



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-1,3,5-triol) and 2,4,6-trinitrophenol (2,4,6-trinitrobenzene-1,3,5-triol) and cation derived from the key synthon 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-tetra-nitro-1,3,5,7-tetraoctane (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-trinitrophenol (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

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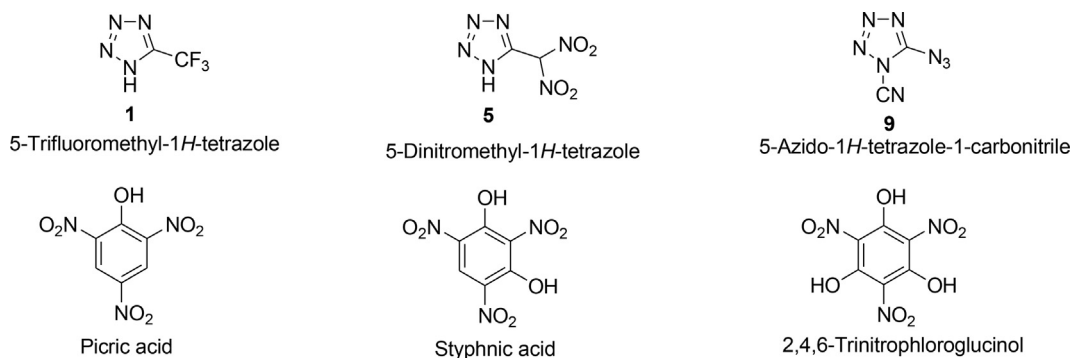


Figure 1. Simple molecular structures of 1, 5, 9, picric acid, styphnic acid and 2,4,6-trinitrophenol.

elevated temperatures. Explosive compounds synthesized using picric acid prove to be powerful, brisant and respond satisfactorily to the impulse of detonation. However, they are distinctively less sensitive to mechanical shock [12].

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 [13].

2,4,6-Trinitrophenol 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 1, 5 and 9 were selected for the design of new ionic based explosives with picric acid, styphnic acid and 2,4,6-trinitrophenol, resulting in the design of some of the new energetic materials such as 2, 3, 4, 6, 7, 8, 10, 11 and 12.

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 Ordnance 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-trinitrophenol 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 halogens but it is also capable of electron donation through its lone pair of electrons which leads to unexpected conformations of the resulting compounds. The higher electron withdrawing ability of CF_3 [σ (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 involves 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 $-\text{CF}_3$ 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].

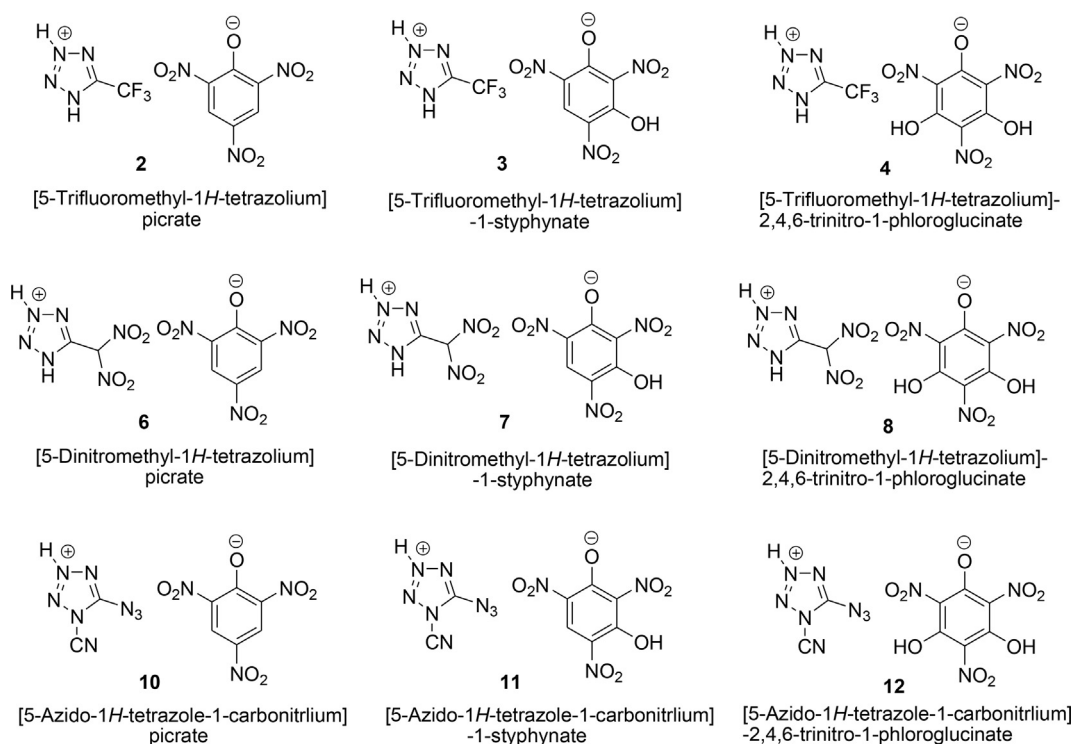


Figure 2. Simple molecular structures of the newly proposed ionic explosive compounds 2, 3, 4, 6, 7, 8, 10, 11, and 12.

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]. The

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

Comp.	Molecular Formula	Molecular Weight	Density (g/cm ³)	Heat of Formation (kcal/mol)	VOD (m/s) (EXPLO-5)	Detonation Pressure (kbar)	Heat of Detonation (kJ/kg)	Volume of Gases (dm ³ /kg)	Explosive Power (kJ/g.cm ³ /g × 10 ⁴)	Power Index (%)	TNT Equivalence	Gurney Velocity (m/s)
TNT	C ₇ H ₅ N ₃ O ₆	227	1.65	-19.25	6824	194	4427	633	280	98	1.00	2298
RDX	C ₃ H ₆ N ₆ O ₆	222	1.81	17	8801	336	5740	784	450	157	1.61	2963
HMX	C ₄ H ₈ N ₈ O ₈	296	1.91	20.07	9193	378	5700	763	435	152	1.55	3095
PA	C ₆ H ₃ N ₃ O ₇	229	1.76	-51.86	7426	234	4567	629	287	100	1.03	2500
SA	C ₆ H ₃ N ₃ O ₈	245	1.82	-111.61	8055	289	5470	638	349	122	1.25	2712
TNPG	C ₆ H ₃ N ₃ O ₉	261	1.89	-156.55	9569	437	5947	591	351	122	1.25	3222
1	C ₂ H ₁ N ₄ F ₃	138.07	1.95	-41.85	8069	298	5739	568	326	114	1.16	2717
2	C ₈ H ₄ N ₇ O ₇ F ₃	367.18	1.84	49.08	8144	322	5413	636	344	120	1.23	2742
3	C ₈ H ₄ N ₇ O ₈ F ₃	383.18	1.89	0.20	8387	352	5652	628	355	124	1.27	2824
4	C ₈ H ₄ N ₇ O ₉ F ₃	399.18	1.94	-22.88	8518	365	5858	634	371	129	1.33	2868
5	C ₂ H ₂ N ₆ O ₄	174.09	1.97	123.95	8670	309	4677	752	352	123	1.26	3061
6	C ₈ H ₅ N ₉ O ₁₁	403.21	1.85	220.52	8587	325	4978	681	339	118	1.21	2792
7	C ₈ H ₅ N ₉ O ₁₂	419.21	1.86	154.96	8847	352	5236	678	355	124	1.27	2891
8	C ₈ H ₅ N ₉ O ₁₃	435.21	1.87	114.72	8918	360	5471	677	370	129	1.32	2974
9	C ₂ N ₈	136.10	1.94	251.10	8549	103	843	719	61	21	0.22	1969
10	C ₈ H ₃ N ₁₁ O ₇	365.22	1.82	328.52	8081	279	3663	662	242	84	0.87	2559
11	C ₈ H ₃ N ₁₁ O ₈	381.22	1.83	282.79	8247	297	3922	662	260	90	0.93	2688
12	C ₈ H ₃ N ₁₁ O ₉	397.22	1.85	241.58	8586	324	4305	661	285	99	1.02	2832

TNT: 2,4,6-Trinitrotoluene; RDX: 1,3,5-Trinitroperhydro-1,3,5-triazine, HMX: 1,3,5,7-Tetranitro-1,3,5,7-tetraoctane, PA: Picric acid, SA: Styphnic acid, TNPG: 2,4,6-Trinitrophenol.

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 tetrazine 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 trinitrophenol 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 4, 5, and 9 show density in the order of 1.94–1.99 g/cm³, which is slightly above the benchmark explosive viz., HMX.

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 synthons 5 and 9 are also found to be positive except compound 1. This is the main reason for the selection of these synthons 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 high positive heat of formation. The picrate salts have high positive heat of formation than that of styphnic acid or trinitrophenol salts. The presence of tetrazole 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

Table 2. Comparison of the theoretically predicted detonation velocity and detonation pressure using different codes.

