Synthesis, characterization and thermolysis of 2,4-dihydro -2,4,5-trinitro-3H-1,2,4-triazol-3-one (DTNTO): A new derivative of 3-nitro-1,2,4-triazol-5-one (NTO)

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A new derivative of 3-nitro-1,2,4-triazol-5-one (NTO, 2), viz., 2,4-dihydro-2,4,5-trinitro-3H-1,2,4-triazole-3-one (DTNTO, **3**) has been obtained by nitration of NTO synthesized during this work using fuming nitric acid and acetic anhydride. The title compound 2 was obtained from 2,4-dihydro-3H-1, 2,4-triazol-3-one (TO, 1). The newly synthesized DTNTO has been characterized by elemental analysis, IR, ^{1}H and ^{13}C NMR. The DTA and DSC of (**3**) showed exothermic decomposition with peak temperature (T_{max}) of 264°C. TG showed 61% weight loss for **3** in the temperature range of 194-264°C. The sensitivity data obtained for the newly synthesized compound indicates its relatively high susceptibility towards external stimuli (Impact height, $h_{50\%}$ explosion 80 cm, 3 kg drop weight and friction insensitive up to 25 kg) in comparison to NTO ($h_{50\%}$ >100 cm, 3 kg drop weight and friction insensitive up to 36 kg). The theoretically predicted performance of compound **3** in terms of velocity of detonation (8.79 km/s) is intermediate to that of NTO (8.75 km/s) and RDX (8.93 km/s). The calculated CJ pressure and sound intensity for DTNTO are found superior in comparison to benchmark high explosives RDX and HMX. Its positive oxygen balance is an attractive feature from the point of view of its application as an eco-friendly oxidizer in propellant formulations.

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Today's benchmark high explosives such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) are beset with the problem of high sensitivity to impact and shock[1]. Attempts are on to realize molecules, which deliver high performance, but are relatively more insensitive despite belonging to UN 1.1 hazard division to permit safe handling. Realization of such explosives can lead to logistic advantages like, reduction of quantity distances between storage sites, decreased battlefield vulnerability of armoured vehicles and personnel as well as increased capacity to carry a large quantity of ordnance. Such attempts have led to the developments of a series of new high-energy materials (HEMs) with promising blend of insensitivity and performance[2-7]. Among the molecules of this class, 1,2,4-triazoles like 5-nitro-2,4-dihydro-3H-1,2,4-triazole-3-one (NTO), 3-amino-5-nitro-1,2,4-triazole (ANTA), 4,6-*bis* (5-amino-3-nitro-1,2,4-triazole-1-yl)-5-nitro-pyrimidine (DAN-TNP) and caged nitramine 4,10-dinitro-2,6,8,12-tetraoxa-4,10 diazatetracyclo $[5.5.0^{5,9}.0.^{3,11}]$ dodecane (TEX) have received great attention. In case of 1,2,4-triazoles, the heterocyclic ring confers high density and thermal stability on the molecule. The high nitrogen content, entails high volume of detonation products and low response to mechanical stimuli. A combination of amino and nitro groups results in the inter and intra molecular hydrogen bonding leading to improved stability and the crystal density. In addition, certain heterocyclic substrates also contribute to the positive heat of formation[1,8]. NTO meets most of the criteria of near ideal explosives[1,8,9]. It has superior performance potential than that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and is much less sensitive to hazard stimuli compared to RDX.

The current synthetic strategy for NTO has been altered only slightly from that reported by Russian workers[10]. The synthetic pathway involves the

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reactions involving the preparation of triazolone and its subsequent nitration to NTO. The two steps can be combined by eliminating the isolation of triazolinone (TO). The method adopted by the Australian workers[1] closely mirrored this route. It involves the reaction of semicarbazide hydrochloride with formic acid followed by nitration using mixed acid in a one-pot reaction.

Crystal packing and molecular dynamics of NTO were studied by Lee and Gilardi[11] as well as Sorescu and Thompson[7]. Crystalline NTO exists in α and β phases, out of which the α phase is the most stable. Prabhakaran et al[9]. evaluated the kinetic parameters of NTO applying various kinetic models and inferred that $C-NO_2$ bond cleavage accompanied, with the rupture of the adjacent C-N bonds is the rate-determining step. The oxidative attack of the NO_2 group on the ring fragments, accounts for the formation of products like CO_2, NO and N_2O. Efforts are on to increase the performance of NTO by altering its structure. The substitution of two hydrogen's of NTO by nitro group may be viable approach in this direction to increase performance. Recently Kulkarni et al [12,13]. have reported the transition and alkali metal salts of NTO as energetic ballistic modifiers.

