A New Thermally-stable Insensitive High Explosive: N,N′-Bis(1,2,3,4-tetrazol-5-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTeDAONAB)

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Abstract: A novel high performance explosive compound, N,N′-bis(1,2,3,4-tetrazol-5-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTeDAONAB), is introduced which is a thermally stable, insensitive high explosive. The presence of $-NH_2$, $-N=N-$ groups and the tetrazole ring simultaneously in the BTeDAONAB unit surprisingly increases its thermal stability. For the identification and characterization of BTeDAONAB, different analytical techniques have been used, including melting point, IR, ^1H NMR, ^{13}C NMR spectroscopy, elemental analysis, differential thermal analysis (DTA), thermogravimetry (TG), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The sensitivity and detonation properties of BTeDAONAB were compared with 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) and N,N′-bis(1,2,4-triazol-3-yl-)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTDAONAB), two well-known, thermally stable, insensitive high explosives, as well as hexanitrostilbene (HNS). These studies show that BTeDAONAB has favorable thermal stability with high performance.

Keywords: synthesis, BTeDAONAB, sensitivity, thermal stability, high explosive

Introduction

Today, it is important for the chemical industry to produce energetic compounds containing high energy, density, heat resistance and safety, as well as good performance, low vulnerability and sensitivity [1, 2]. It has been confirmed that commonly used high explosives such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) show relatively high sensitivity to impact and shock. Thus, it is necessary to look for new explosives with high energy and low sensitivity [1]. Several approaches can be adopted in order to render a system insensitive, *e.g.* by the use of inert and energetic binders [3]. Nitrated products find a broad spectrum of applications in the area of high energy materials (HEMs), pharmaceuticals and fertilizers. HEMs form an essential section of all arms, ammunitions, and weapon systems. A series of energetic compounds, namely 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5,5,0,0^{3,11},0^{5,9}]dodecane (CL-20), 1,3,3-trinitroazetidine (TNAZ), octanitrocubane (ONC), ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF), are key HEMs [4]. These HEMs are at various stages of pilot plant production in different countries. The science and technology of HEMs has experienced a large transformation in the last two decades in terms of the synthesis/scaling-up of exotic energetic materials, newer synthetic routes and their performance evaluation. Some HEM derivatives can be classified on the basis of their properties, *e.g.* (1) CL-20: a high-performance explosive, (2) N,N′-bis(1,2,4-triazol-3-yl-)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTDAONAB): the most thermally-stable explosive, (3) TNAZ: a melt castable explosive, and (4) ADN and HNF: eco-friendly and high-performance oxidizers, which are of recent origin and have considerable potential for large-scale manufacture and future use [5]. Thermal stability and invulnerability of explosive molecules can be achieved by the introduction of amino groups into nitro aromatic rings, the condensation of nitroaryl halides with aminotetrazole, the condensation of nitroaryl halides with aminotriazole, the introduction of conjugation between two nitroaryl compounds or through the introduction of the furoxan group to a nitroaryl compound followed by amino groups [6].

The purpose of the present work was to synthesize and characterize N,N′-bis(1,2,3,4-tetrazol-5-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BTeDAONAB) as a new, thermally stable, insensitive high explosive. Some of the desirable properties of BTeDAONAB are compared with those of 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) and BTDAONAB, two thermally stable, insensitive high explosives, as well as hexanitrostilbene (HNS).

Experimental and Calculation Procedures

Materials

4-Chlorobenzoic acid, as the starting compound for the preparation of BTeDAONAB, oleum 65% (>98%, HPLC), fuming nitric acid 100% (>98%, HPLC), concentrated sulfuric acid 98% (>98%, HPLC), sodium azide (>98%, HPLC), chloroform, ethanol, carbon tetrachloride, acetone and ethyl acetate were purchased from Merck (Germany). 5-Amino-1,2,3,4-tetrazole (purity 97%) was supplied by Sigma-Aldrich Company.

