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Synthesis, characterization and thermolysis of polynitrohexahydropyrimidines: Potential high energy materials

H S Jadhav[a], M B Talawar[a,b*], R Sivabalan[b], D D Dhavale[a], S N Asthana[b] & V N Krishnamurthy[c]

[a]Department of Chemistry, University of Pune, Pune 411 007, India
[a]High Energy Materials Research Laboratory, Pune 411 021, India
[c]Defence Research & Development Organization (DRDO)/Indian Space Research Organization (ISRO) Cell
University of Pune, Pune 411 007, India

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A relatively new entrant to the class of high energy materials, viz., 1,3,5-trinitro-5-methyl-hexahydropyrimidine (MTNP) has been synthesized during this work by nitration of 1,3-di-tert-butyl-5-nitro-5-methyl hexahydropyrimidine with fuming nitric acid. The synthesized molecule (MTNP) has been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR spectroscopy. TG of the compound showed two-step decomposition in the temperature range of 170-200°C and 205-350°C accompanied with 50 and 25% weight loss, respectively. The sensitivity data of MTNP obtained for the synthesized compound indicates its low vulnerability towards external stimuli (impact height, $h_{50\%}$ > 100 cm and friction insensitive up to 36 kg). The velocity of detonation of MTNP has been computed using Linear Output Thermodynamic User-friendly Software for Energetic Systems (LOTUSES) code. The theoretically computed VOD of 7450 m/s is intermediate to that of 2,4,6-trinitrotoluene, TNT (6600 m/s) and 1,3,5-triamino-2,4,6-trinitrobenzene, TATB (7860 m/s) coupled with insensitive nature are attractive features from the point of view of its applications in insensitive munitions. In addition to compound MTNP, synthesis and characterization of some of the promising polynitrohexahydropyrimidines have also been reported.

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The search for the high energy dense materials (HEDMs) has led to the development of vast number of oxidizers, fuels and high explosives with novel as well as fascinating structures for possible use in ordnance. Explosives with thermal decomposition temperature > 250°C usually termed as heat resistant or thermally stable explosives find applications in space vehicles, drilling of deep oil wells and supersonic guided missiles[1-3]. The quest for the development of new and novel high energy dense materials (HEDMs) in the last decade led to path breaking research leading to the emergence of the most powerful explosives known to date, viz., dinitroazoxyfurazan (DNAF), hexanitrohexaazaiso-wurtzitane (HNIW) and octanitrocubane (ONC). In the current scenario, molecules like hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 1,3,5,7-tetranitramino-octahydro-1,3,5,7-tetrazocine (HMX) are the most widely used high explosives[4-8].

Pyrimidines like 1,3,5-trinitrohexahydropyrimidine (TNP) and 1,3,5,5-tetranitro hexahydropyrimidine (TTNP)[9-15] have also evinced interest as HEDMs. The synthesis of TTNP has been reported elsewhere[16,17]. Brill *et al.*[18] reported the thermal decomposition of TTNP applying T-jump/FTIR technique suggesting that TTNP and RDX thermolyse by different routes. They found that the NO is a major product of the thermolysis of TTNP, however it does not exhibit influence on the primary flame zone. Interestingly, the primary flame zone of TTNP appears to be dominated by the reaction of CH_2O and NO_2 in corollary with RDX, leading to similar rate of combustion. Oyumi *et al.*[19] reported the thermal decomposition of nitro hexahydropyrimidine derivatives. Ritter *et al.*[20,21] synthesized 5-azidomethyl 1,3,5-trinitrohexahydropy-rimidine (AMTNP) and nitratomethyl 1,3,5-trinitrohexahydropyrimidine (NMTNP). Wang *et al.*[22] studied the decomposition pathways for trinitropyrimidines. Chapman *et al.*[23] synthesized 5,5-*bis*(difluoramino)hexahydro-1,3-dinitropyrimidine (RN FX) by reacting *N,N′-bis* (substituted alkane- or arenesulfonyl) tetrahydropyrimidin-5 (4H)-ones with fluorimide, and subsequent nitration of the resulting 5,5-*bis* (difluoramino) with simultaneous *N*-desulfonation by a nucleophile. Finally, the cyclization

*For correspondence (E-mail: mbtalawar@yahoo.com)

with formaldehyde led to the formation of RNFX, which is used as a component of propellants and explosives.

