

Synthesis, characterization and thermolysis studies on new derivatives of 2,4,5-trinitroimidazoles: Potential insensitive high energy materials

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Abstract

This paper reports the synthesis of three new derivatives of 2,4,5-trinitroimidazole namely, 1-methyl-2,4,5-trinitroimidazole (**III**), 1-carboethoxy-2,4,5-trinitroimidazole (**V**) and 1-picryl-2,4,5-trinitroimidazole (**VII**). The title compounds (**III**) and (**V**) were synthesized by the nitration of 1-methyl-/1-carboethoxy-(2,4,5-triiodoimidazole) (**II** and **IV**) with fuming nitric acid at 0 °C and (**VII**) was synthesized by condensation of 2,4,5-triiodoimidazole (**I**) with picryl chloride to obtain 1-picryl-2,4,5-triiodoimidazole (**VI**) followed by its nitration with fuming nitric acid at 0 °C. The synthesized compounds have been characterized by elemental analysis, spectral and thermal techniques. The thermolysis studies using TG-DTA revealed exothermic decomposition of the nitroimidazoles (**III**, **V** and **VII**) with T_{\max} in the temperature range of 196–225 °C. The energy of activation obtained for these compounds was in the range 150–170 kJ/mol. The sensitivity data obtained for the newly synthesized compounds (**III**, **V** and **VII**) indicated their safe nature towards external stimuli ($h_{50\%} > 100$ cm; friction > 36 kg) and could be potential candidates for low vulnerable applications in the futuristic systems. The theoretically predicted performance parameters suggest that 1-methyl-2,4,5-trinitroimidazole (**III**), exhibits higher velocity of detonation (VOD: 8.8 km/s) compared to compounds **V** and **VII** (VOD: 7.6 and 8.41 km/s, respectively).
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1. Introduction

Poly nitroimidazoles have attracted renewed attention of high energy materials (HEMs) chemists due to their favourable insensitivity and explosive performance [1,2]. Bulusu et al. [3] synthesized 2,4-dinitroimidazole (2,4-DNI) and found it highly promising insensitive HEM. Attractive features of 2,4-dinitroimidazole are its much less sensitivity than current high explosives (RDX and HMX), and it offers 15–20% more energy potential than insensitive explosive trinitroaminobenzene (TATB). Moreover, it can be prepared from the inexpensive starting materials. Various nitroimidazole derivatives including 2,4-dinitroimidazole [4–7], 4,5-dinitroimidazole [8,9], 2,4,5-trinitroimidazole [10,11] and 4,4',5,5'-tetranitro

2,2'-biimidazole [12,13] have been investigated in the last decade. One of the concerning problem in these molecules is the chemical stability associated with the hydrogen attached to first position, which is known to be quite acidic [14]. The nitration of 1 position is possible and 1,4-dinitroimidazole synthesized is easily isomerised to 2,4-dinitroimidazole (DNI) by heating at a modest temperature in solution or in solid state [6–15]. Further nitration of DNI generates a salt of 2,4,5-trinitroimidazole (TNI) [11]. The salt is formed probably because the hydrogen attached to N₁ atom is labile. Thus, the further nitration at first position of TNI not only increases the explosive performance of nitroimidazole derivatives, but also may stabilize the compounds chemically.

Cho et al. [4] have investigated 1,2,4,5-tetranitroimidazole (TTNI) theoretically using various levels of theories. They reported the optimized geometry of TTNI at AM1, PM3, HF/3-21G, HF/6-31G**, HF/6-311++G** and BP 86/6-31G**. All the calculations conclude that the imidazole ring is planar and C2–N3 and C4–C5 bonds to be substantially short. These

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workers also extended their study to calculate the explosive performance, i.e. CJ pressure and detonation velocity of the above compound. According to the result, explosive performances of trinitroimidazole appear to be in a range between HMX and RDX. It is well known that insertion of picryl group in an organic compound increases the density while insertion of hydrocarbon chain increases the thermal stability [16–21].