Experimental methodology

Melting points were determined in open capillaries. Densities were determined experimentally using Archimedes principle. The IR spectra were recorded on a Shimadzu-IR 470 using a KBr matrix. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz instrument. Chemical shifts were recorded in ppm with reference to tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed on a LECO CHNS-932 elemental analyzer. Sensitivity to temperature was determined by heating 3 mg samples using a deflagration tester Reichel & Partner GmbH-DT400W at a heating rate of 20 °C/min. Differential thermal analysis (DTA) was recorded using a BAHR Thermoanalyse STA503 apparatus at a heating rate of 25 °C/min with 3 mg samples in the presence of static air. Thermogravimetric and differential scanning calorimetric (TG-DSC) studies were conducted using a NTEZSCH STA 449C instrument at a heating rate of 5 °C/min under argon at a flow rate of 2mL/min and 2.84 mg sample. X-ray diffraction (XRD) patterns were obtained on a X'PERT PRO of PANALYTICAL diffractometer. The impact, 2.5 kg drop-weight, and friction sensitivity were determined using a 'BAM Apparatus'.

Calculated detonation properties

Heat of detonation

The effectiveness of an explosive depends on the amount of energy it contains and the rate of its release, which can be described by the heat of detonation. For $C_aH_bN_cO_d$ explosives a useful method considers four different reaction pathways, where all nitrogens are assumed to go to N_2, while a portion of the oxygens form H_2O and the carbons are preferentially oxidized to CO rather than CO_2 [7, 8]. The heat of detonation was calculated on the basis of water being in the gaseous phase.

Detonation pressure and velocity

The detonation velocity and pressure have for many years been regarded as the principal measures of the performance of detonating explosives. Detonation pressure is not easy to determine accurately because non-equilibrium effects in the reaction zones may contribute to a large uncertainty, spanning a range of 10-20%. Suitable empirical relationships [7, 9] have been used to predict the detonation pressure and velocity.

Adiabatic exponent

The adiabatic (gamma) exponent shows the rate of pressure (and energy) release along the C-J adiabat. It can also be coupled with the C-J pressure as an index of an explosive's ability to accelerate metal, which may also be used for estimating the detonation pressure from the measured detonation velocities of explosives through the hydrodynamic relation:

$$P_{C-J} = \frac{\rho_0 D_{C-J}^2}{\gamma_{C-J} + 1} \tag{1}$$

where P_{C-J}, D_{C-J} and γ_{C-J} are the C-J detonation pressure, velocity and adiabatic exponent respectively at a given loading density, ρ_0. A reliable equation has been used for the prediction of the adiabatic exponent of explosives at any loading density, and describes the detonation isentrope [10].

Gurney velocity of explosives

The Gurney velocity provides a more relevant, absolute indicator of the ability of an explosive to accelerate metal under a wide variety of loading conditions and geometries of interest. A suitable correlation was used to calculate the Gurney velocity in which the chemical composition of the high explosive is an essential factor [11].

Specific impulse

Rocket propellant performance is characterized widely by means of the specific impulse [5, 12], which is defined as the thrust divided by the propellant consumption rate. A high explosive can be designated as a monopropellant for which the specific impulse depends upon chemical and structural factors [12]. In general, a high detonation velocity and pressure, for the purposes of illustration, are promoted by light gaseous detonation products and a high positive heat of formation per unit weight of explosive. A suitable method was used to estimate the specific impulse of the new explosive from the detonation velocity of the explosive [13].

Synthesis of BTeDAONAB

For the synthesis of BTeDAONAB four stages were used, using 4-chlorobenzoic acid as the starting material. The first three-stages are similar to the method of Mehilal *et al.* [6] for the synthesis of BTDAONAB. The final step for the synthesis of BTeDAONAB in our method is completely different, and will be discussed below.

4,4′-Dichloro-2, 2′,3,3′,5,5′,6,6′-octanitroazobenzene (5 g, 8.18 mmol) was transferred to a three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser and addition funnel, followed by ethanol (100 mL). 3-Amino-1,2,3,4-tetrazole (3.5 g, 41.14 mmol) was added slowly to the solution with occasional swirling. The reaction mixture was heated under reflux during 5 h. After completion of the reaction, it was cooled to room temperature and poured into ice-cooled water. The resulting brown solid was allowed to settle overnight. The product was filtered off, was washed thoroughly with cold distilled water and dried to give the product. This compound was further washed with ethyl acetate to remove any impurities and finally air dried. The purity of the synthesized compound was about 98%.

Yield: 4.9 g (~84%), DTA exotherm at 275 °C.

IR (KBr) υ (cm^{-1}): 3547 (m, NH str), 3415 (m, N=N-NH str), 1591 (s, N=N str), 1545 and 1343 (s, NO$_2$ asym and sym str), 1232 (m, N-N str), 876 (m, NO$_2$ out of plane wagging), 703 (w, CH bending vibration).