In view of the above observations coupled with scanty information available on the nitro hexahydropyrimidine derivatives, we report here the well established lab scale synthesis of 1,3,5-trinitrohexahydropyrimidine **(TNP, 3),** 1,3,5,5-tetranitrohexahydro pyrimidine **(TTNP, 4)** and 5-azidomethyl-1,3,5-trinitrohexahydropyrimidine **(AM-TNP, 7)**, 5-nitroxymethyl-1,3,5-trinitrohexahydropyrimidine **(MTNP, 8)** and 1,3,5-trinitro-5-methyl-hexahydropyrimidine **(TNMP, 10)** based on the lines of the reported methods[9,12,24,25]. During this work, azidomethyl, nitro and nitratomethyl groups were introduced in TNP at carbon position 5 with the aim of realizing a combination of density and energetic performance. The information on the synthesis of AMTNP, TNMP and MTNP available literature[25] is limited. The synthesized compounds have been characterized spectroscopically (IR and NMR) and subjected to thermal studies (DTA/TGA) as well as sensitivity test (impact and friction). The results are discussed in the light of the reported findings. Various detonation parameters have been theoretically computed using Linear Output Thermodynamic User-friendly Software for Energetic Systems (LOTUSES) code and compared with those of well-known explosives, RDX, HMX, trinitro toluene (TNT), dinitro imidazole (DNI) and nitrotriazolone (NTO).

Materials and Methods

Procedure

The melting point of the synthesized compounds was measured using Thomas Hoover capillary melting point apparatus. Elemental analysis was carried out on Perkin-Elmer instrument. The IR spectra were determined as nujol mull on a Perkin Elmer-1600 FTIR spectrophotometer. Proton NMR spectra were recorded on Varian 300 MHz spectrometer with tetramethyl silane as internal standard. The 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 cm^3/min. DSC was obtained on Perkin-Elmer –7 system at a heating rate of 10 °C/min in nitrogen atmosphere. Energy of activation was calculated from TG data by applying the method of Madhusudnan *et al*.[26]. The impact test was conducted using a set-up similar to that used in Naval Ordnance Laboratory (NOL), USA. The test specimens (30-35 mg of powder) were kept between two hardened stainless steel 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. The results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample. The friction test was conducted with the sample kept between a fixed corrugated (rough) and a movable stainless steel plate. The pulling of the movable plate at varying lever loads subjected sample to friction stimuli of different orders. The sample size and the procedure were same as followed for impact testing. The performance parameters of the newly synthesized compounds were also predicted using Linear Output Thermodynamic User friendly Software for Energetic Systems (LOTUSES) code[27-29].

Materials

The starting materials of AR grade were used directly as purchased from the trade. All the chemicals were of Merck and Aldrich make.

Preparation of 1,3-Di-tert-butyl-5-(tert-butylaminomethyl)-5-nitro-hexahydropyrimidine (1)

An aqueous solution of formaldehyde (32 cm^3, 0.40 mol; ≈ 37% solution) was added to a solution of *t*-butylamine (22.0 g, 26.8 mmol) in methanol (200 cm^3) and the mixture was stirred at 0°C for 10 min. Subsequently, nitromethane (5.4 cm^3, 0.10 mol) was added. A white solid precipitate was obtained after 2 h. The flask was allowed to cool down in ice, and the crystals were isolated by filtration to obtain 26 g (yield 75 %) of title compound (**1**), having melting point of 104-106ºC.

Preparation of –5(tert-butylaminomethyl) –1,3,5-trinitro-hexahydropyrimidine (2)

Compound (**1**) (2.47 g, 7.5 mmol) was added to 98% sulphuric acid (25 cm^3, 0.5 mol) under stirring for over 2 h while maintaining the temperature less than 10ºC until solution acquired orange colour. Stirring was continued for another 20-30 min at 0°C, and then conc. nitric acid (6.25 cm^3, 0.15 mol) was added dropwise. The solution was stirred for additional 20-30 min at 0°C. The reaction was quenched by pouring the contents on ice water slurry. The precipitate formed was isolated by filtration and washed with ether as well as acetone to obtain the nitrate salt (**2**) as white solid (2.0 g, 73% yield), having melting point of 152-154°C.

Preparation of 1,3,5-trinitrohexahydropyrimidine (TNP, 3)

Compound (**2**) (6.32 g, 17 mmol) was dissolved in aqueous ethanol (30 cm^3, 81 %) and contents were refluxed for 2 h to obtain the title compound (**3**), which precipitated out on cooling as sparkling white crystal in the from of plates (2.5 g, 75% yield) having the melting point of 140-142 °C. IR in cm^{-1}(ν max): 763, 954 (ring), 1560 (C-NO_2), 1580 (N-NO_2), 1377, 1457, 1572, 3172 (-CH stretching). ^{1}H NMR (300 MHz, $CDCl_3$): 4.55 (2H, dd, J=4.7&16.7), 5.20 (2H, dd, J=4.77, 16.7), 5.27 (1H, quin.), 5.60 (1H,d, J=16.7), 6.71 (1H,d, J=16.7);. C, H, N, O content analysis calculated for $C_4H_7N_5O_6$: C: 21.72, H: 3.19, N: 31.68%; Found: C: 21.77, H: 3.18, N: 31.78%.