Compound	Density (g/cm ³)	EXTEC		EXPLO-5		Keshavarz Method		LOTUSES	
		VOD (m/s)	P (kbar)	VOD (m/s)	P (kbar)	VOD (m/s)	P (kbar)	VOD (m/s)	P (kbar)
TNT	1.65	6881	195	6824	194	7397	230	6664	181
RDX	1.85	8936	346	8801	336	8963	358	9050	354
HMX	1.91	9296	393	9193	378	9279	396	9246	408
CL-20	2.04	9600	467	9489	390	9485	429	9515	461
PA	1.76	7500	246	7426	234	8070	285	7557	265
SA	1.82	7590	250	8055	289	9400	195	7794	276
TNPG	1.80	7254	214	9569	437	8776	382	7998	352
1	2.07	9426	443	8069	298	5790	161.04	9184	436
2	1.88	7820	290	8144	322	8376	319.25	8074	306
3	1.93	8070	315	8387	352	8714	350.83	8196	324
4	1.94	8197	325	8518	365	8863	364.00	8308	335
5	1.97	9576	397	8670	309	8912	369	9100	402
6	1.85	8289	304	8587	325	8121	298	8593	342
7	1.86	8534	328	8847	352	8355	320	8689	359
8	1.87	8748	348	8918	360	8554	340	8777	374
9	1.94	8714	323	8549	103	7715	262	9050	362
10	1.82	8079	289	8081	229	7732	267	8547	332
11	1.83	8250	306	8247	259	7879	283	8658	352
12	1.85	8632	350	8586	298	8286	319	8758	372

CL-20: Hexanitrohexaazaisowurtzitane.

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 Keshvraj 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 benchmark 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 benchmark 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

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

Comp.	Empirical Formula	Balanced explosive reaction	Volume of gas products (dm ³ /kg)	Oxygen Balance (%)	Impact Sensitivity (cm)	Electrostatic Spark Sensitivity (J)
1	C ₂ H ₁ N ₄ F ₃	HF+2N ₂ +2C+1F ₂	568	-52.14	24.91	12.29
2	C ₈ H ₄ N ₇ O ₇ F ₃	7CO+3HF+0.5H ₂ +3.5N ₂ +1C	636	-47.93	45.71	9.038
3	C ₈ H ₄ N ₇ O ₈ F ₃	8CO+3HF+0.5H ₂ +3.5N ₂	628	-41.75	41.75	9.108
4	C ₈ H ₄ N ₇ O ₉ F ₃	1CO ₂ +7CO+3HF+0.5H ₂ +3.5N ₂	634	-36.07	38.41	9.322
5	C ₂ H ₂ N ₆ O ₄	1CO ₂ +1CO+1H ₂ O+3N ₂	752	-09.19	108.2	10.61
6	C ₈ H ₅ N ₉ O ₁₁	1CO ₂ +7CO+2H ₂ O+0.5H ₂ +4.5N ₂	681	-29.76	81.66	10.86
7	C ₈ H ₅ N ₉ O ₁₂	2CO ₂ +6CO+2H ₂ O+0.5H ₂ +4.5N ₂	678	-24.80	73.52	11.24
8	C ₈ H ₅ N ₉ O ₁₃	3CO ₂ +6CO+2H ₂ O+0.5H ₂ +4.5N ₂	677	-20.21	66.71	11.67
9	C ₂ N ₈	4N ₂ +2C	719	-47.02	56.67	3.134
10	C ₈ H ₃ N ₁₁ O ₇	7CO+0.5H ₂ +5.5N ₂ +1C	662	-45.99	62.30	7.729
11	C ₈ H ₃ N ₁₁ O ₈	8CO+1.5H ₂ +5.5N ₂	662	-39.87	56.14	7.963
12	C ₈ H ₃ N ₁₁ O ₉	8CO+1H ₂ O+0.5H ₂ +5.5N ₂	661	-34.23	51.01	8.305

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 tetrazole rings in compounds 5-8 has a higher predicted impact sensitivity. Electric spark (ES) sensitivity plays a vital role in the safety of the newly 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-trinitrophenol 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

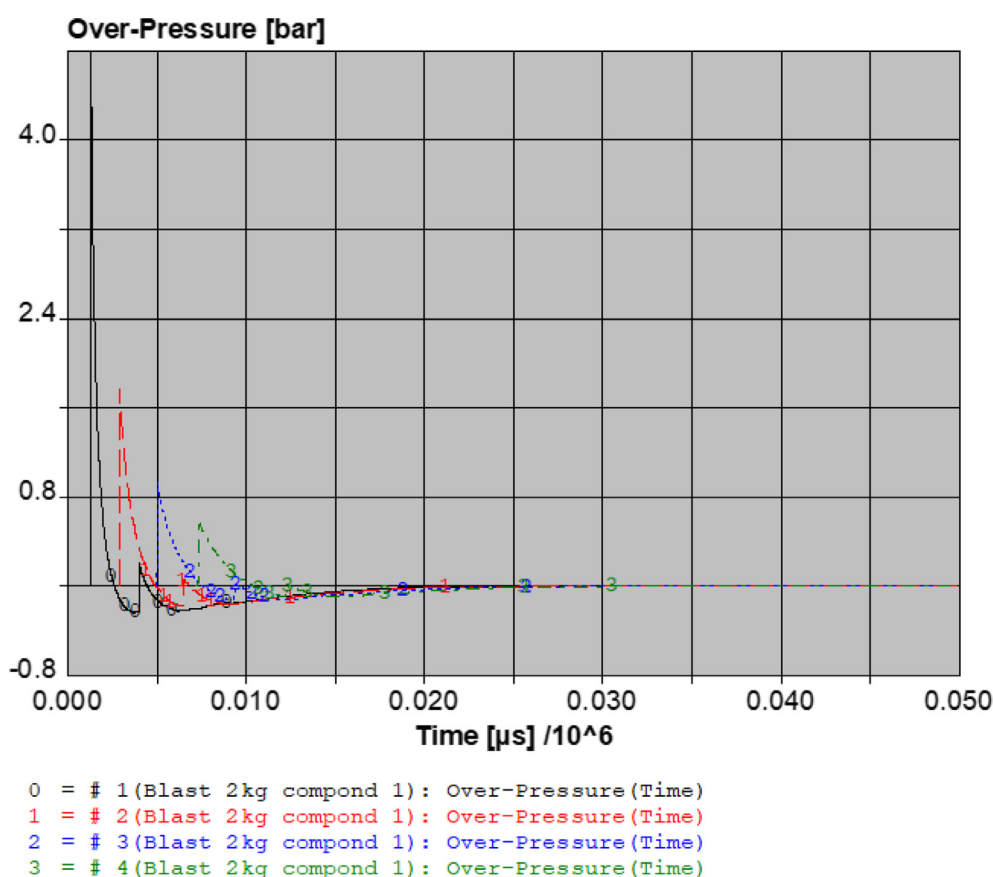
A numerical simulation of the newly designed molecules was carried out using SPEED software [22]. In this modelling study, an explosive charge quantity of 2 kg was considered for the prediction of blast peak over pressure and blast impulse. Some of the selected compounds such as 1, 2, 3, 5, 6, 8, 9, 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 synthon 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, 7, 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 4. Percentage composition of elements.

Compound	Empirical Formula	Molecular Weight	% of H	% of C	% of N	% of O	% of F
1	C ₂ H ₁ N ₄ F ₃	138.07	0.73	17.39	40.58	-	41.28
2	C ₈ H ₄ N ₇ O ₇ F ₃	367.18	1.09	26.16	26.70	30.50	15.52
3	C ₈ H ₄ N ₇ O ₈ F ₃	383.18	1.05	25.07	25.59	33.40	14.87
4	C ₈ H ₄ N ₇ O ₉ F ₃	399.18	1.01	24.07	24.56	36.07	14.27
5	C ₂ H ₂ N ₆ O ₄	174.09	1.15	13.79	48.28	36.76	-
6	C ₈ H ₅ N ₉ O ₁₁	403.21	1.24	23.83	31.27	43.64	-
7	C ₈ H ₅ N ₉ O ₁₂	419.21	1.20	22.92	30.07	45.79	-
8	C ₈ H ₅ N ₉ O ₁₃	435.21	1.15	22.07	28.97	47.79	-
9	C ₂ N ₈	136.10	-	17.65	82.35	-	-
10	C ₈ H ₃ N ₁₁ O ₇	365.22	0.82	26.30	42.19	30.66	-
11	C ₈ H ₃ N ₁₁ O ₈	381.22	0.79	25.20	40.42	33.57	-
12	C ₈ H ₃ N ₁₁ O ₉	397.22	0.76	24.19	38.79	36.25	-

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

Charge Quantity: 2 kg			Blast POP (bar)				Blast Impulse (bar. ms)			
Compound	Density (g/cm ³)	VOD (m/s) EXTEC method	Distance from Charge				Distance from Charge			
			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

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

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 layout 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

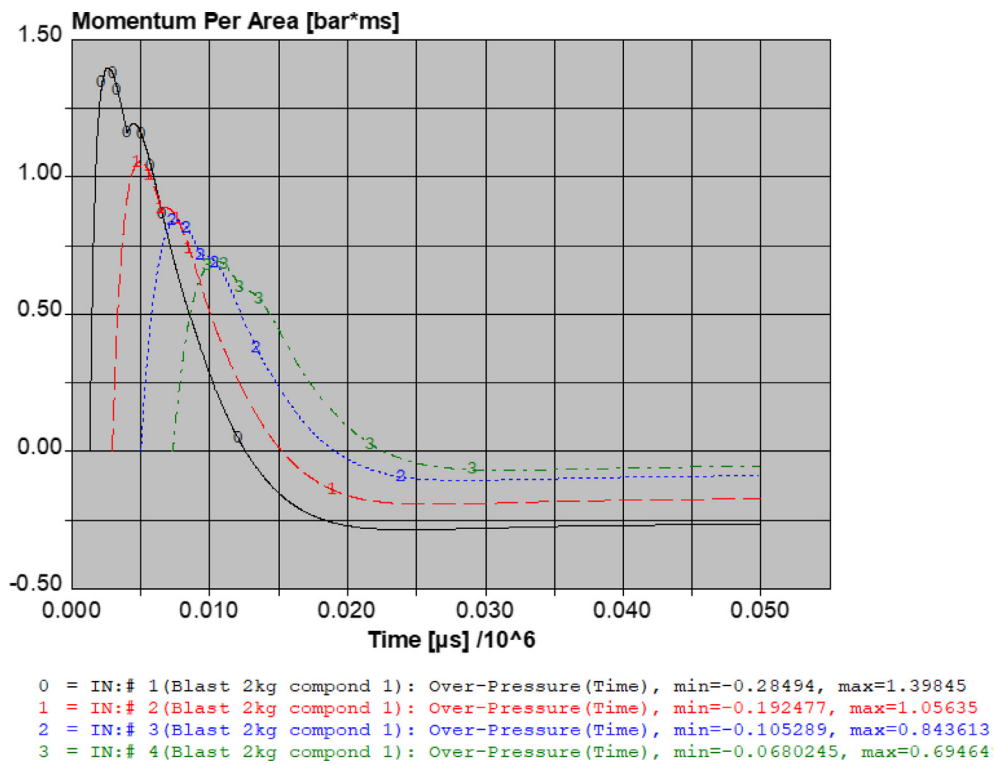


Figure 4. The graph of blast impulse Vs time for compound 1.