Polynitroimidazole have been also investigated for their antibacterial, fungicidal and chemotherapeutical properties [11,22]. The aryl derivatives of imidazoles are also reported as potential antibacterial agents [23]. 4-Nitro-5-haloimidazole forms an important class of ring substituted nitroimidazole derivatives useful as chemotherapeutic agents [24], potential radio sensitizers and also intermediates in the synthesis of variety of biologically important nitroimidazole derivatives because of the ease of replacement of the halogen [25]. Bhujang Rao et al. [26] reported the electrophilic iodination of 4-nitroimidazole employing the systems KI–HNO₃–AcOH as a new route for the synthesis of 4-nitro-5-iodoimidazoles and 2,5-diiodo-4-nitroimidazoles. The iodination of imidazole was originally investigated by Pauley et al. [27–29]. Under alkaline conditions, C-2 position which gets initially substituted, undergoes substitution at C-4 to offer 2,4(5)-diiodoimidazole. This conclusion was shown to be erroneous by Naidu and Bensusan [30] and Holoway et al. [31], each of whom independently and correctly assigned the sequential products of mono and disubstitution as 4(5)-iodoimidazole and 4,5-diiodoimidazole, respectively. It was left to Hamill and co-workers [32] to unambiguously identify the structure of diiodoimidazole [30].

In view of the above observations coupled with broad spectrum applications of nitroimidazoles and scanty reports on N(1) substituted nitroimidazoles, we are herewith reporting the synthesis and characterization of three new *N*-methyl, *N*-ester and *N*-picryl derivatives of 2,4,5-trinitroimidazole. This paper also reports the theoretical performance prediction of the newly synthesized compounds in comparison to the well known insensitive energetic materials such as nitrotriazolone (NTO), diaminodinitro ethylene (FOX-7), triaminotrinitrobenzene (TATB), diamino trinitrobenzene (DATB), dinitroimidazole (DNI), tetranitro tetraazapentalene (TACOT) and benchmark explosives viz., trinitrotoluene (TNT), hexahydro trinitro triazine (RDX) and tetranitramino octahydro tetrazocine (HMX).

2. Experimental

2.1. Materials and methods

The starting materials used in the present study were of AR grade and purchased from the trade. The melting point of the compounds was measured using Thomas Hoover capillary melting point apparatus. The IR spectra were determined as nujol mulls on a Perkin-Elmer-1600 FTIR spectrophotometer. Proton NMR spectra were recorded on Varian 300 MHz spectrometer (TMS as an internal standard). Elemental analysis was carried out on Perkin-Elmer instrument. Thermal analysis (with about 2 mg samples) was performed on Mettler Toledo star TG-DTA

system at a heating rate of 10 °C/min in nitrogen atmosphere at a flow rate of 80 cm³/min. DSC was performed on Perkin-Elmer-7 system at a heating rate of 10 °C/min in nitrogen atmosphere. Energy of activation and selected Avogadro's data were calculated by applying the Madhusudanan et al. method [33]. The Impact test was conducted using a set up similar to that used in Naval Ordnance Laboratory (NOL), USA. Test specimens (30–35 mg of powder) were kept between two hardened anvils and a 3 kg drop weight was allowed to fall freely from different heights. Both open and aluminum foil encapsulated specimens were used for evaluation. Ten tests were conducted for each compound. The results are reported in terms of height for 50% probability of explosion (*h*_{50%}) of the sample. The friction test was also conducted in a test set up similar to the one employed by NOL. The sample was kept between a fixed corrugated (rough) stainless steel plate and a movable stainless steel plate. Pulling of the movable plate at varying lever loads caused friction. The impact and friction sensitivity studies of bench mark explosives such as RDX and TNT was also carried out under identical conditions to validate the data obtained for the newly synthesized compounds. The explosive properties of the synthesized compounds have been computed using Linear Output Thermodynamic User friendly Software for Energetic Systems (LOTUSES) code [34–37]. The results are compared with the well-known HEMs.

2.2. Synthesis

2.2.1. Preparation of 2,4,5-triiodoimidazole (I)

The title compound (I) was synthesized and characterized by following the reported method [12]. The procedure is described as follows: an aqueous solution (50 ml) of iodine (6.77 g, 0.053 mol) and potassium iodide (8.85 g, 0.069 mol) was added drop wise to a stirred solution of imidazole (0.453 g, 0.0066) in aqueous sodium hydroxide (2 M, 70 ml) at room temperature and left stirring for 24 h. The reaction mixture solution was neutralized with 25% acetic acid to obtain a creamy precipitate, which was filtered, washed with water and air-dried. The compound was then recrystallized from ethanol to yield colorless crystals of (I), (2.17 g, yield: 81.7%) having a melting point of 192 °C (lit. 191 °C). IR (ν_{\max} , cm⁻¹): 660 (Iodide absorption band), 1525 (C=N), 3320 (–NH stretching). ¹H NMR (300 MHz, DMSO-*d*₆): 10.5 (bs, –NH). The elemental analysis data obtained for compound (I, C₃HN₂I₃). Calculated: C, 8.07; H, 0.24; N, 6.27; found: C, 8.16; H, 0.34; N, 6.30%.