Preparation of 1,3,5,5-tetranitrohexahydropyrimidine (TTNP, 4)

Compound **3** (0.750 g, 3.339 mmol) was dissolved in a solution of sodium hydroxide (0.162 g, 4.05 mmol) in water (10 cm^3) and cooled down to 0°C. A chilled solution of sodium nitrite (2.34 g, 27 mmol) and potassium ferricyanide (1.11 g, 3.339 mmol) in water (10 cm^3) was added, followed by sodium persulphate (1.28 g, 10.6 mmol). The temperature increased rapidly to 30°C. Subsequently, the contents were stirred for 1 h, and then extracted with dichloromethane. The combined extracts were dried on sodium sulphate, and the solvent was evaporated to obtain the compound **4**, having the melting point 150-152°C (lit.153-154°C). IR in cm^{-1} (ν_{max}): 862 (ring), 1342 (-CH_2), 1377, 1460, 1533(-C-NO_2) and 1558 (Gem dinitro). ^{1}H NMR (300 MHz, DMSO-d_6): 5.24 (s, 4H), 6.71(s, 2H). C, H, N, O content analysis calculated for $C_4H_6N_6O_8$: C, 18.04; H, 2.25; N, 31.58%. Found: C, 18.0; H, 2.36; N, 31.30%.

Preparation of 5-hydroxymethyl 1,3,5-trinitrohexahydrop-yrimidine (5)

A saturated solution of potassium carbonate (1.5 cm^3) in formalin (5 cm^3, 0.1 mol: 37%) was added to the solution of **3** (5.55 g, 25 mmol) in ethyl acetate (250 cm^3). The reaction mixture was stirred for 4 hours at room temperature, and then the ethyl acetate solution was decanted from the solid residue. The solution was dried over anhydrous sodium sulphate, and concentrated to obtain viscous oil. The product was subjected to column chromatography (hexane/ethyl acetate 3:7) to obtain the title compound **5** (5.6 g, 89%), having the melting point 138-140° C, (rep. 140-142°C). IR in cm^{-1} (ν_{max}): 868 (ring), 1342, 1355, 1420, 1565 (-C-NO_2), 3450 (-OH group). ^{1}H NMR (300 MHz, DMSO-d_6): 4.12 (1H, d), 4.16 (1H, d), 5.17 (2H, d), 5.21 (2H, d), 6.71 (1H,d), 6.88 (1H,d), 3.8 (1H, bs, - OH). Elemental Analysis calculated for $C_5H_9N_5O_7$: C, 23.90; H, 3.58; N, 27.88%. Found: C, 23.53; H, 3.76; N, 28.12%.

Preparation of 5-tosylmethyl-1,3,5-trinitrohexahydropyrimidine (6)

Compound **5** (1 g, 3.9 mmol) was dissolved in pyridine (10 cm^3) and *p*-toluene sulphonyl chloride (1.2 g, 6.3 mmol) was mixed with 10 cm^3 of pyridine separately. Both the liquids were transferred to a refrigerator. After cooling down to ~15°C, the liquids were mixed and stirred for 30 min. This mixture was placed into a refrigerator for 12 h, then poured onto crushed ice. A yellow precipitate obtained was filtered and washed with water. It was recrystallized from methanol to obtain **(6)** as a pale yellow solid (1.5 g, 78%) having the melting point of 187-190°C. IR in cm^{-1}(ν_{max}): 890 (ring), 1070 (S=O stretching), 1365, 1520 (Aromatic), 1565 (-C-NO_2). 1H NMR (300 MHz, $CDCl_3$): 2.5 (3H, s), 4.2 (2H, s), 4.5 (2H, d), 4.7 (2H, d), 5.7 (1H, d), 5.8 (1H,d), 7.4 (2H, d), 7.82 (2H, d); C, H, N, O content analysis calculated for $C_{12}H_{15}N_5SO_9$: C, 35.55; H, 3.70; N, 17.28%. Found: C, 35.63; H, 3.76; N, 18.00%.

Preparation of 5-azidomethyl 1,3,5-trinitrohexahydropyrimidine (AMTNP, 7)

A mixture of (**6)** (0.500 g, 1.97 mmol) and sodium azide (0.256 g, 3.9 mmol) in anhydrous DMF (10 cm^3) was stirred at 100°C for 12 h. The contents were extracted with ethyl acetate. The organic layer was dried and concentrated to obtain azido compound (**7)** (0.255 g, 75 %) as a pale yellow solid, having melting point 125-127°C (rep.128-129°C). IR in cm^{-1} (ν_{max}): 835 (ring), 1379, 1454, 1527 (-C-NO_2), 1568 (-N-NO_2) and 2142 (-N_3). ^{1}H NMR (300 MHz, $CDCl_3$): 3.05 (2H,s), 4.31 (2H,d), 4.75 (2H, d) 5.86 (2H, AB quartet) C, H, N, O content analysis calculated for $C_5H_8N_8O_6$: C, 21.73; H, 2.89 N, 47.57%. Found: C, 21.75; H, 2.92; N, 47.57%.