^{1}H NMR (DMSO-d$_6$) δ (ppm): 9.6 (br, NH protons of the tetrazole rings) 7.1 (br, NH protons attached to the benzene ring).

^{13}C NMR (DMSO-d$_6$) δ (ppm):161, 137, 132, 138 and 135.

Elemental analysis for $C_{14}H_4N_{20}O_{16}$ (mol. wt. 708); Calcd: C 23.75, H 0.56, N 39.55%; Found: C 23.73, H 0.57, N 39.52%.
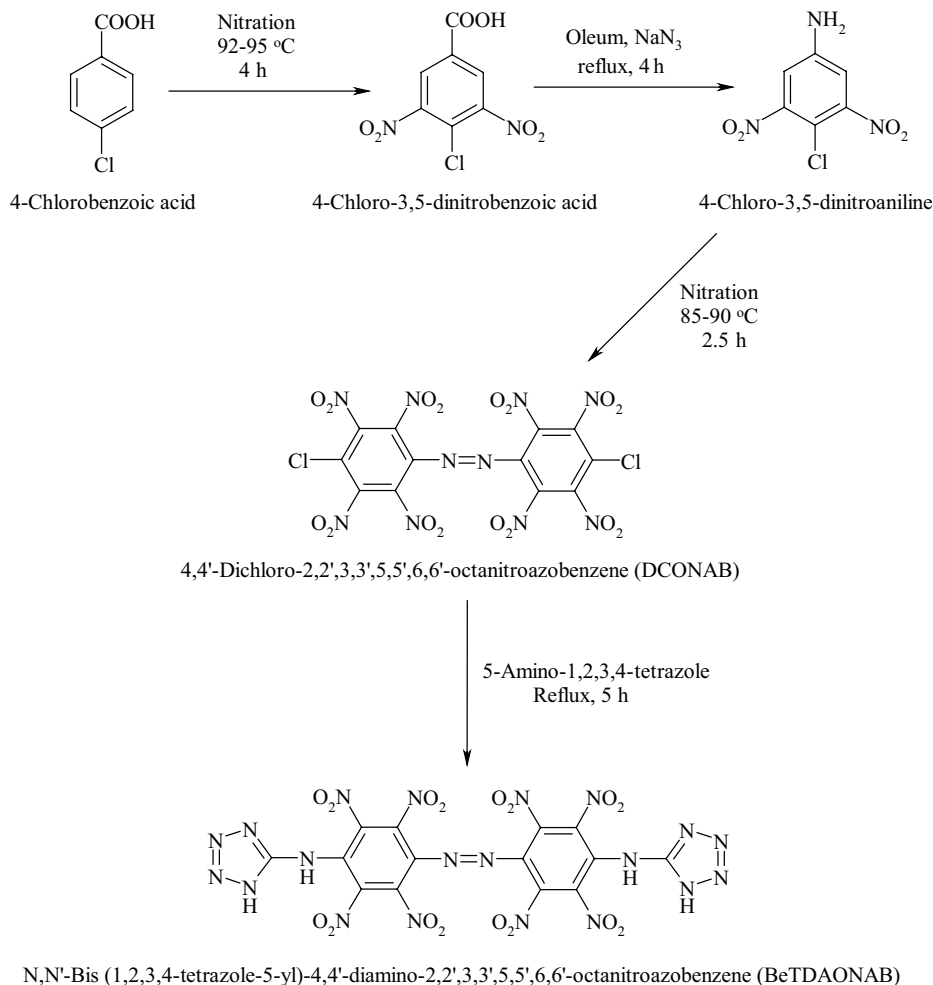

Results and Discussion

Synthesis

The synthetic route is shown in Figure 1. For the three first steps, some modifications have been made to the method of Mehilal *et al.* [6], in order to increase the yield in each step.

Using fuming nitric acid (100%) and oleum (65%) with higher concentrations than were used in the method of Mehilal *et al.* [6], the yield of stage 1 was increased from 12.8 g (81.2%) to 13.88 g (88.1%). The yields of stages 2 and 3 were also improved from 7.4 g (84%) to 8.1 g (92%) and 11.0 g (78%) to 11.3 g (80%), respectively. In all three steps, high purity products were produced.

In order to increase the purity of the product in stage 3, ethyl acetate and carbon tetrachloride were also used.