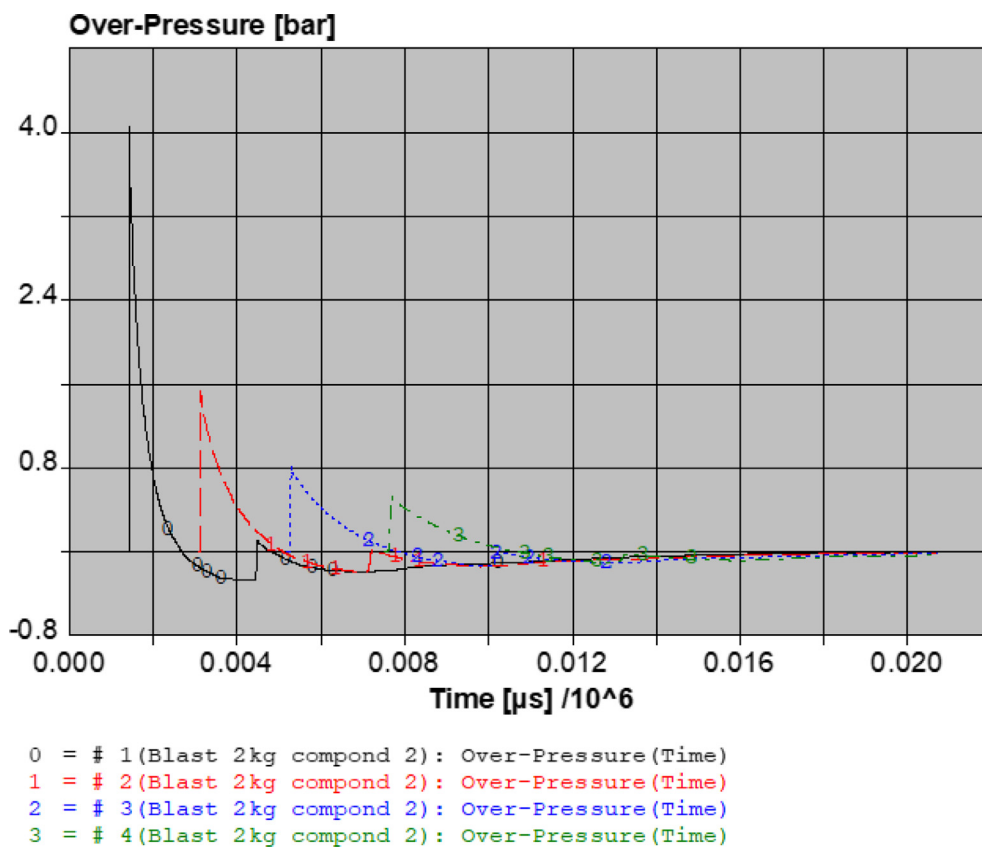


Figure 5. The graph of peak over pressure Vs time for compound 2.

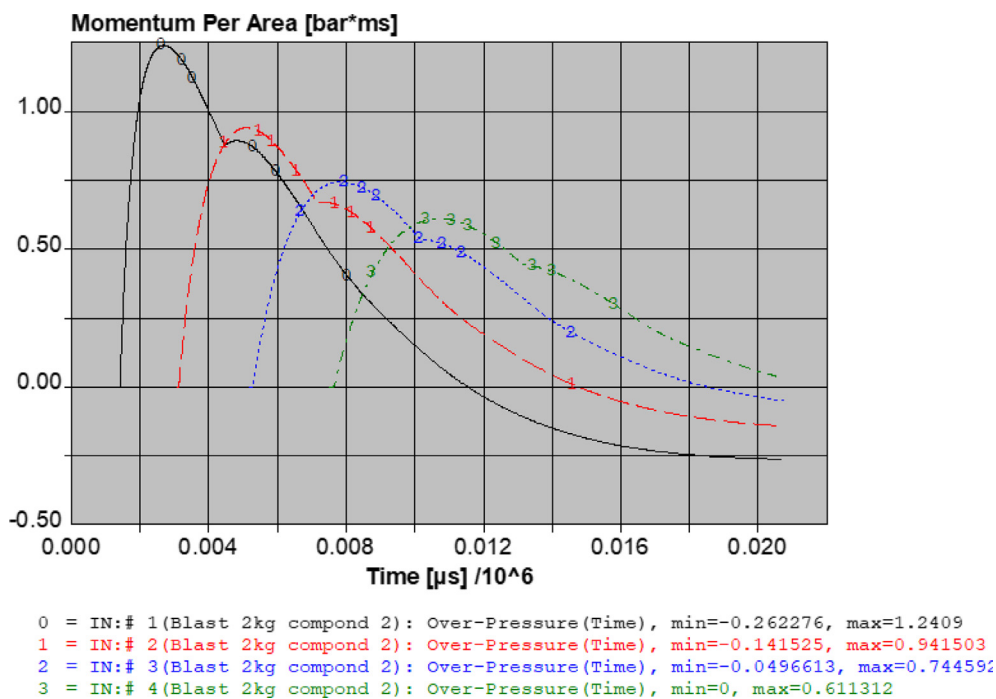


Figure 6. The graph of blast impulse Vs time for compound 2.

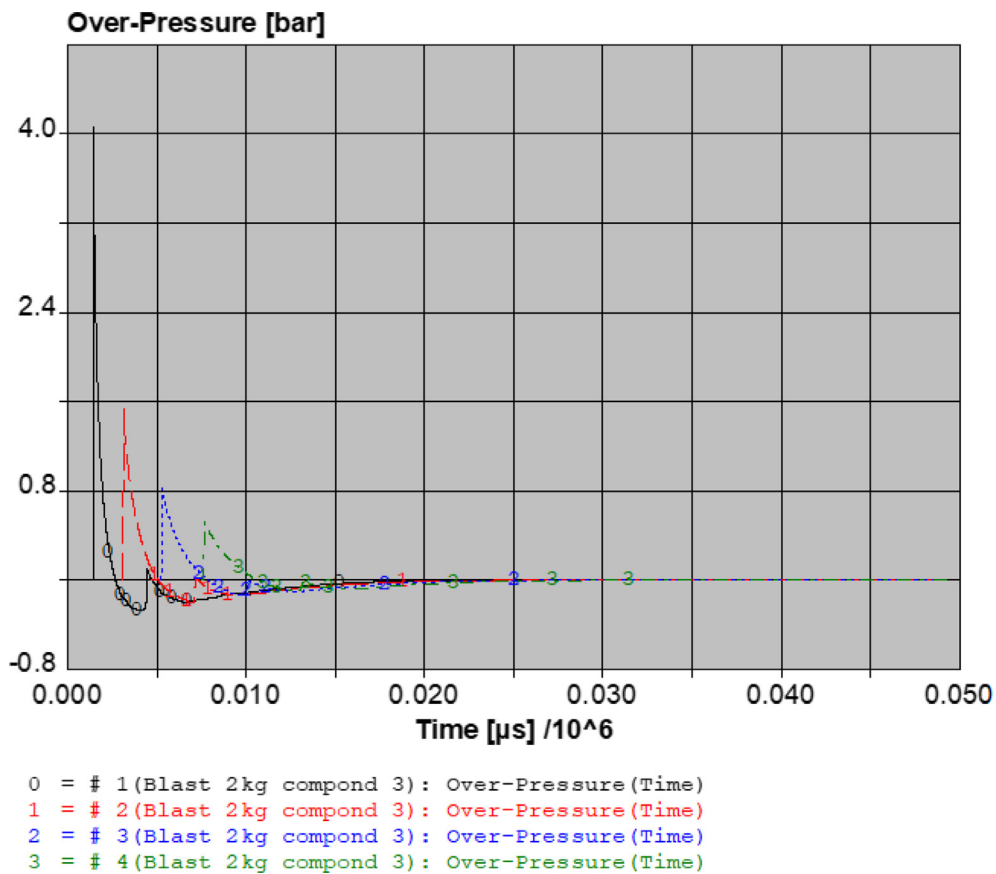


Figure 7. The graph of peak over pressure Vs time for compound 3.