2.2.2. Preparation of 1-methyl-2,4,5-triiodoimidazole (II)

Potassium carbonate (30 g, 2.2 mmol) was added to the stirred solution of 2,4,5-triiodoimidazole (I) (0.500 g, 1.12 mmol) in dimethylformamide (10 cm³). Reaction mixture was kept under stirring for an hour, and then methyl iodide (0.159 g, 1.1 mmol) was added slowly in nitrogen atmosphere. The stirring was continued for 4 h at room temperature. DMF was evaporated *in vacuo*. The product was extracted with ethyl acetate and dried on sodium sulphate. Evaporation of ethyl acetate yielded white creamy compound (II) of 0.28 g (yield: 55%), which melts at 210 °C. IR (ν_{\max} , cm⁻¹): 662 (Iodide absorption band), 1342

(C–N stretching vibration), 1570 (C=N). ^1H NMR (300 MHz, DMSO- d_6): δ 2.89 (3H, s). The elemental analysis data obtained for compound (II, $\text{C}_4\text{H}_3\text{N}_2\text{I}_3$). Calculated: C, 10.43; H, 0.65; N, 6.08; found: C, 10.76; H, 0.59; N, 6.30%.

2.2.3. Preparation of 1-methyl-2,4,5-trinitroimidazole (III)

About 0.250 g of 1-methyl-2,4,5-triiodoimidazole (II) was added in small portions to the solution of fuming nitric acid (5 cm^3) stirred at 0°C . The stirring of the reaction mixture was continued for an hour at 100°C , and then the contents were cooled to room temperature. Subsequently, the reaction mixture was poured into crushed ice to obtain compound (III) of 0.046 g (yield: 40%), which melts at $240\text{--}242^\circ\text{C}$. IR (ν_{max} , cm^{-1}): 1575 (–C–NO $_2$), 1560 (C=N), 2800. ^1H NMR (300 MHz, DMSO- d_6): δ 3.73 (3H, s). Elemental analysis for (III), $\text{C}_4\text{H}_3\text{N}_5\text{O}_6$: Calculated: C, 22.11; H, 1.38; N, 32.25; found: C, 22.16; H, 1.49; N, 32.30%.

2.2.4. Preparation of 1-carboethoxy-2,4,5-triiodoimidazole (IV)

To the stirred solution of potassium carbonate (0.30 g, 2.24 mmol) in dry dimethylformamide (8 cm^3), triiodoimidazole (I) (0.500 g, 1.12 mmol) was added in small installments at room temperature. The reaction mixture was stirred for an hour and ethylbromoacetate (0.185 cm^3 , 1.12 mol) was added drop wise under nitrogen atmosphere. The stirring of the mixture continued for 4 h at room temperature and the product was extracted with ethyl acetate. The extract was dried over sodium sulphate. Evaporation of the ethyl acetate yielded compound (IV) (0.310 g, yield: 52%), having melting point at 196°C . IR (ν_{max} , cm^{-1}): 650 (Iodide absorption band) cm^{-1} : 1672 (Ester), 1520 (C=N), and 2840 (C–H). ^1H NMR (300 MHz, DMSO- d_6) δ 3.9 (2H, s, N–CH $_2$ –CO), 4.2 (2H, quar.), 1.1 (3H, t). Elemental analysis for compound (VI) $\text{C}_7\text{H}_7\text{I}_3\text{N}_2\text{O}_2$: Calculated: C, 15.78; H, 1.31; N, 5.26; found: C, 15.76; H, 1.49; N, 5.30%.