In view of the our continued interest[14-18] in the synthesis of high energy materials, we report here the synthesis of NTO variant: 2,4-dinitramino -5-nitro - 1,2,4-triazol-3-one (DTNTO). The synthesized DTNTO was characterized by elemental analysis and spectroscopic techniques as well as subjected to thermal studies.

Experimental Procedure

Methods and materials

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 Infrared (IR) spectra were determined as nujol mulls on a Perkin-Elmer-1600 FTIR spectrophotometer. Proton Magnetic Resonance (NMR) spectra were recorded on Varian 300 MHz spectrometer with tetramethyl silane as an internal standard. The thermal analysis (with about 2 mg samples) was performed on Mettler Toledo Star Thermogravimetry-Differential Thermal Analyzer (TG-DTA) system at a heating rate of $10^oC/min$ in nitrogen atmosphere at a flow rate of 80 cm^3/min. DSC was obtained on Perkin-Elmer DSC-7 system at a heating rate of 10°C/min in nitrogen atmosphere. Energy of activation was obtained from

TG data by applying the Madhusudnan et al[19]. equation. 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 end 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) and a movable stainless steel plate. The pulling of the movable plate at varying lever loads subjected sample to different extent of friction. The sample size and the procedure were same as followed for impact testing. The impact and friction sensitivity studies on benchmark explosives such as RDX, HMX and tetryl were also carried out under identical conditions to validate the experimental set-up. The performance parameters of the newly synthesized compounds were predicted using Linear Output Thermodynamic User friendly Software for Energetic Systems (LOTUSES) code[20-22].

Synthesis

The starting materials used in the present study were of AR grade and used directly as purchased from the trade. Acetic anhydride was obtained from High Explosive (HE) Factory Khadaki, Pune, India. The synthesis of 2,4-dihydro-3H- 1,2,4-triazol-3-one (TO) and 5-nitro - 2,4-dihydro-3H- 1,2,4-triazol-3-one (NTO) was carried out on the lines of reported method[2,3].

2,4-Dihydro-3H- 1,2,4-triazol-3-one (TO) (1)

Semicarbazide hydrochloride (6.6 g) was added to the stirred solution of formic acid (6.9 cm^3). The reaction mixture was kept under stirring until all the semicarbazide hydrochloride dissolved completely. Subsequently, the excess of formic acid was removed by distillation until crystallization commenced, and then 10 cm^3 of water was added. The distillation was continued to dryness and the residue was recrystallized from ethanol to obtain **1** as white solid (9.56 g, 75%), having the melting point of 232°C. IR in cm^{-1} (ν max): 985, 1690, 1716 ((-NH)$_2$-C=O), 2900 (C-H) 3100 (-NH Stretching). ^1H NMR (300 MHz, DMSO-d_6): 7.4 (1H, s), 11.2 (2H, bs). Anal. Calc. for

$C_2H_3N_3O$ (MW 85) C, 28.23; H, 3.52; N, 49.41; found: C, 28.76; H, 3.49; N, 49.33%.
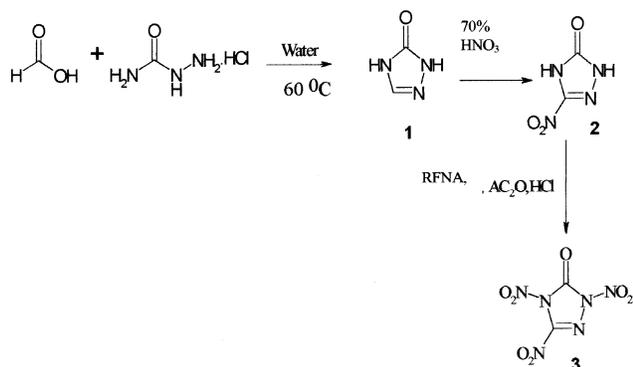
5-Nitro - 2,4-dihydro-3H- 1,2,4-triazol-3-one (NTO) (2)

The synthesized TO (1.0 g) was added to the stirred solution of nitric acid (10 cm^3) at 0°C, and the mixture was heated to 70°C for 16 h with constant stirring. An exothermic reaction occurred with the evolution of brown fumes. The product precipitated out, on completion of the reaction. The reaction mixture was allowed to cool down in ice bath. The precipitate was filtered and washed with water to remove the excess of nitric acid. The product obtained was recrystallised from water to obtain **2** (1.18 g, 70 %), having the melting point of 272-274°C. IR in KBr, cm^{-1} (v max): 1359, 1546 (-C(NO$_2$) and 1714 ((-NH)$_2$-C=O), 2923, 3211 (-NH Stretching). ^{1}H NMR (300 MHz, DMSO-d_6): 12.8 broad singlet due to –NH. ^{13}C NMR (75 MHz, DMSO-d_6): 147.8, 154.2. Anal. Calc. for $C_2H_2N_4O_3$ (MW 130) C, 18.46; H, 1.53; N, 43.07; found: C, 18.0; H, 1.36; N, 43.30%.