Preparation of 5-nitroxymethyl 1,3,5-trinitrohexahydrop-yrimidine (NMTNP, 8)

The compound (**5)** was added to 15.6 cm^3 (216 mmol) of cold conc. nitric acid in small portions under stirring 6.25 g (24.9 mmol) while maintaining temperature at 0-5°C. The stirring was continued for two hour. The compound (**8)** precipitated out on drop-wise addition of 15 cm^3 of sulfuric acid. The solid was filtered, washed with ice water and dried to obtain 4.93g (80%) of the title product. The product was recrystallized from methanol to yield white

crystals, having melting point 145-147°C. IR in cm^{-1} (ν_{max}): 738 (ring), 1377, 1458, 1508, 1544 (C-NO_2), 1560 (N-NO_2), 1627 (ONO_2). ^1H NMR (300 MHz, $CDCl_3$): 3.88 (2H,d), 4.06 (2H,s), 5.00 (1H, d), 5.21 (2H, d), 6.81 (1H, d); C, H, N, O content analysis calculated for $C_5H_8N_6O_9$: C, 20.27; H, 2.70; N, 28.37%. Found: C, 20.52; H, 2.62; N, 28.38%.

The synthesis of compounds **(1), (2), (3), (4), (5), (6), (7)** and **(8)** have been presented in Scheme 1.

Preparation of 1,3-Di-tert-butyl-5-nitro, 5-methyl–hexahydropyrimidine (9)

5 cm^3 of 37% formaldehyde solution along with tert-butylamine (1.4 g, 10.07 mmol) was added to a solution of nitroethane (1.5 g, 17.8 mmol) in 15 cm^3 of methanol. The mixture was stirred overnight, and then cooled to –10°C. The precipitated solid was collected by filtration and dried. It was purified by column chromatography (15% ethyl acetate/hexane) to obtain the title compound **9** (1.2 g, 50%) as a white crystalline solid, having melting point 75-77 °C. IR in cm^{-1} (ν_{max}): 870 (ring), 1300, 1535 (-C-NO_2). ^1H NMR (300 MHz, $CDCl_3$): 1.1 (18H, s), 1.5 (3H, s), 2.34 (2H, d), 2.88 (2H, d), 3.62 (2H, d), 3.85 (2H, s). Elemental analysis calculated for $C_{13}H_{27}N_3O_2$: C, 60.70; H, 10.50; N, 16.34%. Found: C, 60. 56; H, 10.20; N, 16.46%.

Preparation of 5-methyl 1,3,5-trinitrohexahydropyrimidine (MTNP, 10)

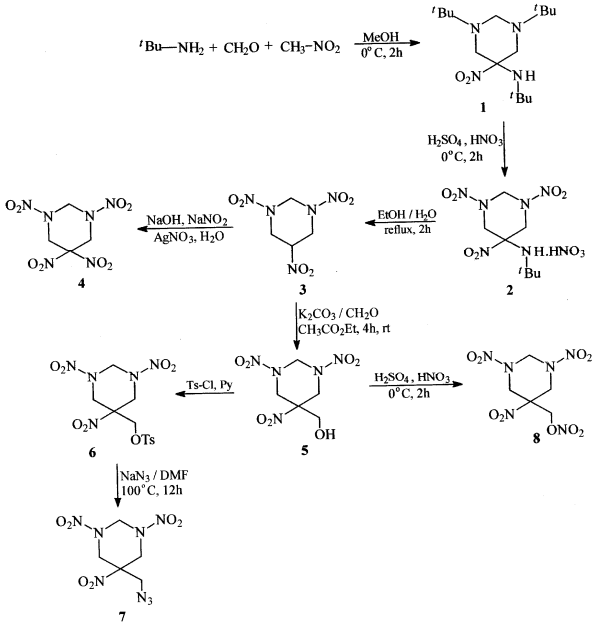
Compound **9** (0.500 g, 1.94 mmol) was added slowly to the cooled fuming nitric acid (8 cm^3) at rate such that the temperature was maintained at about 10°C. The mixture was stirred for 1 h, and then poured on crushed ice. The white precipitate obtained was isolated by filtration and recrystallised from ethanol (0.338 g, 74% yield). It gave melting point of 164-166 °C (rep. 167-168°C). IR in cm^{-1} (ν max): 885 (ring), 1384, 1452, and 1539 (-C-NO_2), 1560 (-N-NO_2). ^1H NMR (300 MHz, $CDCl_3$): 1.69 (3H, s), 4.04 (2H,d, J= 15 Hz), 5.18 (2H, d, J=15 Hz), 5.26 (1H, d, J= 15 Hz), 6.76 (1H, d, J= 15 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): 20.0 (-CH_3), 51.76 (C4, 6), 59.00 (C2) and 81.97 (C5). Elemental analysis calculated for $C_5H_9N_5O_6$: C, 25.52; H, 3.83; N, 29.79%. Found: C, 25.87; H, 3.60; N, 30.00%. Scheme 2 represents the synthesis of **MTNP (10)** and its precursor **(9)**.