2.2.5. Preparation of 1-carboethoxy-2,4,5-trinitroimidazole (V)

1-Carboethoxy-2,4,5-triiodoimidazole (IV, 0.500 g) was added to the solution of fuming nitric acid (10 cm^3) stirred at 0°C . Reaction mixture was kept stirring for 1.5 h at 0°C , and subsequently for 4 h at 100°C . The contents were cooled and poured into crushed ice. Yellow precipitate obtained, was filtered and dried *in vacuo* resulting in the isolation of the title compound (V) of 0.139 g (yield: 45%) having melting point at $248\text{--}250^\circ\text{C}$. IR (ν_{max} , cm^{-1}): 1690 (ester), 1580 (–C–NO $_2$), 1560 (–C=N), 2900 (–CH). ^1H NMR (300 MHz, DMSO- d_6): 1.31 (3H, t), 4.23 (2H, quar. –OCH $_2$ –CH $_3$), 4.56 (2H, s, –N–CH $_2$ –CO–). Elemental analysis results of compound (V, $\text{C}_7\text{H}_7\text{N}_5\text{O}_8$): C, 29.06; H, 2.42; N, 24.22; found: C, 29.2; H, 2.49; N, 24.30%.

2.2.6. Preparation of 1-picryl-2,4,5-triiodoimidazole (VI)

Anhydrous potassium carbonate (0.30 g, 2.2 mol) was added to the stirred solution of 2,4,5-triiodoimidazole (0.500 g, 1.12 mmol) in dimethylformamide (10 cm^3) and the reaction mixture was kept stirring for an hour. Picryl chloride (0.277 g,

1.12 mmol) was added to it slowly. The contents were kept stirring for overnight at room temperature. The DMF was evaporated *in vacuo*, and compound was extracted with ethyl acetate. The extract was dried on sodium sulphate. The solvent was evaporated to dryness to yield the compound (VI) (0.73 g, yield: 53%), which melts at $202\text{--}204^\circ\text{C}$. IR (ν_{max} , cm^{-1}): 690 (iodide), 1560, 1585 (aromatic –C–NO $_2$), 2875 (–CH). ^1H NMR (300 MHz, DMSO- d_6): 8.90 (2H, s). Elemental analysis data obtained for $\text{C}_9\text{H}_2\text{I}_3\text{N}_5\text{O}_6$: Calculated: C, 16.43; H, 0.30; N, 10.65; found: C, 16.56; H, 0.44; N, 10.30%.

2.2.7. Preparation of 1-picryl-2,4,5-trinitroimidazole (VII)

1-Picryl-2,4,5-triiodoimidazole (VI, 0.500 g) was added in installments to the stirred solution of nitric acid (10 cm^3) at 0°C . The reaction mixture was stirred for additional 1 h at 0°C , and subsequently for 4 h at 100°C (until the evolution of iodine vapors ceases). Reaction mixture was cooled and poured into the crushed ice. The yellow precipitate obtained, was filtered and dried *in vacuo* to yield the title compound (VII) of 0.084 g (yield: 30%) having a melting point at $248\text{--}250^\circ\text{C}$. IR (ν_{max} , cm^{-1}): 1540 (C–N), 1572 (C=N), 1600 (C–NO $_2$) and 2900 (–C–H). ^1H NMR (300 MHz, DMSO- d_6): 9.17 (2H, s). Elemental analysis data obtained for $\text{C}_9\text{H}_2\text{N}_8\text{O}_{12}$: Calculated: C, 26.08; H, 0.48; N, 27.05; found: C, 26.22; H, 0.50; N, 27.23%.

