Synthesis of 1,3-bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene and its thermal and explosive behaviour

J. P. Agrawal,* Mehilal, U. S. Prasad and R. N. Surve

High Energy Materials Research Laboratory, Sutarwadi, Pune–411 021, India

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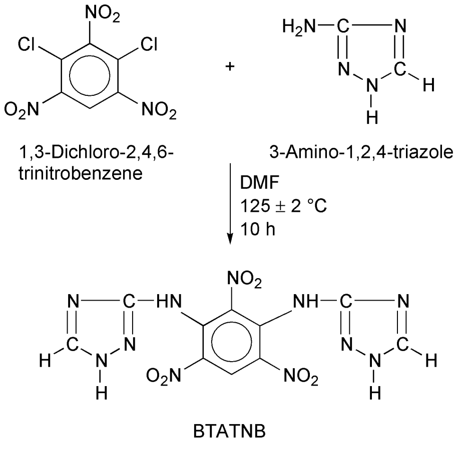
1,3-Bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene (BTATNB) has been synthesized by condensing 1,3-dichloro-2,4,6-trinitrobenzene and 3-amino-1,2,4-triazole in dimethyl formamide (DMF) at 125 ± 2 °C. The product has been characterized by elemental analysis, Fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and mass spectrometry. The data on thermal and explosive properties indicate that BTATNB is slightly more thermally stable than 3-picrylamino-1,2,4-triazole (PATO). At the same time, it is safer towards impact and friction.

Safety, reliability and stability are given prime consideration when developing explosives and propellants. Of course, in recent times, cost-effectiveness, eco-friendliness and the hazards involved in demilitarization are also being given due consideration, in addition to better explosive performance.[1,2] The mechanical integrity of conventional explosive compositions is disturbed by aerodynamic heating, thereby affecting the performance of warheads and shells. In order to obviate these shortcomings, there is a need to develop explosives with high melting points and as a result, better stability.[3]

From an analysis of the structures of a large number of thermally stable explosives reported so far in the literature, Agrawal[4] suggested that there are four general approaches to impart thermal stability to explosive molecules, these being (*i*) introduction of amino groups in aromatic nitro compounds, (*ii*) condensation of triazole ring to aromatic nitro compounds, (*iii*) salt formation and (*iv*) introduction of conjugation.

With the use of concept (*ii*), 3-picrylamino-1,2,4-triazole (PATO) was synthesized by condensing picryl chloride with 3-amino-1,2,4-triazole[5,6] or by condensing tetryl with 3-amino-1,2,4-triazole.[7] It was initially thought that PATO would replace 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), a well-known and the most thermally stable explosive,[8,9] but its performance is inferior to TATB. With these ideas in mind, a new explosive molecule, 1,3-bis(1,2,4-triazol-3-amino)-2,4,6-trinitrobenzene (BTATNB), not reported so far in the literature, was conceived, designed and synthesized by the condensation of 1,3-dichloro-2,4,6-trinitrobenzene with 3-amino-1,2,4-triazole (Scheme 1).



Scheme 1

In the present paper, we report the synthesis and characterization of BTATNB along with its thermal as well as explosive properties. Furthermore, its properties have been compared to those of PATO.

Experimental

Materials

1,3-Dichloro-2,4,6-trinitrobenzene[10] (prepared from styphnic acid by treatment with pyridine and phosphorus oxychloride), m.p. 128–129 °C, and 3-amino-1,2,4-triazole[11] (prepared by condensing amino guanidine bicarbonate and formic acid), m.p. 152–156 °C, were used as starting materials. Dimethylformamide, SQ grade from Glaxo, was used as a solvent.