Results and Discussion

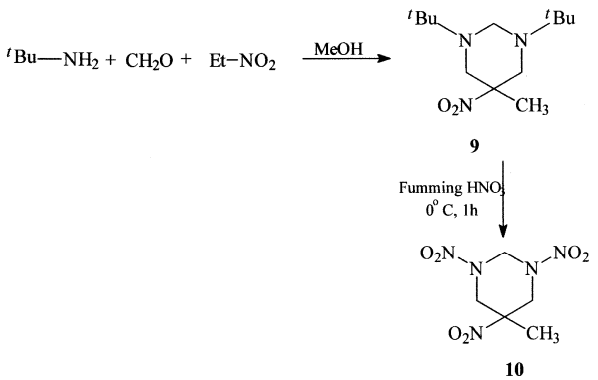
Spectroscopic studies

IR spectra of TNP **(3)** showed peaks at 1560 and 1580 cm^{-1} indicating the presence of C-NO_2 and N-NO_2 groups respectively. The bands observed at 763 and 954 cm^{-1} suggest the formation of ring. In the ^1H NMR spectra, C2 protons appeared as a doublet with a geminal coupling constant of 16.7 Hz and C5 protons appeared at δ 5.27. The C4, and C6 protons appeared as doublet of doublet (dd) at δ 4.7 and 16.7 respectively. ^{13}C NMR showed signal at the δ 48 (C4 and C6), 62 (C5) and 76 (C2). The IR spectra of **(TTNP, 4)** exhibited band at 862 cm^{-1} confirming the ring structure. The IR bands at 1377 and 1533 cm^{-1} confirmed the presence of geminal dinitro functional groups in the molecule and the absorption at 1558 cm^{-1} revealed the presence of N-NO_2 groups. The ^1H NMR spectra of the synthesized compounds showed two singlets at δ 5.24 and 6.72 with integration corresponding to its structure.

The conversion of TNP **(3)** to 5-hydroxymethyl-1,3,5-trinitrohexahydro-pyrimidine **(5)** followed by tosyalation to **(6)** and subsequent azidation yielded 5-



Scheme 1



Scheme 2

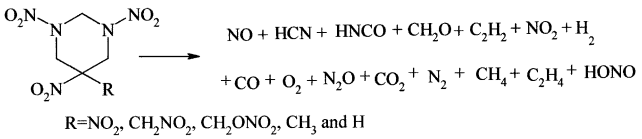
azidomethyl-1,3,5- trinitrohexahydropyrimidine **(AM TNP, 7).** The IR spectrum of **(7)** exhibited band at 2142 cm^{-1} confirming the presence of azide functional group. The absence of aromatic region in ^1H NMR is indicative of the complete replacement of tosyl group by azide. The IR peaks at 1527 and 1568 cm^{-1} can be accounted for C-NO_2 and N-NO_2 respectively. In ^1H NMR spectrum, compound **(7)** resonated and shows singlet at δ 3.05, doublet at δ 4.31 and δ 4.75 as well as quartet at δ 5.80.

The nitration of **(5)** with concentrated nitric and sulphuric acid combination yielded 5-nitroxymethyl-1,3,5-trinitrohexahydropyrimidine **(NMTNP, 8).** The IR peaks obtained for compound **(8)** at 1508, 1560 and 1627 cm^{-1} may be attributed to C-NO_2, N-NO_2 and O-NO_2 respectively indicating the presence of nitro, nitramino and nitrate ester functional groups in the molecule. The band observed at 738 cm^{-1} suggests ring structure. The ^1H NMR spectra showed the presence of methylene protons by a singlet at δ 3.88.

The condensation of *t*-butylamine with formaldehyde and nitroethane yielded 1,3-ditertiarybutyl-5-nitro-5 methylhexahydropyrimidine **(9)**, which on nitration by fuming nitric acid afforded 5-methyl-1,3,5-triniitrohexahydro pyrimidine **(MTNP, 10)**. The IR spectrum of **10** showed the presence of nitro group at 1384 and 1539 cm^{-1}. In ^1H NMR, compound **10** showed C5 methyl proton at δ 1.69 and C2 methylene protons as doublet at δ 5.26 and 6.76. The methylene protons at C4 and C6 appeared at δ 4.04 and 5.18. The ^{13}C data exhibited four singlets at δ 20 (methyl), 51 (C4, 6), 59 (C2) and 82 (C5) in line with the structure features. The spectral data obtained for these compounds synthesized during this work are in agreement with the reported values[15-17].