Figure 1 Reaction scheme text labels:

4-Chlorobenzoic acid → (Nitration 92-95 °C, 4 h) → 4-Chloro-3,5-dinitrobenzoic acid → (Oleum, NaN$_3$, reflux, 4 h) → 4-Chloro-3,5-dinitroaniline

(Nitration 85-90 °C, 2.5 h) →

4,4'-Dichloro-2,2',3,3',5,5',6,6'-octanitroazobenzene (DCONAB)

(5-Amino-1,2,3,4-tetrazole, Reflux, 5 h) →

N,N'-Bis (1,2,3,4-tetrazole-5-yl)-4,4'-diamino-2,2',3,3',5,5',6,6'-octanitroazobenzene (BeTDAONAB)

Figure 1.   Synthetic route for BTeDAONAB.

BTeDAONAB is a new, high performance explosive that has relatively high thermal stability and low sensitivity to impact and friction. As shown in Figure 1, the initial nitration of 4-chlorobenzoic acid with oleum (65%) and fuming nitric acid (100%) was performed at 92-95 °C, to form 4-chloro-3,5-dinitrobenzoic acid. In the second step, the 4-chloro-3,5-dinitrobenzoic acid was treated with sodium azide in the presence of oleum under reflux to perform

a Schmidt reaction, which gave 4-chloro-3,5-dinitroaniline. Subsequently the 4-chloro-3,5-dinitroaniline was nitrated with concentrated sulfuric acid and fuming nitric acid (100%) at 85-90 °C to produce 4,4′-dichloro-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (DCONAB). In the final step, DCONAB was reacted with 5-amino-1,2,3,4-tetrazole in ethanol under reflux, producing BTeDAONAB as a brown solid. Both the purity and overall yield in this synthesis are very good. The yield of BTeDAONAB was found to be about 84%. The BTeDAONAB has a decomposition temperature of 275 °C. Some thermal and explosive properties of this product have also been studied. The experimental data indicate that BTeDAONAB possesses a remarkable thermal stability and is, at the same time, safe for handling, transportation and storage**.**

Spectral studies

The product has been characterized by elemental analysis and spectral data (IR and NMR). The IR spectrum of BTeDAONAB showed the presence of –NH groups at 3547 and 3415 cm^{-1} and the absence of C-Cl groups in the molecule, which supports the complete substitution of DCONAB with 5-amino-1,2,3,4-tetrazole. The ^{1}H NMR spectrum of BTeDAONAB reveals a broad peak at δ 9.6 for the −NH protons of the tetrazole rings and a singlet at δ 7.1 for the –NH protons attached to the benzene ring. The ^{13}C NMR spectrum of BTeDAONAB gives 5 different types of carbon *i.e.*, 161, 137, 132, 138 and 135 for 2,2′,6,6′ (4C), 3,3′,5,5′(4C), 1,1′(2C), 4,4′(2C) and positions C3 in the substituted tetrazole rings. From the elemental analysis, the percentages of the elements in BTeDAONAB are in good agreement with the calculated values, which indicates a high purity of the synthesized product.

Thermal, sensitivity, XRD and performance studies

Various thermal, sensitivity and performance properties of TATB, HNS, BTDAONAB and BTeDAONAB are presented in Table 1. The BTeDAONAB has sensitivity to temperature at 260 °C, as indicated by the DTA thermogram of the corresponding exotherm at 275 °C. The TG-DSC plot of BTeDAONAB is shown in Figure 2. The DSC curve shows that an exothermic peak begins at 162 °C with a peak maximum at 268 °C. The TG curve shows no weight loss until about 162 °C. Beyond 162 °C, the weight loss is slow up to 360 °C. After 360 °C, the weight loss continues very slowly and the total weight loss becomes about 59% by 600 °C. However, the compound is stable up to 162 °C and it decomposes only slowly and exothermically beyond 162 °C. Thus, the sensitivity to temperature of BTeDAONAB is less than those for BTDAONAB, TATB and HNS. The higher thermal stability of BTeDAONAB may arise from the