2,4-Dinitramino -5-nitro - 1,2,4-triazol-3-one (DTNTO) (3)

Acetic anhydride (1.56 g) was added slowly to the stirred mixture of fuming nitric acid (0.580 g,) and HCl (0.124 g)., After stirring the reaction mixture for half an hour at 0°C, NTO (**2**) (0.500 g) was added in small portions. The reaction mixture was stirred overnight at room temperature and for 1-2 h at 35-40°C. The colour of the contents changed from red to white during the progress of the reaction monitored by TLC. After completion of reaction, the mixture was poured onto crushed ice. The precipitate was filtered and dried to obtain title compound (**3**) (0.294 g, 36 %), having a melting point at 248-250°C (Scheme 1).

IR (in KBr) cm^{-1} (v max): 939, 1342,1460, 1569 (C-NO$_2$), 1554 (N-NO$_2$), 1583 (N-NO$_2$). ^{1}H NMR (300 MHz, DMSO-d_6): no peak ^{13}C (75 MHZ, DMSO-d_6): 148.2, 154.5 Anal. Calc. for $C_2N_6O_7$ (MW 220) C, 10.91; N, 38.18; found: C, 10.77; N, 38.20%.

Results and Discussion

Spectroscopic studies

The title compound triazolinone (**1**) showed major IR stretching frequencies at 1690, 2900 and 3300 cm^{-1} due to C=O, CH and NH respectively. The ^{1}H NMR of TO displayed resonating signals at δ 7.4 and 11.2 due to CH and NH respectively. The formation of NTO was confirmed by the absence of IR peak at 2900 cm^{-1} and the appearance of bands at 1546 and 1359 cm^{-1} due to NO$_2$ asymmetric and symmetric stretching vibrations. The NMR spectrum of NTO also revealed substitution of C-H proton as it gave broad singlet at δ, 12.8 only due to amide NH. The formation of NTO was further confirmed by ^{13}C NMR wherein resonating peaks at 147.8 and 154.2 were observed due to carbon atoms in two different environments in the molecule. The results obtained for TO and NTO are in agreement with the reported data[2,3]. The IR spectrum of DTNTO clearly indicates the conversion of secondary amide of NTO to nitramide as revealed by the appearance of absorption bands at 1569 and 1583 cm^{-1} due to -N-NO$_2$ moieties with the disappearance of bands at 3211 cm^{-1} (NH). DTNTO s was ^{1}H NMR inactive due to the absence of NH proton (δ 12.8). ^{13}C NMR revealed marginal downfield shift of carbon signals in DTNTO compared to NTO which may be due to the electron withdrawing effect of the NO$_2$.

Thermal analysis studies

The thermal and explosive properties of the newly synthesized compounds obtained during this work are

Scheme 1: Synthesis of DTNTO

Table 1—Thermal and sensitivity characteristics of nitrotriazoles

Property	NTO	DTNTO
DTA ^{O}C Exotherm (Peak temperature ^{o}C)	274	264
TG` (%) wt. Loss; 1st step ^{o}C	73 (197-274)	61 (194-264)
2nd Step,^{o}C		29(475)
Ea kJ/mol	100	89
Frequency factor (*A*)	6	5.12
Correlation co-efficient (*r*)	0.903	0.998
Impact sensitivity h$_{50\%}$, cm	>100	80
Friction sensitivity (kg)	36	25

Sensitivity to impact: RDX, 28-30 cm; HMX, 22-25 cm
Sensitivity to friction: RDX, 32 kg, HMX, 12 kg.

presented in Table 1. The DSC curve of NTO (**2**) and DTNTO (**3**) showed sharp exothermic peak decomposition with maxima at 273°C and 264°C respectively. A similar trend was observed in DTA. The TG of NTO revealed major weight loss (73%) in the temperature range of 197-274°C with maxima at 271°C as recorded in DTG. The TG thermogram of target molecule DTNTO revealed the maximum weight loss (61%) in almost similar temperature range of (194-264°C) followed by slow weight loss (29%) up to 475°C. 28% residue was left in case of NTO, whereas 10% residue was left in case of DTNTO. This can be co-related with their relative oxygen balance. Although many groups have examined the thermal decomposition of NTO, a consensus has not emerged at the decomposition pathway or even the initial step in the thermal decomposition of NTO. The most probable mechanism of decomposition is reported to be the cleavage of $C-NO_2$ bond in case of NTO. The FTIR studies on decomposition products of NTO evolved during TG revealed of gaseous products such as CO_2 and oxides of nitrogen as well as gaseous species containing OH and $C≡N$ group species. The labeling studies undertaken with ^{15}N by Coburn et al[23]. indicated the evolution of nitrogen gas from adjacent ring nitrogen. Similar decomposition process is expected to be operative in DTNTO.