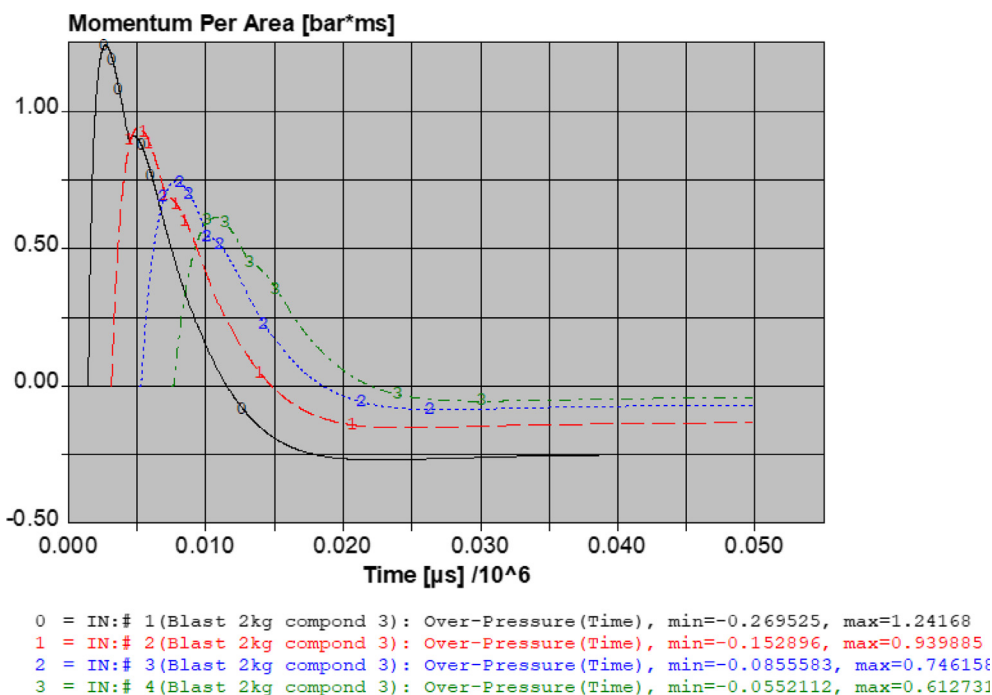


Figure 8. The graph of blast impulse Vs time for compound 3.

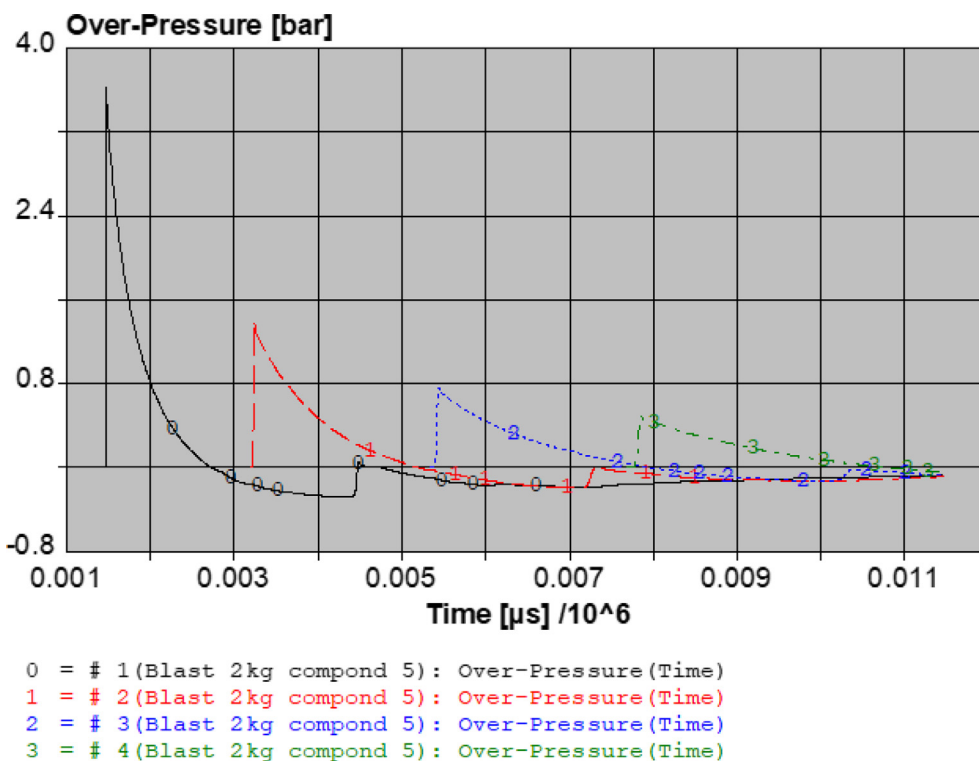


Figure 9. The graph of peak over pressure Vs time for compound 5.

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

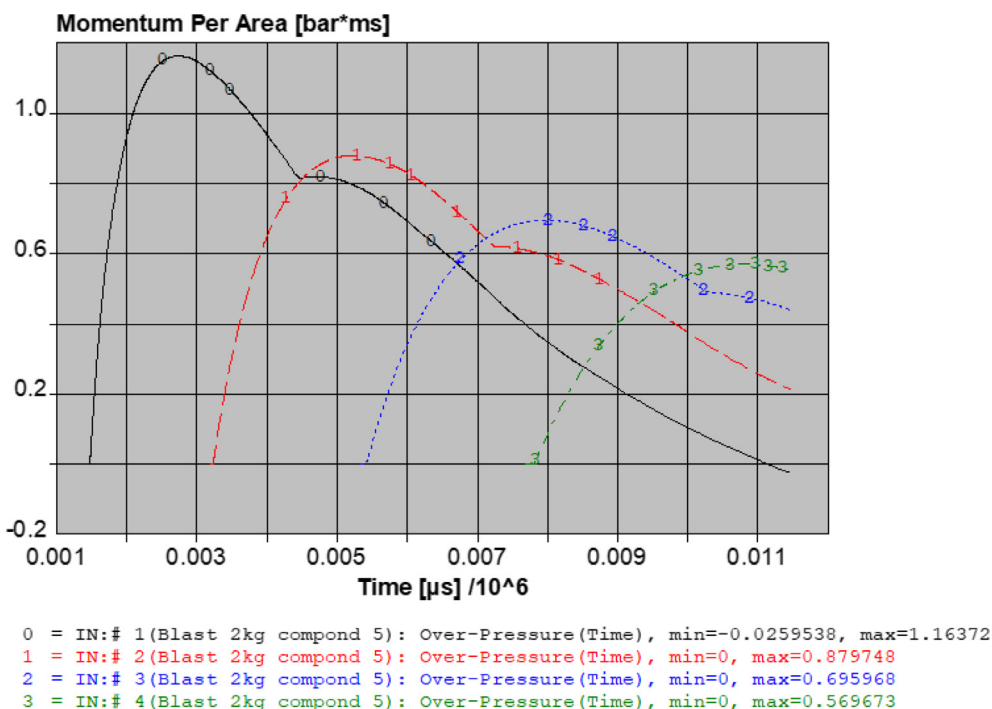


Figure 10. The graph of blast impulse Vs time for compound 5.

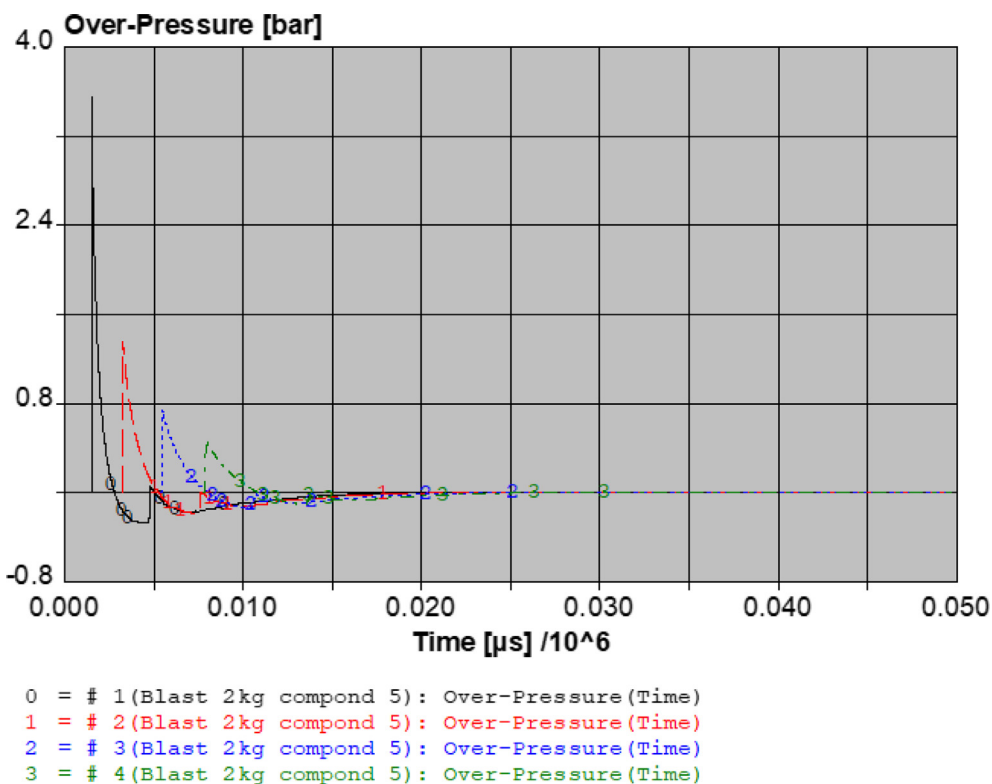


Figure 11. The graph of peak over pressure Vs time for compound 6.

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.