Thermal analysis

TG of trinitrohexahydropyrimidine (**TNP**, **3**) revealed that it decomposes in two consecutive steps, in the temperature range of 142-160°C and 160-500 °C accompanied with the weight loss of 75 and 14% respectively. The energy of activation of its decomposition was found to be 200 kJ/mol. Other compounds such as **TTNP (4**), **AMTNP (7), NMTNP (8)** and **MTNP (10**) also decompose in two steps. The decomposition temperature with corresponding weight loss along with energy of activation is presented in Table 1. The decomposition of hexahydro nitropyrimidine have established as per the following general scheme[18,19].



They observed that the substitution of groups at the 5th position of TNP have major influence on the decomposition of most of these molecules. TG data obtained during this work suggests that the major decomposition step shifted to higher temperature on insertion of methyl group **(10)** at 5th position in TNP whereas introduction of nitro **(4)**, nitratomethyl **(8)** and azidomethyl **(7)** at this position resulted in the shift to lower temperature.

Sensitivity evaluation

The title compound trinitrohexahydropyrimidine (**TNP**, **3**) gave $h_{50\%}$ > 100 cm in impact sensitivity test and was found friction insensitive up to 36 kg load. These results (Table 1) reveal that TNP (**3**) is safer

Table 1—Explosive and thermal properties of compounds (**3**), (**4**), (**7**), (**8**) and (**10**)

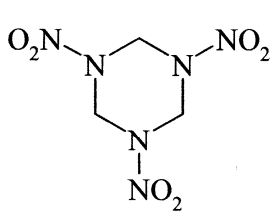
Properties	TNP (**3**)	TTNP (**4**)	AMTNP (**7**)	MTNP (**8**)	MTNP (**10**)
TGA % weight loss (Temperature range, °C)					
1st step	75 (142-160)	57 (120-283)	45 (125-192)	60 (110-156)	50(170-200)
2nd step	14 (160-500)	18 (190-400)	18 (192-400)	25 (160-395)	25(205-350)
Activation energy (kJ/mol) (Major step)	200	153	115	102	205
Frequency factor (*A*) (Major step)	20.97	14.28	11.56	9.87	22.34
Correlation co-efficient (*r*)	0.9987	0.9985	0.9867	0.9889	0.9874
Order (*n*)	1.8	1.8	1.8	1.8	1.8
Impact sensitivity ($h_{50\%}$), cm	> 100	85	90	85	>100
Friction insensitivity (kg)	>35	35	35	30	>35

Sensitivity to impact: RDX, 28-30 cm; HMX, 23-25, Tetryl, 74-78 cm

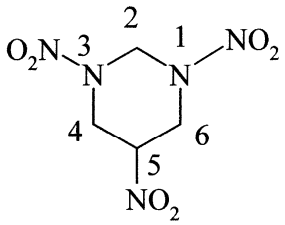
Table 2—Theoretical performance properties of compounds (**3**), (**4**), (**7**), (**8**) and (**10**)

HEM	MW	Elemental composition (%)				OB	ρ	ΔH_f	DF	VOD	CJP	RS	SI	HOE	PI	ET	VDP
		C	H	N	O	(%)	g/cm^3	kJ/mol		km/s	(GPa)	(%)	(db)	kJ/kg	(%)	(K)	(l/kg)
MTNP (**10**) $C_5H_9N_5O_6$	235	25.53	3.85	29.7	40.8	-57.82	1.72	0	4.35	7.451	24.77	145	306	3405	152	2800	1205
NMTNP (**8**) $C_5H_8N_6O_9$	296	20.28	2.72	28.4	48.6	-27.0	1.79	-132	4.8	8.30	31.80	160	336	4710	167	3900	957
AMTNP (**7**) $C_5H_8N_8O_6$	276	21.74	2.91	40.5	34.7	-46.34	1.74	+275	4.82	8.304	31.05	155	333	3897	160	3300	1112
TTNP (**4**) $C_4H_6N_6O_8$	266	18.05	2.27	31.5	48.0	-18.03	1.82	+8.37	5.12	8.835	36.43	173	353	5498	180	4900	887
TNP (**3**) $C_4H_7N_5O_6$	221	21.72	3.19	31.6	43.0	-39.79	1.78	-40.08	4.71	8.091	30.02	153	329	4029	159	3300	1068
TATB $C_6H_6N_6O_6$	258	27.9	2.34	32.56	37.18	-55.78	1.79	-139	4.58	7.86	28.46	80	322	2057	84	2100	1098
DNI $C_3H_2N_4O_4$	158	22.97	1.27	35.44	40.48	-30.36	1.77	+21	5.11	8.82	35.54	120	349	3782	125	3700	897
TNT $C_7H_5N_3O_6$	227	37.01	2.21	18.50	42.26	-73.96	1.66	-63	3.92	6.66	19.26	100	275	2676	113	2600	1114
NTO $C_2H_2N_4O_3$	130	18.47	1.55	43.08	36.90	-24.60	1.93	-112	5.07	8.752	37.46	88	356	2719	91	2700	908
RDX $C_3H_6N_6O_6$	222	16.22	2.72	37.84	43.21	-21.61	1.77	+71	5.17	8.93	36.48	174	353	5098	181	4400	957
HMX $C_4H_8N_8O_8$	296	16.22	2.72	37.84	43.21	-21.61	1.77	+87	5.23	9.04	39.49	173	355	5073	180	4400	957