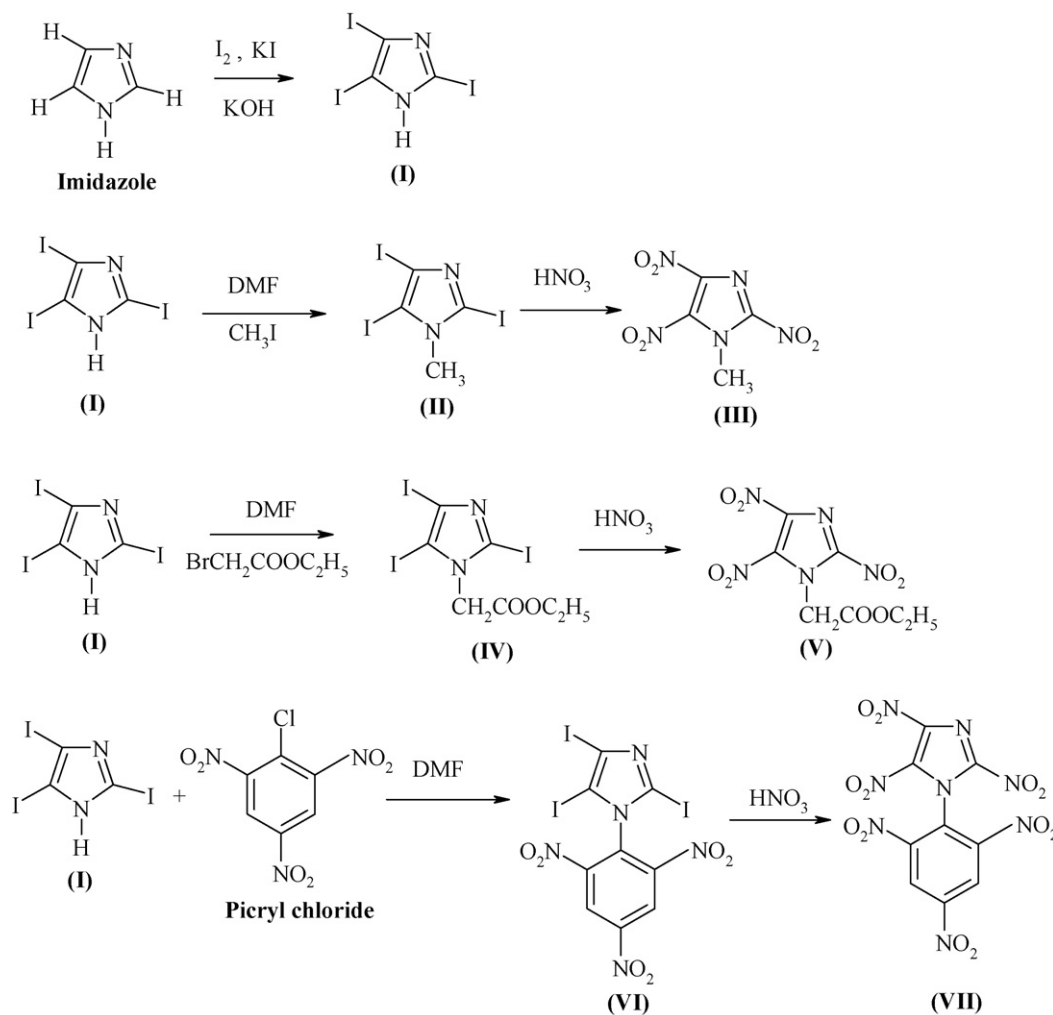
The various reaction steps involved in the synthesis of the above compounds are represented in Scheme 1.

3. Results and discussion

The preparation of 2,4,5-triiodoimidazole (I) by treatment of imidazole with aqueous alkaline iodine was first described by Dimorth and Hartmann [38] and Brunings [39] prepared (I) by a heterogeneous iodination procedure. However, we found that both methods are inconvenient and each yielding multiple component mixtures from which isolation of pure product was difficult. Idonn and co-workers [40] claimed the preparation of compound (I) by treatment of imidazole with aqueous potassium iodide/iodine. However, Lindell and Turner [41] reported that following Idonn's procedure also gave 4,5-diiodoimidazole. Katritzky et al. [12] have reported a convenient and high yielding method for the multigram preparation of (I) by the treatment of imidazole with aqueous alkaline potassium iodide/iodine. In addition, they also reported the conversion of di- to triiodoimidazole (I) in 97% yield.

3.1. Spectral study

The formation of compound 1-methyl-2,4,5-trinitroimidazole (III) was confirmed by infrared spectroscopy, in which nitro groups exhibited bands at 1575 cm^{-1} and the –N–CH, stretching frequency appeared at 2800 cm^{-1} . In the case of 1-carboethoxy-2,4,5-trinitroimidazole (V), ester functional group appeared at 1690 cm^{-1} , and the nitro group absorbs at 1580 cm^{-1} whereas in the case of 1-picryl-2,4,5-trinitroimidazole (VII), peaks at 1572 cm^{-1} (nitro group) as well as the –N–CH, stretching frequency at 2900 cm^{-1} confirms the presence of picryl moiety in the compound. Further, absence



Scheme 1. Synthesis scheme of imidazole derivatives.

of band at 660 cm^{-1} (carbon–iodine bond) again confirms the replacement of iodine by nitro group in all the compounds (**III**, **V** and **VII**). IR spectroscopy provided evidence in support of realization of nitro group and absence of carbon–iodine absorption band in the synthesized compounds.