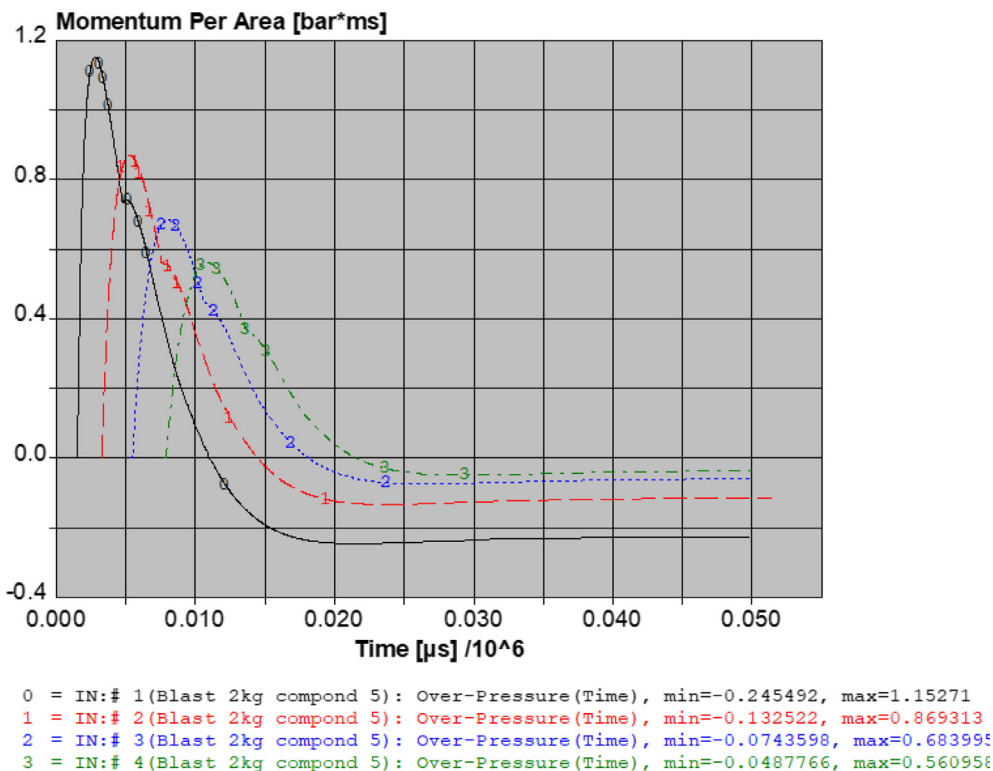


Figure 12. The graph of blast impulse Vs time for compound 6.

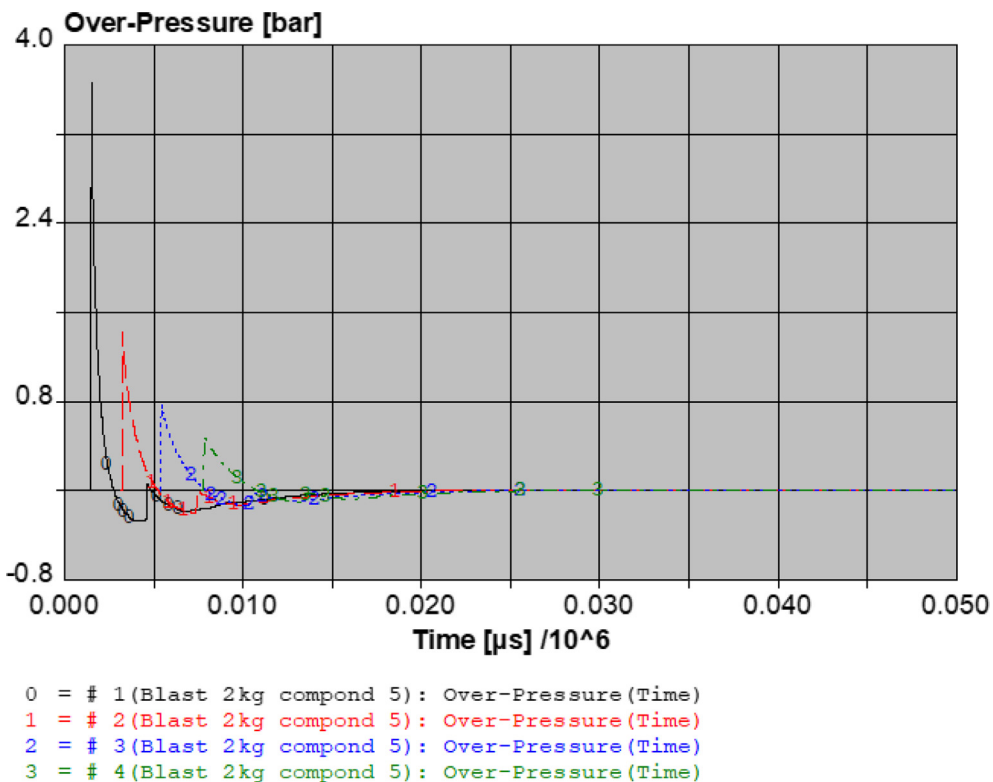


Figure 13. The graph of peak over pressureVs time for compound 8.

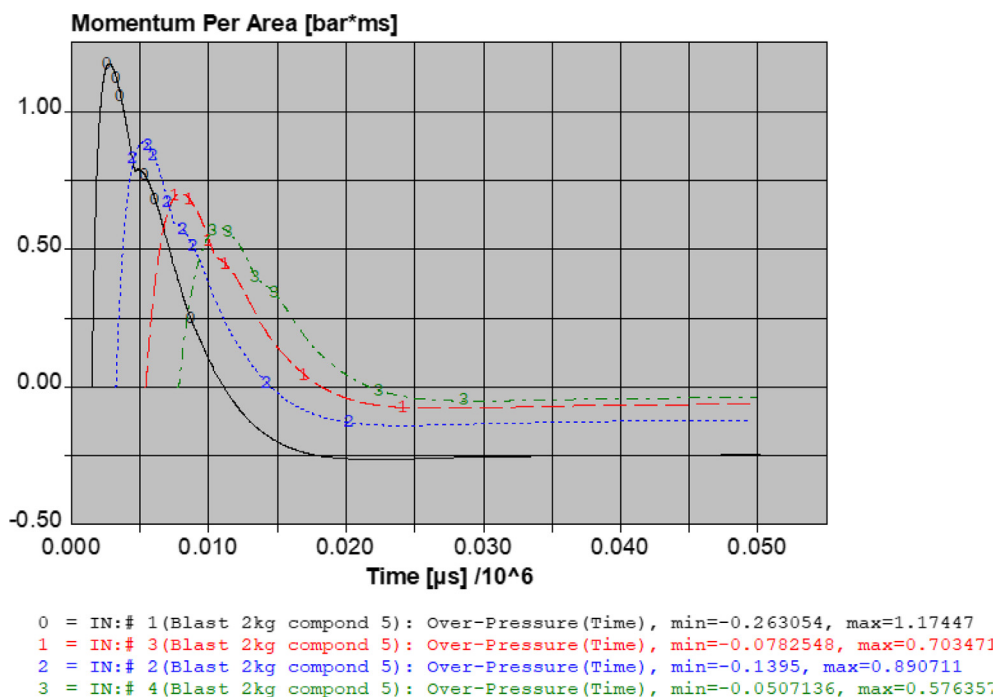


Figure 14. The graph of blast impulse Vs time for compound 8.

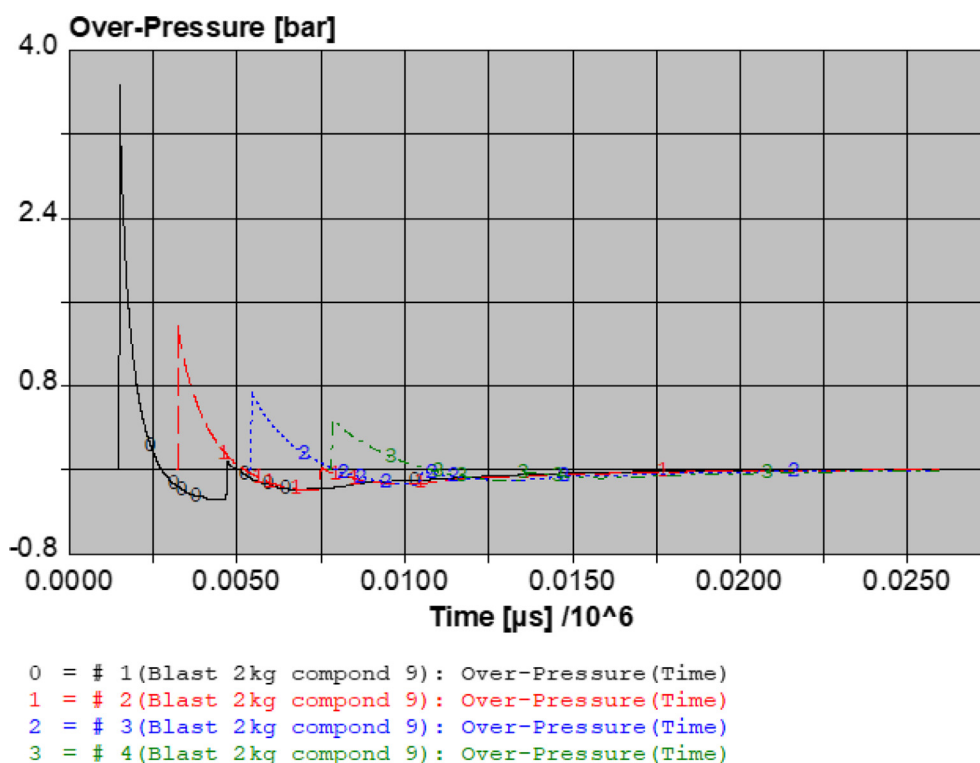


Figure 15. The graph of peak over pressure Vs time for compound 9.

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.