To a one-litre 4-necked round bottom flask, placed in an oil bath and equipped with a mechanical stirrer, reflux condenser and thermometer pocket, 500 ml of dimethylformamide (DMF) was transferred and 25 g (0.09 mole) of 1,3-dichloro-2,4,6-trinitrobenzene was added slowly with stirring. After this, 37 g (0.44 mole) of 3-amino-1,2,4-triazole was added slowly over a period of 10 min with vigorous stirring. On complete addition, the temperature of the reaction mixture was raised to and maintained at 125 ± 2 °C for 10 h. As the BTATNB product is insoluble in the reaction medium, a pale yellow solid started precipating slowly. The reaction mixture was cooled down to ambient temperature and the product was filtered on a Buchner funnel. It was washed thoroughly with hot DMF and finally with acetone, followed by drying. The yield of BTATNB as pale yellow, free flowing crystals was 25.27 g (76%) and its melting point 319–321 °C (decomp.).

Characterization

The melting point was recorded on a Veego melting point apparatus and is uncorrected.

Structural aspects. Elemental analysis was performed on a Carlo Erba elemental analyzer, model EA 1108. The Fourier transform infrared (FTIR) spectrum was recorded at room temperature by the KBr matrix method on a Perkin–Elmer FTIR spectrophotometer, model 1600. The ^{1}H NMR spectrum was recorded with Bruker 90 MHz, model WG-90 spectrometer using sulfuric acid-d$_2$ (97 ± 1% sulfuric acid-d$_2$ solution in D$_2$O, 99.5 + atom% D, Acros, Belgium) as a solvent and tetramethylsilane (TMS) as an internal standard. The electron impact mass spectrum (EIMS) was recorded on a

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double focussing JEOL-DS mass spectrometer at 70 eV usingthe direct insertion technique.

Thermal and explosive properties. The deflagration temperature was determined by heating 0.02 g of the sample in a glass tube in a Wood's metal bath[12] at a heating rate of 5 °C min^{-1}. The temperature at which the sample ignited was recorded as the deflagration temperature. Differential thermal analysis (DTA) was recorded on a DTA apparatus by heating 10 mg of the sample at a heating rate of 10 °C min^{-1}, in the presence of static air. The activation energy of decomposition was determined by the Ozawa[13] and Kissinger[14] methods. The impact sensitivity was determined by the fall hammer method using a 2.0 kg drop weight and friction sensitivity on a Julius Peter's apparatus by standard methods.[15] The velocity of detonation[16] (VOD) and detonation pressure[17] (DP) were calculated by methods reported in the literature.

Results and discussion

Synthesis and structure

The synthesis of the title compound requires a temperature of 125 ± 2 °C and a period of 10 h, compared to 100 °C and 5 h for PATO. PATO is soluble in DMF while the title compound is insoluble in almost all common organic solvents. Therefore, as the reaction proceeds, it starts precipitating in the reaction medium and it is very difficult to recrystallise. However, it was washed thoroughly with hot DMF to remove any adhering impurities. Some physical properties of BTATNB are given in Table 1. The compound has been characterized by spectral data and elemental analysis. The spectral data of BTATNB are given in Table 2. The FTIR spectrum of BTATNB shows characteristic absorption bands at 3240, 3102, 2860, 1614, 1518 and 1324 cm^{-1}.

Table 1 Some physical properties of BTATNB

Property	Value
Melting point/°C	Decomp. at 325
Density/g cm^{-3}	
Calcd.[a]	2.03
Exptl. (flotation method)	1.98
Particle size/μm	6–7

[a] Calculated density from ref. 18.

The title compound is insoluble in almost all common organic solvents, hence the only choice left to us was to record the ^{1}H NMR spectrum in deuterated sulfuric acid with TMS as an internal standard. Since the D_2SO_4 used for recording the spectrum is not 100% deuterated, the residual signal was also recognized at δ 11.0 from the blank spectrum and accordingly, chemical shifts of the remaining protons were assigned. In the spectrum, there are only two sharp singlets at δ 9.63 and 9.37, which correspond to one picryl proton and two C-5 protons of the triazole rings, respectively. A noticeably high deshielding effect could be attributed to the highly polar solvent in which the spectrum was recorded and involved hydrogen bonding. In the NMR spectrum, the signals for the secondary NH protons are absent because of rapid exchange with the acidic solvent. The chemical shifts reported here are the results from two independent NMR spectra recorded at different time intervals and therefore, support the chemical stability of the compound in D_2SO_4. The molecular structure shown in Scheme 1 is also well-supported by the IR, mass spectral and elemental analysis data. (Values reported herein are the results of three independent analyses).