In ^1H NMR spectrum, the protons of methyl group in compound (**III**) resonated downfield (δ 3.73) than those of methyl group (δ 2.89) of (**II**), due to the greater electro negativity of nitro groups than that of iodo group, and thereby further confirming the N-nitration. The insertion of ester functional group as well as nitro substitution in compound (**V**) is confirmed with the help of NMR results. In compound (**IV**), the $-\text{N}-\text{CH}_2$ protons were observed at δ 3.9 while in compound (**V**), a downfield shift (δ 4.5) was noticed due to introduction of strong electron attracting groups in the ring. The protons of picryl ring of compound (**VII**) appeared at δ 9.17, in contrast to δ 8.9 in case of (**VI**) in NMR spectrum.

3.2. Thermal characterization

The TG curve of compound (**III**) revealed weight loss in the temperature range of $130\text{--}200^\circ\text{C}$. Maximum weight loss

occurred at 196°C . The overall weight loss during this stage was about 80% whereas compound (**V**) exhibited 30% weight loss in TG, in the temperature region of $198\text{--}246^\circ\text{C}$. The compound left residue of 63.89% during decomposition, which may be due to the high negative oxygen balance (-58.28%) of the compound (**V**) compared to that of (**III**). The TG revealed two-stage decomposition for compound (**VII**). The first stage decomposition commenced at $175\text{--}239^\circ\text{C}$, with around 20% weight loss and the second stage accompanied with 24% loss in weight in the temperature region of $239\text{--}368^\circ\text{C}$. The compound left 50% residue during decomposition, probably due to its aromatic moiety. The higher thermal stability may be attributed to the presence of picryl group in the title compound (**VII**). The calculated energy of activation obtained from TG experiments for the title compounds (**III**), (**V**) and (**VII**) was 147, 172 and 169 kJ/mol, respectively.

3.3. Sensitivity study

The synthesized compounds such as 1-methyl-2,4,5-trinitroimidazole (**III**), 1-carboethoxy-2,4,5-trinitroimidazole (**V**) and 1-picryl-2,4,5-trinitroimidazole (**VII**) were subjected

Table 1
Theoretical performance properties of imidazole derivatives in comparison with other insensitive high-energy materials

HEM	MW	Elemental composition (%)				ρ (g/cm ³)	DF	VOD (km/s)	CJP (GPa)	RS (%)	SI (db)	HOE (kJ/kg)	PI (%)	ET (K)	VDP (l/kg)
		C	H	N	O										
Compound (III), C ₄ H ₃ N ₅ O ₆	217	22.11	1.38	32.25	44.21	1.78	5.10	35.58	138	350	4472	144	4500	870	
Compound (V), C ₇ H ₇ N ₅ O ₈	289	29.06	2.42	24.22	44.26	1.63	4.46	24.91	134	307	3543	139	3300	1062	
Compound (VII), C ₉ H ₂ N ₈ O ₁₂	414	26.08	0.48	27.05	46.35	1.91	4.88	34.36	124	345	4375	129	4500	798	
DNI, C ₃ H ₂ N ₄ O ₄	158	22.79	1.28	35.44	40.48	1.77	5.11	35.54	120	349	3782	125	3700	897	
TATB, C ₆ H ₆ N ₆ O ₆	258	27.91	2.34	32.56	37.18	1.79	4.58	28.46	101	322	2598	106	2600	1098	
DATB, C ₆ H ₅ N ₅ O ₆	243	29.63	2.07	28.8	39.48	1.84	4.49	27.9	104	320	2759	109	2700	1069	
NTO, C ₂ H ₂ N ₄ O ₃	130	18.47	1.55	43.08	36.9	1.93	5.07	37.46	116	356	3579	120	3400	908	
FOX-7, C ₂ H ₄ N ₄ O ₄	148	16.22	2.72	37.84	43.21	1.88	5.29	40.05	131	364	3873	137	3400	957	
TACOT, C ₁₂ H ₄ N ₈ O ₈	388	37.12	1.04	28.87	32.97	1.85	4.14	23.16	136	298	3486	141	3900	1095	
TNT, C ₇ H ₅ N ₃ O ₆	227	37.01	2.21	18.50	42.26	1.65	3.93	19.2	100	275	2685	113	2700	1114	
RDX, C ₃ H ₆ N ₆ O ₆	222	16.22	2.72	37.84	43.21	1.77	5.18	37.3	174	353	5041	181	4500	957	
HMX, C ₄ H ₈ N ₈ O ₈	296	16.22	2.72	37.84	43.21	1.77	5.23	39.49	173	355	5159	180	4500	957	