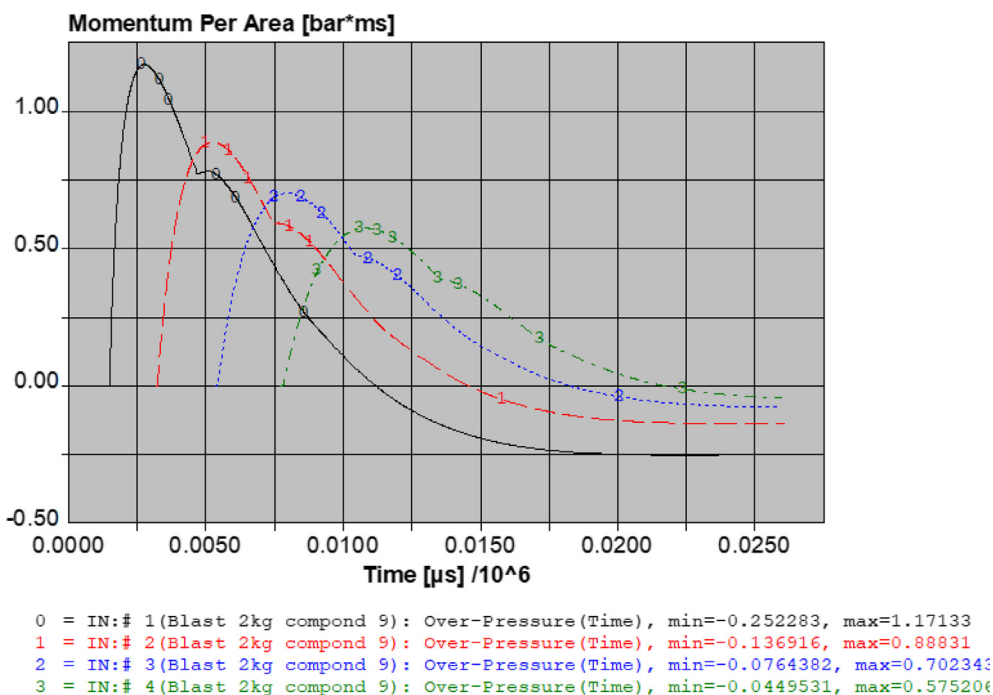


Figure 16. The graph of blast impulse Vs time for compound 9.

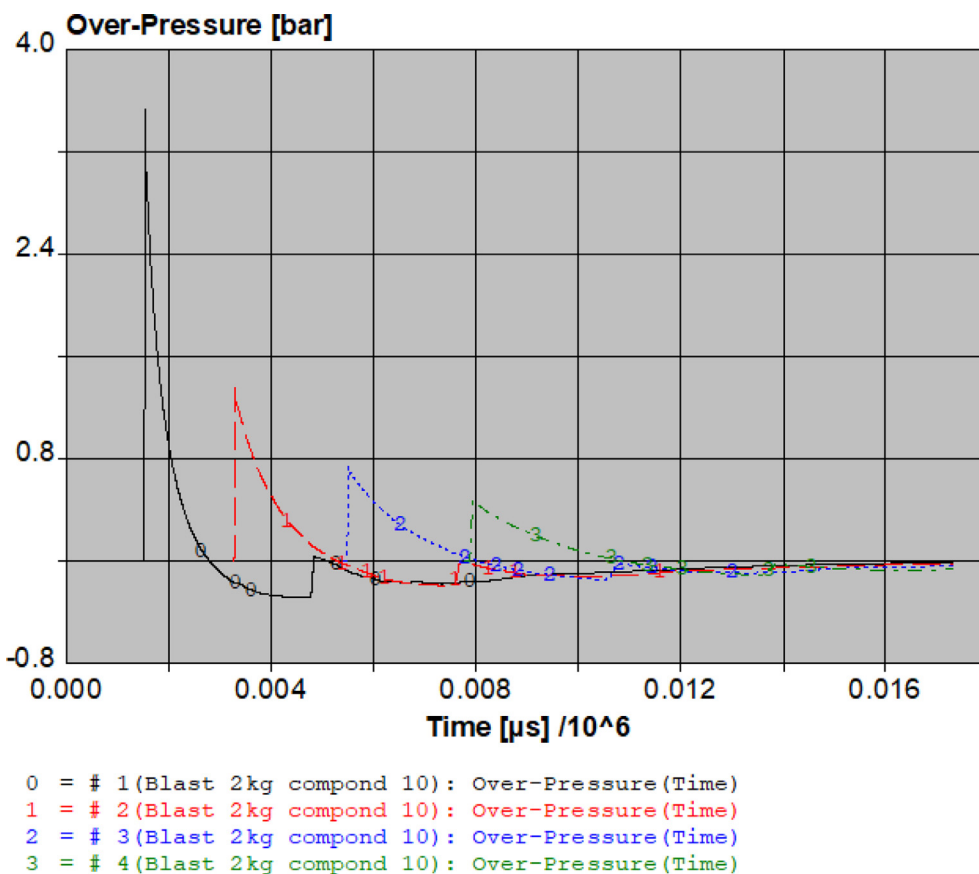


Figure 17. The graph of peak over pressure Vs time for compound 10.

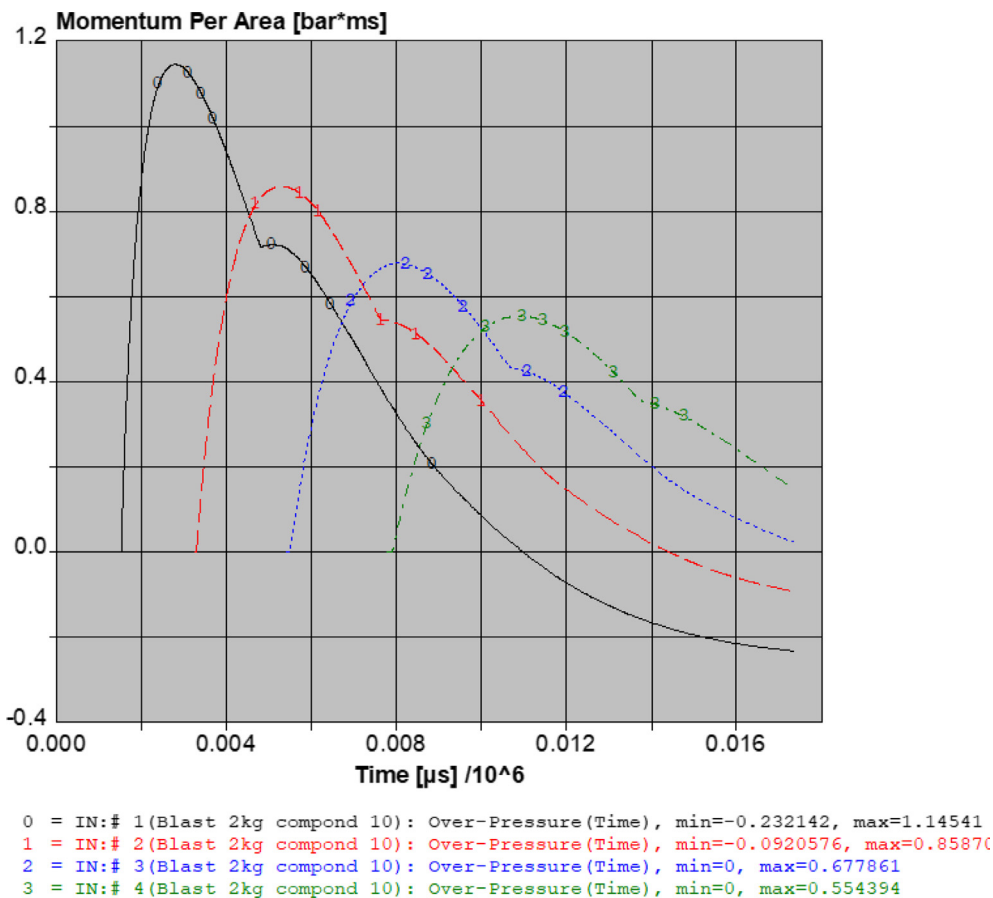


Figure 18. The graph of blast impulse Vs time for compound 10.

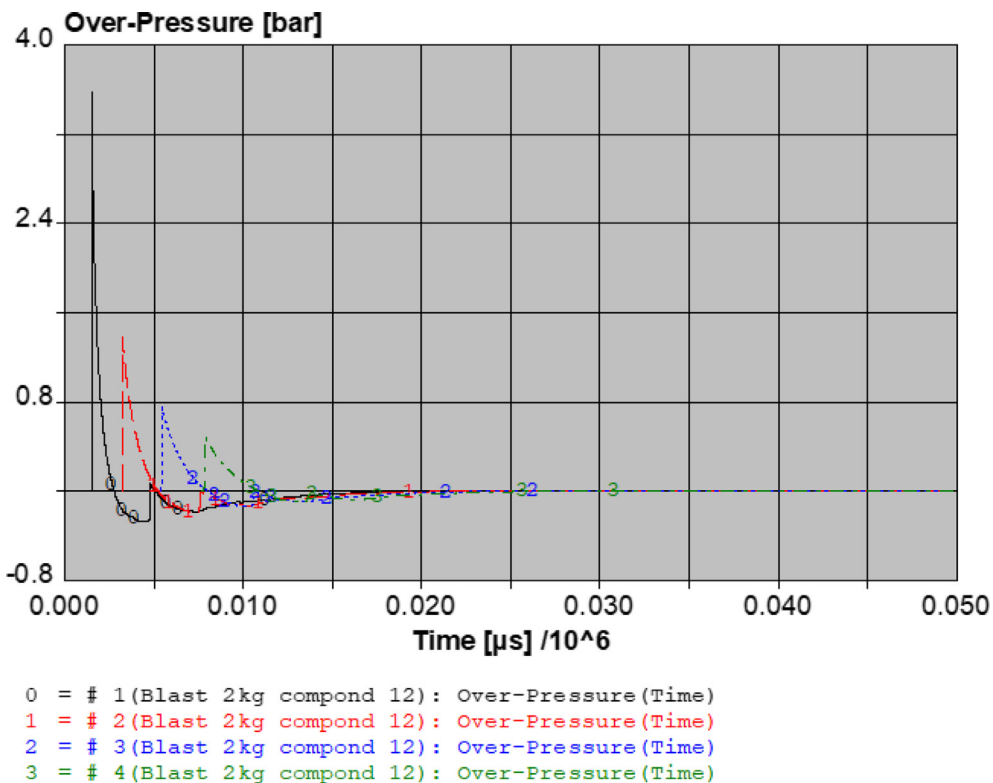


Figure 19. The graph of peak over pressure Vs time for compound 12.