The electron impact mass spectrum of BTATNB shows a negligible abundance of the molecular ion peak at m/z 377. The $[M - NO_2]^+$ ion at m/z 331 is characteristic of the EIMS of nitroaromatic compounds. The low intensity ion at m/z 314 probably arises from consecutive loss of NO_2 and OH radicals from the M^+ peak. The ion at m/z 286 is formed as a result of the loss of $2NO_2$ with protonation while the loss of $3NO_2$ with protonation produces an ion at m/z 240 from M^+. The ion at m/z 213 is the stable trinitrobenzene species. The ion at m/z 91, which constitutes the base peak in the spectrum, arises most probably from the molecular ion by the loss of 286 mass units. Another significant ion at m/z 83 corresponds to the 3-imino-1,2,4-triazole ion.

Thermal and explosive properties

The title compound deflagrates or ignites at 325 °C. The DTA curve shows an exotherm at 320–321 °C, indicating a good

Table 2 Spectral data and elemental analysis of BTATNB

Peak/cm^{-1}	Assignment
3240	NH (stretching)
3102	Ar–H (stretching)
2860	N=CH–N (triazole ring)
1614	C=N (stretching)
1518 and 1324	NO_2 (asym. and sym. stretching)
1238	N–N (stretching)
1100	C–N (ring bending)
980	N→O (stretching)
870	Penta-substituted benzene ring
738	NO_2 (out-of-plane wagging CH bending vibration)
^{1}H NMR (D_2SO_4)	
δ	Assignment
9.37 (2H, s)	C–H protons of triazole ring
9.63 (1H, s)	Ar–H proton
EIMS (70 eV) m/z	
377, 331(7), 314(1.5), 286(100), 240(28), 213(32), 91(100), 83(52)	
Elemental analysis	
For $C_{10}H_7N_{11}O_6$ (MW 377)	
Calcd. %	C 31.83, H 1.85, N 40.84
Found %	C 32.01, H 1.93, N 40.76

Table 3 Some thermal and explosive properties of BTATNB and PATO

Property	BTATNB	PATO
Deflagration temperature/°C	325	318
DTA/°C	320–321 (exotherm)	318 (exotherm)
AED/kcal mol^{-1}		
Kissinger method	135.8	50.43
Ozawa method	134.1	51.18
Impact sensitivity/cm (height for 50% explosion)	165–170	137
Friction sensitivity/kg (Does not explode below)	>36	>36
Calc. VOD/m s^{-1}	7609	7469
Calc. DP/GPa	29.8	27.0

thermal stability of the compound. The activation energies of decomposition (AED) of the title compound and PATO have been determined by the Ozawa and Kissinger methods and the data are given in Table 3. The results show that the activation energy of decomposition of BTATNB is higher than that of PATO, suggesting that BTATNB is more thermally stable than PATO. This is also supported by the higher deflagration temperature and T_{max} of 321 °C derived from the DTA curve.

The study on explosive properties of the title compound indicates that it is very insensitive towards impact and friction (Table 3), being less sensitive to impact than PATO. The calculated VOD and DP of BTATNB are 7609 m s^{-1} and 29.8 GPa while those of PATO are 7469 m s^{-1} and 27.0 GPa, respectively. Thus, it is more energetic than PATO.

In conclusion, a comparison of the properties of BTATNB and PATO indicates that BTATNB is a slightly more thermally stable explosive than PATO. At the same time, it is also more powerful and insensitive to impact.

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