HEM: high energy material; MW: molecular weight; OB: oxygen balance; ρ : density; DF: detonation factor; VOD: velocity of detonation; CJP: Chapman-Jouguet pressure; SI: sound intensity; RS: relative strength; HOE: heat of explosion; PI: power index; ET: explosion temperature; VDP: volume of detonation products; compound (III): 1-methyl-2,4,5-trinitroimidazole; compound (V): 1-carboethoxy-2,4,5-trinitroimidazole; compound (VII): 1-picryl-2,4,5-trinitroimidazole; DNI: dinitroimidazole; TATB: 1,3,5-triamino-2,4,6-trinitrobenzene; DATB: diamino trinitro benzene; NTO: nitrotriazolone; FOX-7: diamino dinitroethylene; TACOT: tetranitro tetraaza pentalene; TNT: trinitrotoluene; RDX: hexahydro-1,3,5-trinitro-1,3,5-triazine; HMX: 1,3,5,7-tetranitramino octahydro-1,3,5,7-tetrazocine.

for impact and friction sensitivity tests to understand the safe nature of these materials. The experimentally determined friction sensitivity results revealed that all the three compounds are insensitive to friction stimuli (>36 kg). The experimentally determined impact sensitivity data for the title compounds **III**, **V** and **VII** was found 105, 108, and 102 cm, respectively. The sensitivity data obtained for the benchmark explosives such as RDX and TNT under identical conditions was in agreement with the reported sensitivity data.

3.4. Theoretical performance evaluation

The explosive properties of the synthesized compounds viz., 1-methyl-2,4,5-trinitroimidazole (**III**), 1-carboethoxy-2,4,5-trinitroimidazole (**V**) and 1-picryl-2,4,5-trinitroimidazole (**VII**) have been theoretically predicted by applying LOTUSES code and the results are presented in Table 1. The computed density for the newly synthesized compounds (**III**), (**V**) and (**VII**) are 1.78, 1.63 and 1.91 g/cm³, respectively. The theoretically computed velocity of detonation (VOD) for compound (**III**) was found on par with that of RDX, DNI and NTO. The calculated VOD values of compound (**III**) and (**V**) are superior to conventional explosives such as TATB, DATB, TACOT and TNT. The predicted heat of explosion of (**III**) and (**V**) are of 4472 and 4375 kJ/kg, respectively.

The relative strength (RS), power index (PI), sound intensity (SI), heat of explosion (HOE), CJ pressure and explosion temperature (ET), of these compounds (**III** and **V**) are also higher than TATB. Compound (**VII**) possesses a lower VOD and CJ pressure whereas it produces reasonable amount of gas volume of the order of 1062 l/kg. The predicted explosive properties of compound (**VII**) are on par with DATB and TNT. However the theoretically predicted performance parameters call for the in depth studies on the title compounds for their utility as an insensitive high performance high-energy material.

4. Conclusions

The present investigation demonstrates the synthesis of three new derivatives of 2,4,5-trinitroimidazole namely, 1-methyl-2,4,5-trinitroimidazole (**III**), 1-carboethoxy-2,4,5-trinitroimidazole (**V**) and 1-picryl-2,4,5-trinitroimidazole (**VII**). The newly synthesized compounds have been characterized by elemental and spectral analysis data. The thermal analysis of these compounds revealed the exothermic decomposition establishing their possible candidature as HEMs. Sensitivity data obtained suggested the insensitive nature of these compounds towards impact and friction stimuli. The theoretically predicted performance potential of compounds (**III**) is on par with the RDX and compound (**V**) is on par with the TNT. The theoretically predicted performance parameters coupled with experimentally obtained sensitivity characteristics indicated the potential of these nitroimidazoles for futuristic low vulnerable applications.

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