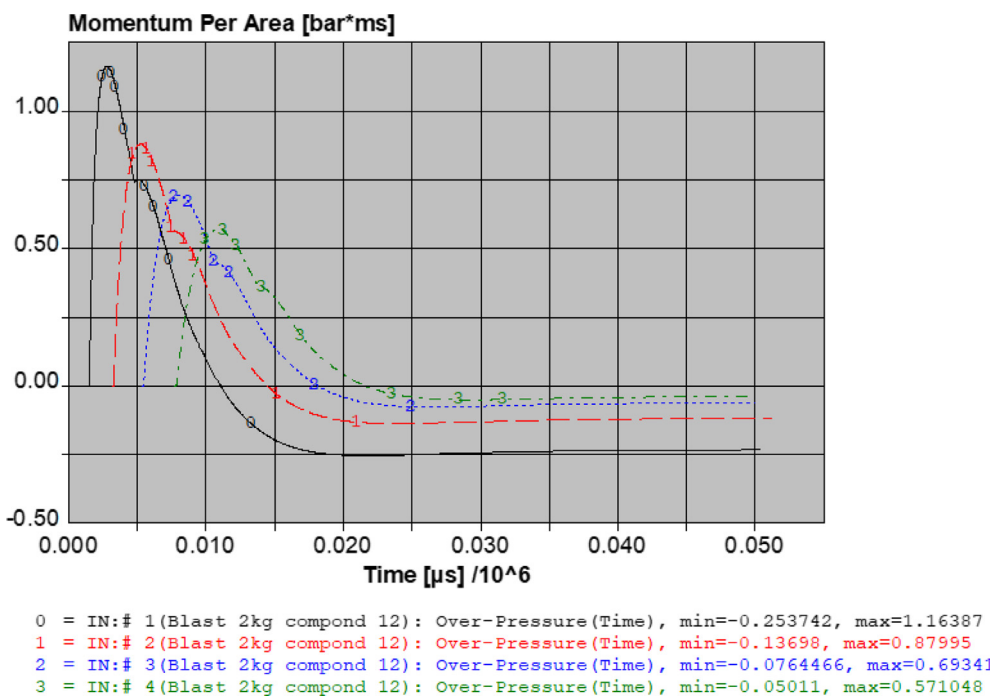


Figure 20. The graph of blast impulse Vs time for compound 12.

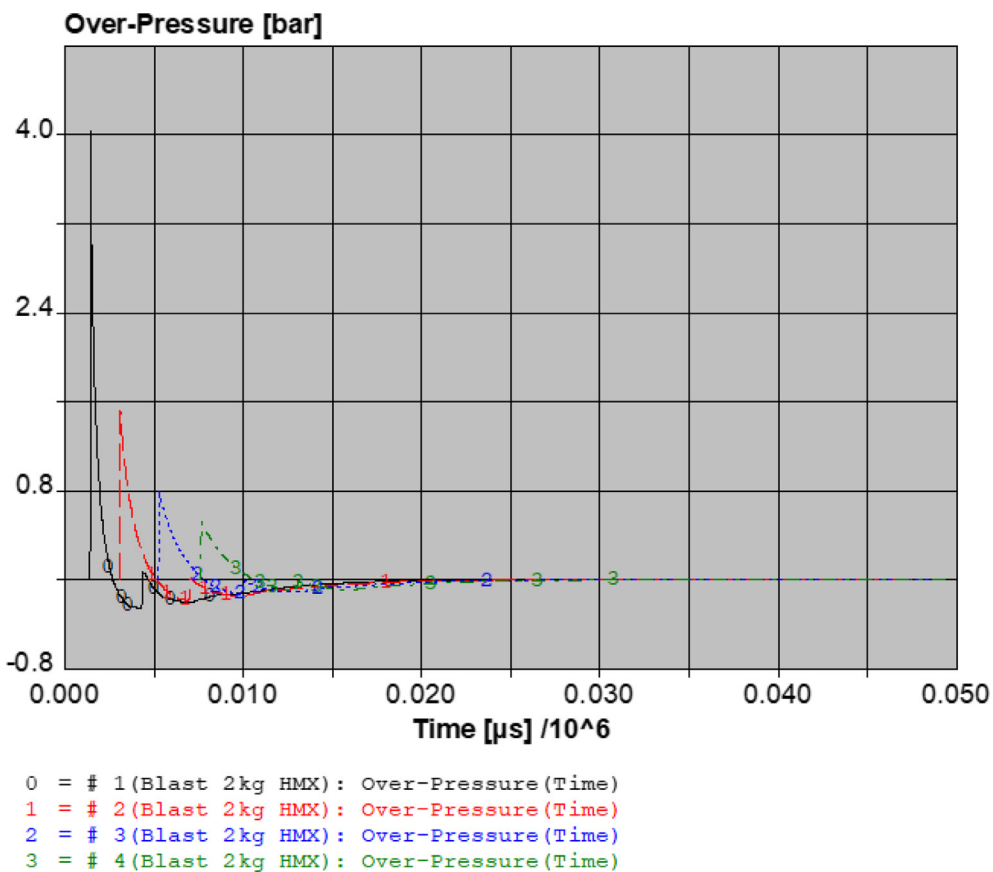


Figure 21. The graph of peak over pressure Vs time for HMX.

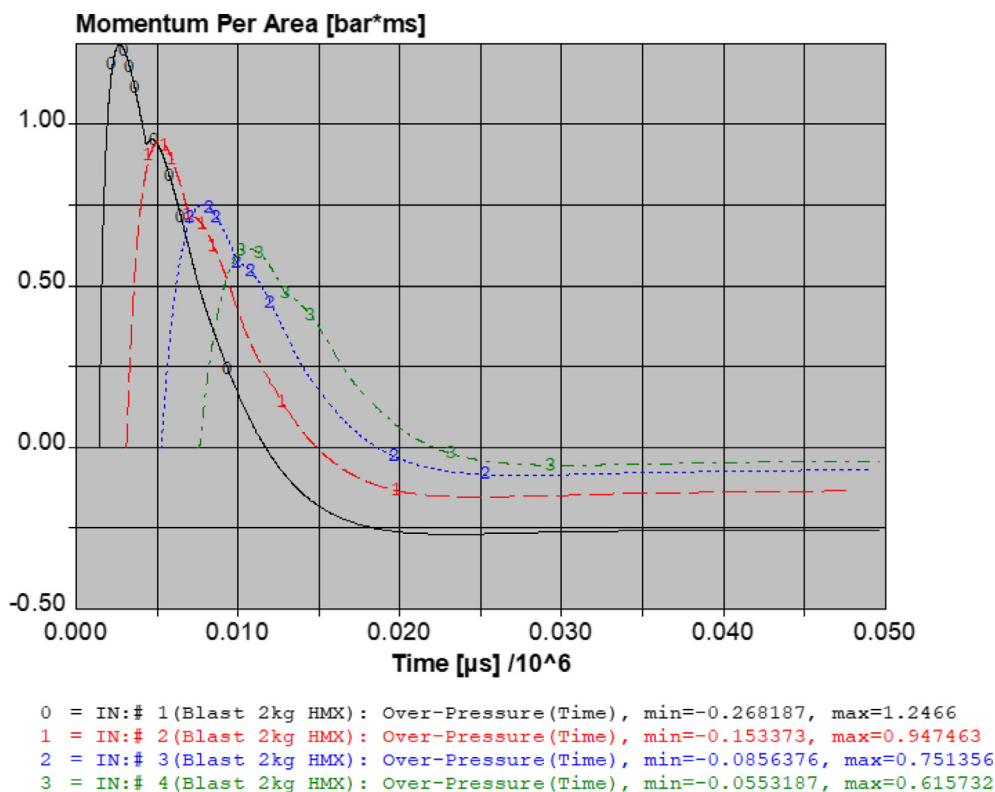


Figure 22. The graph of blast impulse Vs time for HMX.

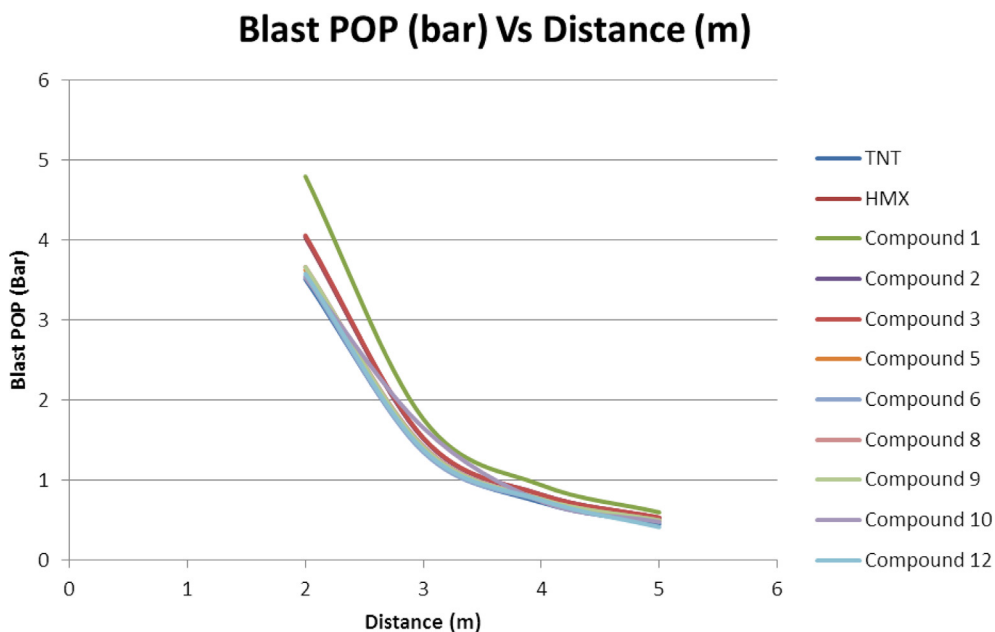


Figure 23. Blast POP Vs distance for compounds 1, 2, 3, 5, 6, 8, 9, 10 and 12.

