangamali, Synthesis, spectral, and computational studies of some energetic picrates, J. Mol. Struct. 1195 (2019) 378–386.

[21] H. Muthurajan, R. Sivabal, M.B. Talawar, S.N. Anitha, Computer simulation for prediction of performance and thermodynamic parameters of high energy materials, J. Hazard Mater. 112 (2004) 17–33.

[22] M. Suizasca, EXPLO-5: Computer Program for Calculation of Detonation Parameters, in: Proceeding of 32nd International Annual Conference of ICF, Karlsruhe, Germany, 2001, p. 116.

[23] SPEED (Shock physics explicit eulerian/lagrangian dynamics), 3.2.1, Numerics Software, Developed by NUMERICS Software GmbH-Mozarring 3-85238 Petershausen, Germany, 2019. E-mail: info@numerics-gmbh.de, https://www.numerics-gmbh.de.

[24] M.H. Keshavarz, A. Zamani, A simple and reliable method for predicting the detonation velocity of CHNOFCl and aluminized explosives, Cent. Eur. J. Energ. Mater. 12 (2015) 13–33.

[25] D. Cooper, PROPEP 3 Software Programme by 2012 MS Windows 7 for Free Distribution Expanded Data File (pecoded.Daf) for the PROPEP Program, 2012. https://www.nakka-rocketry.net/softw.html or https://www.ckolgover.com.

[26] C. Ye, J.M. Shreeve, Rapid and accurate estimation of densities of room-temperature ionic liquids and salts, J. Phys. Chem. A 111 (2007) 1456–1461.

[27] S. Zeman, M. Jungova, Sensitivity and performance of energetic materials, Propellants, Exptls. Pyrotech. 16 (2001) 426–451.

[28] J.R. Stine, Prediction of Crystal Densities of Organic Explosives by Group Additivity, Report LA-8920, Los Alamos National Laboratory, Los Alamos, New Mexico, USA, 1981.

[29] P.W. Cooper, Explosives Engineering, Wiley-VCH Verlag GmbH, Weinheim, Germany, 1996.

[30] X. Hu, T. Zhang, X. Qiao, J.H. Yi, B. Yan, H.X. Ma, K.Z. Xu, J.R. Song, R.Z. Hu, Crystal structure and thermal behaviors for 3,5-dinitrobenzoic acid of 3,5-diamino-1,2,4-triazole, J. Anal. Appl. Pyrolysis 102 (2013) 89–96.

[31] H. Martinez, The Role of Fluorine in Energetic Materials and its Impact on Long Duration Expanded Data File (pepcoded.Daf) for the PROPEP Program, 2012. https://www.nakka-rocketry.net/softw.html or https://www.ckolgover.com.

[32] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[33] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[34] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[35] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[36] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[37] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[38] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[39] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[40] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[41] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.

[42] H. Martinez, A. Zheng, W.R. Dolbier Jr., Energetic materials containing fluorine. Aromat. Compd. 37 (2017) 327–335.