HEM: High energy material; MW: Molecular weight; OB: Oxygen balance; ρ: Density; ΔHf: Heat of formation; 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; MTNP: 5-Methyl-1,3,5-trinitro-hexahydropyrimidine; TTNP: 5-Nitro-1,3,5-trinitro-hexahydropyrimidine; TNP: 1,3,5-trinitro-hexahydro pyrimidine AMTNP: Azidomethyl-1,3,5-trinitro-hexahydropyrimidine; NMTNP: 5-nitroxymethyl-1,3,5-trinitro-hexahydropyrimidine; TATB: 1,3,5-Triamino-2,4,6-Trinitrobenzene; DNI: Dinitroimidazole; TNT: Trinitrotoluene; NTO: Nitrotriazolone; RDX: hexahydro-1,3,5 -trinitro-1,3,5-triazine; HMX: 1,3,5,7-tetranitramino octahydro-1,3,5,7-tetrazocine.



RDX



TNP

than RDX ($h_{50\%}$ of >32 cm and friction insensitive up to 17-18 kg load), which may be due to the presence of a C-NO_2 group in the molecule in place of N-NO_2 group in RDX.

5-methyl- 1,3,5-trinitrohexahydropyrimidine **(MTNP, 10)** gave sensitivity test results similar to those for **(TNP, 3).** The title compounds **(TTNP, 4), (AMTNP, 7)** and **(NMTNP, 8)** were marginally more sensitive to impact ($h_{50\%}$ 85-90 cm) and friction (30-35 kg) stimuli in comparison to **(TNP, 3)** and **(MTNP, 10).** It is difficult to pin point the mechanism, as the initiation of explosives by impact and friction stimuli is a complex phenomenon, which does not depend only on the molecular structure but also on several physical factors such as crystal hardness, shape and size as well as thermal conductivity. However, the relatively low vulnerability of compound (**3**) and (**10**) to initiation compared to **TTNP** (**4**), **AMTNP** (**7**) and **NMTNP** (**8**) can be correlated with their relatively higher value of their energy of activation (198 and 205 kJ/mol respectively).

Performance evaluation

The performance parameters of (**3**), (**4**), (**7**), (**8**) and (10) have been theoretically predicted by applying LOTUSES code are given in Table 2. The computed density for the newly synthesized compound (**10**) was found to be 1.72 g/cm^3. The velocity of detonation (VOD) of (**4**) as computed by applying LOTUSES code was found on par with that of RDX, DNI and NTO whereas compounds (**3**), (**7**) and (**8**) gave theoretical VOD higher than that of the conventional explosives such as triaminotrinitrobenzene (TATB) and trinitrotoluene (TNT). The higher VOD, relative strength (RS) power index (PI), sound intensity (SI), heat of explosion (HOE), volume of detonation products (VDP) and explosion temperature (ET) of compound (**4**) may be due to optimization of the oxygen balance resulting in desirable combination of the flame temperature and mean molecular weight of decomposition product. The introduction of methyl group (**10**) at C5 in trinitrohexahydropyrimidine led to

increase in RS, HOE, ET and VDP in comparison to those of the well known explosives, viz., TATB, NTO and TNT. The predicted velocity of detonation and CJ pressure of **10** were higher than those of TNT. However, the theoretically predicted performance potential of compound (**10**) was found lower than that of (**8**), (**7**), (**4**) and (**3**). This may be attributed to decrease in density as well as increase in negative value of oxygen balance (Table 2).

Conclusions

1,3,5-Trinitro-5-methyl hexahydropyrimidine (**TN MP**, **10**) – a derivative of 1,3,5-trinitrohexahydropyrimidine was synthesized by the nitration of 1,3-ditert butyl-5-methyl hexahydropyrimidine using nitric acid. In addition to **(10)**, a lab scale process for the synthesis of most sought after potential poynitro hexahydropyrimidines viz., 1,3,5-trinitrohexahydropyrimidine **(3),** 1,3,5,5-tetranitrohexahydropyrimidine **(4),** 5-azidomethyl-1,3,5-trinitrohexahydro pyrimidine **(7)** and 5-nitromethyl-1,3,5-trinitrohexahydropyrimidine **(8)** was also established. The thermal analysis studies indicated that the compound **(10)** is relatively more stable and less vulnerable to mechanical stimuli than polynitrohexahydropyrimidines **(4), (7)** and **(8)**. The title compound **(4)** could be of interest as high performance energetic ingredient for high explosive formulations whereas the title compound **(7)** may find application as melt castable high explosive ingredient. However, one has to establish the non-conventional process for its melting in view of its melting point of the order of 128°C. Compound (**3)** may find application in insensitive munitions (IM). Compound (**10)** may be of interest for relatively thermally stable low vulnerable ammunition (LOVA) and explosives (LOVEX). These compounds can be synthesized in large scale from inexpensive starting materials, and thereby are attractive for futuristic applications.