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-trinitrophenol 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.

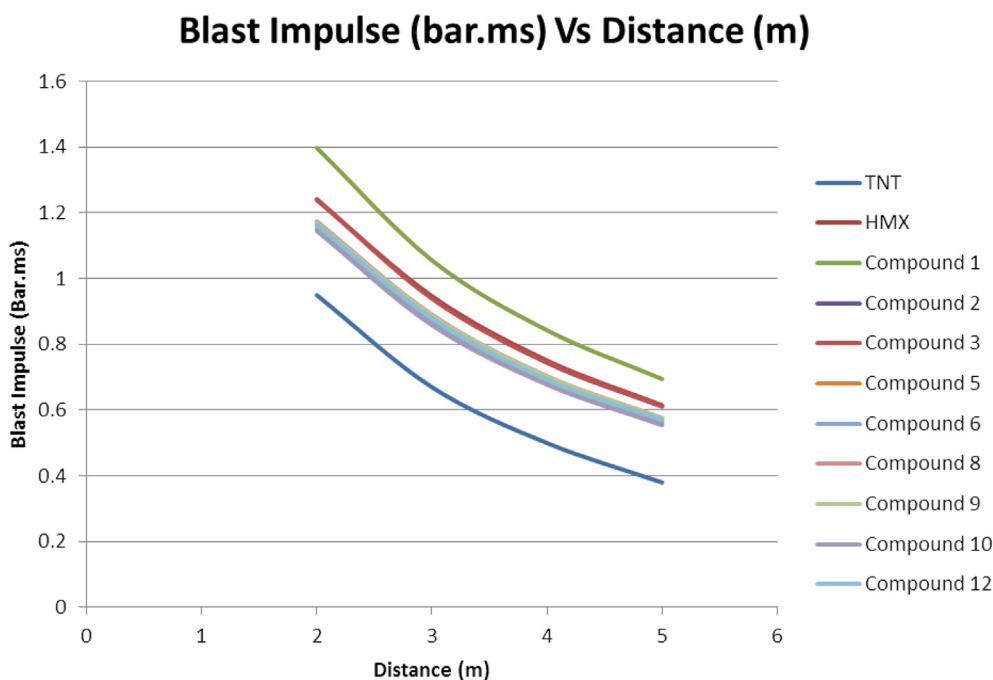


Figure 24. Blast impulse Vs distance for compounds 1, 2, 3, 5, 6, 8, 9, 10 and 12.

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

S. No.	Molecular formula	Density composition (g/cm ³)	Heat of Formation (cal/g)	Molecular Weight (g/mol)	Flame Temperature	Impulse specific (s)	C* (m/s)	Density Impulse
TNT	C ₇ H ₅ N ₃ O ₆	1.737	-366	24.448	3168	261.6	1566	454
RDX	C ₃ H ₆ N ₆ O ₆	1.754	-368	24.775	3300	264.7	1586	464
HMX	C ₄ H ₈ N ₈ O ₈	1.761	-368	24.775	3300	264.7	1586	466
CL-20	C ₉ N ₁₂ H ₆ O ₁₂	1.773	-354	25.13	3342	264.7	1586	469
PA	C ₆ H ₃ N ₃ O ₇	1.748	-397	24.94	3231	261.4	1565	457
SA	C ₆ H ₃ N ₃ O ₈	1.754	-420	23.85	2410	239.9	1415	421
TNPG	C ₆ H ₃ N ₃ O ₉	1.784	-434	23.851	2404	239.1	1410	427
1	C ₂ H ₁ N ₄ F ₃	1.775	-314	24.943	3333	268.5	1609	477
2	C ₈ H ₄ N ₇ O ₇ F ₃	1.759	-369	24.931	3258	264	1581	464
3	C ₈ H ₄ N ₇ O ₈ F ₃	1.764	-375	25.008	3275	264.2	1582	466
4	C ₈ H ₄ N ₇ O ₉ F ₃	1.764	-380	25.081	3290	264.3	1583	466
5	C ₂ H ₂ N ₆ O ₄	1.764	-360	25.155	3309	263.2	1576	464
6	C ₈ H ₅ N ₉ O ₁₁	1.757	-384	25.036	3262	262	1569	460
7	C ₈ H ₅ N ₉ O ₁₂	1.761	-388	25.108	3277	262.2	1570	462
8	C ₈ H ₅ N ₉ O ₁₃	1.764	-393	25.175	3290	262.3	1571	463
9	C ₂ N ₈	1.749	-256	24.752	3158	259.1	1555	453
10	C ₈ H ₃ N ₁₁ O ₇	1.754	-348	24.868	3205	261	1563	458
11	C ₈ H ₃ N ₁₁ O ₈	1.759	-362	24.959	3217	261	1562	459
12	C ₈ H ₃ N ₁₁ O ₉	1.764	-360	25.027	3247	261.8	1567	462
Reference		1.765	-434	25.599	3388	263.8	1579	466

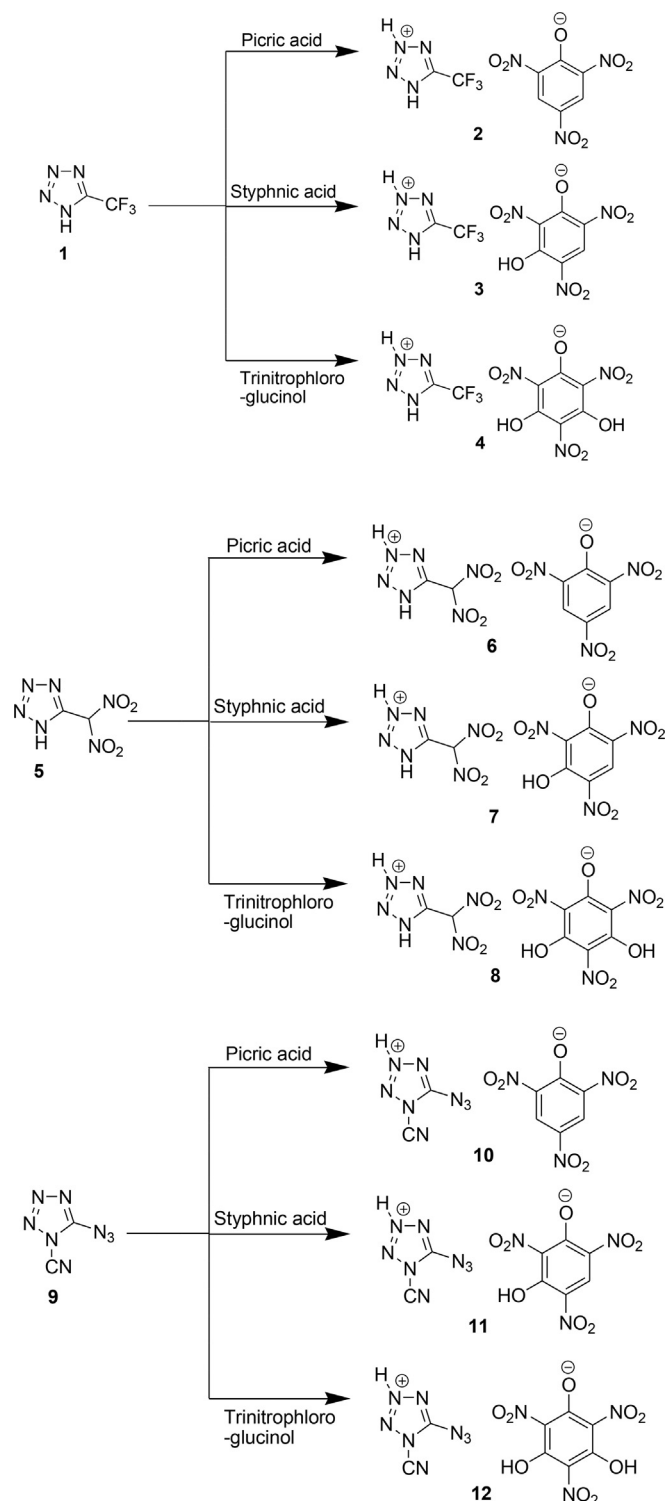
Control sample: Ammonium perchlorate 68%, Al 18% Dioctyl adipate 3%, Hydroxy terminated polybutadiene 11%.

Test sample compound 1 to 12 (10%) + Ammonium perchlorate 58%, Al 18% Dioctyl adipate 3%, Hydroxy terminated polybutadiene 11%.

The major requirement of Navies all over the world is that of requirement 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 newly designed energetic materials are anticipated to meet the insensitive requirements as well as that of higher thermal stability. 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



Scheme 1. Proposed method of synthesis of newly designed molecules.

effects but a higher energy release partitioned over different stages. 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 the 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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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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