Sensitivity studies

The DTNTO gave $h_{50\%}$ of 80 cm in impact sensitivity test and was friction insensitive up to 25 kg load suggesting its relatively higher sensitivity in comparison to NTO ($h_{50\%}$ of >100 cm and friction insensitivity upto 36 kg). The trend can be directly co-related with the relative oxygen balance of NTO (-24%) and DTNTO (+21.81). The energy of activation obtained from TG experiments for NTO and DTNTO (89 and 100 kJ/mol respectively) can also be co-related with their relative susceptibility to initiation. However, DTNTO is much less vulnerable than RDX and HMX to mechanical stimuli ($h_{50\%}$ of 22-30 cm and friction insensitive upto 12-16 kg) under identical experimental conditions. It is difficult to pin point the mechanism, as the initiation of NTO and DTNTO 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.

Performance

The theoretically predicted performance potential of DTNTO by LOTUSES method was found on par with that of NTO despite superior oxygen balance of the former. It is surprising that the introduction of two nitro groups in NTO has not shown any remarkable incremental effect on the performance. This may be because of interplay between the temperature and molecular weight of the detonation products. It is pertinent to state that the thermodynamic calculations for explosion processes including detonation have yielded significantly lower velocity of detonation

Table 2.— Performance parameters (predicted by LOTUSES) for nitro triazoles and conventional HEMs

HEM	MW	% Composition (wt.)				OB (%)	ρ (g/cm^3)	VOD (km/s)	C-J-P (Gpa)	SI (db)
		C	H	N	O					
NTO	130.07	18.47	1.55	43.08	36.90	-24.60	1.93	8.752	37.46	356
DTNTO	220.08	10.92	-	38.19	50.89	21.81	2.08	8.795	40.14	364
DNI	158.0	22.97	1.27	35.44	40.48	-30.36	1.77	8.82	35.54	349
TATB	258.2	27.9	2.34	32.56	37.18	-55.78	1.79	7.86	28.46	322
RDX	222.1	16.22	2.72	37.84	43.21	-21.61	1.77	8.93	36.48	353
HMX	296.1	16.22	2.72	37.84	43.21	-21.61	1.77	9.04	39.49	355
TNT	227.1	37.01	2.21	18.50	42.26	-73.96	1.66	6.66	19.26	275

MW = Molecular weight of HEM; OB = Oxygen Balance; VOD = Velocity of
detonation; C-J-P = Chapman Jueget Pressure; SI = Sound Intensity;
ρ = Density; DNI-Dinitro imidazole; TATB: Triaminotrinitrobenzene;
TNT: 2,4,6-trinitrotoluene ; RDX: Hexahydro-1, 3,5-trinitro-1, 3,5-triazine;
HMX**:** Octahydro-1, 3,5,7-tetranitro-1, 3,5,7-tetrazocine

(VOD) as compared to experimentally determined values in zero hydrogen organic explosives[24]. The actual explosive properties of DTNTO may be significantly higher than the those of C, H, N and O explosives. This warrants the further in depth studies on the experimental determination of VOD of DTNTO. The VOD experiment requires nearly 100 g of DTNTO to obtain accurate results. It is also worth mentioning that the calculated CJ pressure and sound intensity after blast for DTNTO are superior in comparison to well known explosives such as RDX and HMX (Table 2).

Conclusions

DTNTO was successfully synthesized by replacing the hydrogen of NH group of NTO by NO_2. The thermal analysis studies bring out that it decomposes in more or less similar manner as NTO. It was found to be relatively more sensitive than NTO. However it was much less sensitive than RDX and HMX despite superior oxygen balance. Surprisingly, introduction of NO_2 group did not lead to incremental effect on the performance of the newly synthesized compound. This may be due to absence of hydrogen in the molecule. The actual experimental performance of DTNTO may be far superior to the theoretically obtained VOD data. This needs detailed investigations. However, positive oxygen balance of DTNTO is an indicative of its potential as oxidizer/energetic additive in clean burning propellants.

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