References

1 Licht H H & Ritter H, *Propellant, Explos, Pyrotech,* 22 (1997) 333.

2 Heming X, Jianfen F & Xuedong G, *Propellants, Explos, Pyrotech***,** 22 (1997) 360.

3 Mehilal, Salunke R B, Sikder A K & Agarwal J P, *J Hazard Mater*, A84 (2001) 117.

4 Sikder A K, Maddala G, Agarwal J P & Singh H, *J Hazard Mater*, A 84 (2001) 117.

5 Krishnamurthy V N, *Proc Third Int Conf High Energy Materials and Exhibit,* Thiruvananthapuram, India, Dec. 6-8, 2000, 72.

6 Krishnan S, Chakravarthy S R & Athithan S K, *Propellants and Explosive Technology*, Course notes of the Professional Development Short Term Course conducted at IIT Madras, India, Dec. 6-7 (1998).

7 Varghese T L & Nainan K N, *Propellants and explosives technology* (Allied Publishers Limited, Chennai, India) 1998, 419.

8 Delvin S, *Explosives*, 1st ed, (Sarup and Sons Publishers, New Delhi, India), 2000.

9 Ritter H & Licht H H, *Propellants, Explos, Pyrotech,* 10 (1985) 147.

10 Senkus M, *J Am Chem Soc,* 72 (1946) 10.

11 Cichra D A & Adolph H G, *J Org Chem,* 47 (1982) 2474.

12 Levins D A, Bedford C D & Staats S J, *Propellant, Explos, Pyrotech,* 8 (1983) 74.

13 Urbanski T, *Synthesis*, 54 (1974) 613.

14 Baer H H & Urbas L, *Chemistry of nitro and nitroso groups*, edited by Feuer H (John Wiley & Sons, New York), Pt 2 (1970) 75.

15 Prabhakaran K V, Naidu S R & Kurian E M, *Propellants, Explos, Pyrotech*, 20 (1995) 238.

16 Remennikov G Y, Shavaran S S, Boldyrev I V, Kurilenko L K, Klebanov B M, Kukhar V P, *Inst Bio-org Khim. Neftekhim*., Kiev, USSR. Khimiko- Farmatsevticheskii Zhurnal 25(3) (1991) 35-37. CAN 115:71520 AN 1991:471520.

17 Blackburn M G, Beadham I G, Adams H, Hutchinson A P & Nicklin S, *J Chem Soc, Perkin Trans,* 1 (2) (2000) 225.

18 Brill T B, Patil D G, Duterque J & Lengelle G, *Combust Flame*, 95 (1993) 183.

19 Oyumi Y & Brill T B, *Combust Flame*, 62 (1986) 225.

20 Ritter H & Robert P, Report, (1986), ISL,-RT-506/86 order no. PB87- 181632/GAR, 24 pp CAN: 107:179536.

21 Ritter H, Kriegel G & Licht H H, Report (1985), ISL-R-112/85 order no PB 86- 161635/GAR 16 pp, CAN: 106: 198745 v.

22 Wang J, Brower K R & Naud D L, *J Org Chem*, 62 (1997) 9055.

23 Chapman R D & Nguyen Ba Van, US6310204 B1 2001. CAN 135:346536.

24 Boileau J, Piteau M & Jacob G, *Propellants, Explos, Pyrotech*, 15 (1990) 38.

25 Licht H H, Ritter H, *Proc. 21st Int Annual Conf ICT*, Karlsruhe, Germany, 1990, 9/1-9/13.

26 Madhusunan P M, Krishnan K & Ninan K N, *Thermochim Acta*, 97 (1986) 189.

27 Muthurajan H, Sivabalan R, Talawar M B & Asthana S N, *J Hazard Mater,* A112 (2004) 17-33.

28 Muthurajan H, Sivabalan R, Venkatesan N, Talawar M B & Asthana S N, *Proc 4th Int High Energy Materials Conf & Exhibit,* HEMRL, Pune, India, 18-20 Nov 2003, 470.

29 Muthurajan H, Sivabalan R, Talawar M B & Asthana S N, *Proc the 14th Nat Symp Thermal Analysis*, M S University, Baroda, India, 20-22 Jan 2004, 225.