introduction of the −N=N− bond, which subsequently enhances conjugation of the molecule, and also of the aminotetrazole rings. Thus, BTeDAONAB may be introduced as a new, thermally stable explosive. The study of the sensitivity of BTeDAONAB reveals that its impact and friction sensitivities are close to the reported values for BTDAONAB. The calculated performance parameters of BTeDAONAB, *i.e.* detonation pressure, detonation velocity, heat of detonation, Gurney velocity and specific impulse, are greater than those of HNS, TATB and BTDAONAB. Since the overall performance of BTeDAONAB is better than the best available explosives, this compound is more interesting for further investigation in propellant and explosive formulations. Furthermore, the density of BTeDAONAB is 1.98 g/cm^3, which is higher than those of BTDAONAB, TATB and HNS.
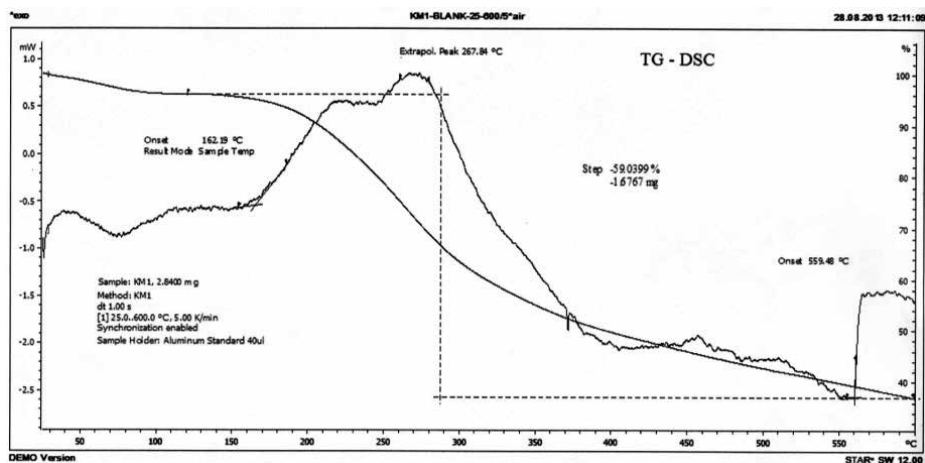
Figure 2. TG-DSC diagram of BTeDAONAB.

XRD was used to determine whether BTeDAONAB was crystalline or amorphous. The peak intensities were plotted as a function of the diffraction angle (2θ) in this analysis. Figure 3 indicates that BTeDAONAB is amorphous.
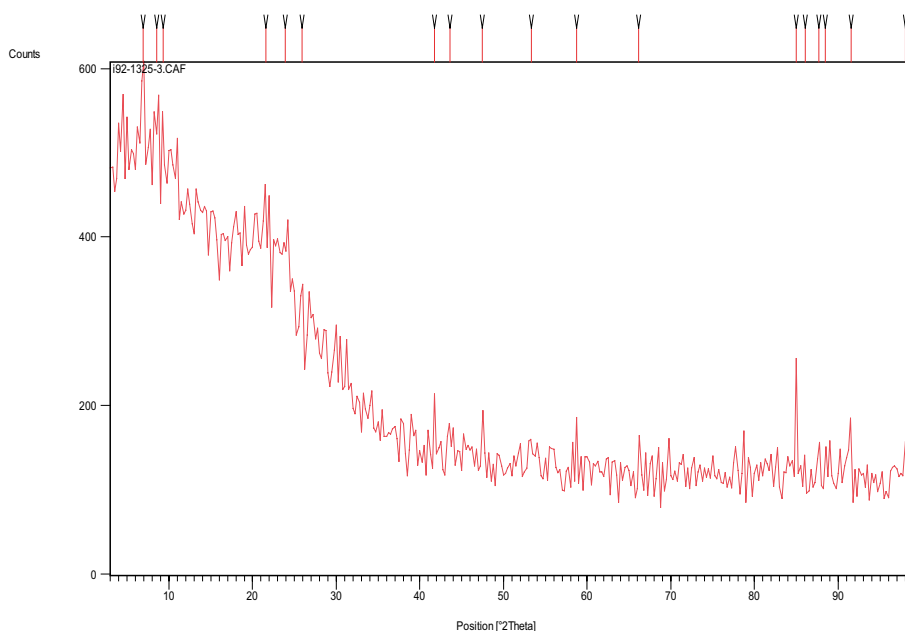
Figure 3. XRD patterns of BTeDAONAB.

Table 1. Comparative data on the thermal and explosive properties of TATB [6], HNS [14], BTDAONAB [6] and BTeDAONAB

Property	TATB	HNS	BTDAONAB	BTeDAONAB
Density, g/cm^3	1.94	1.74	1.97	1.98
Sensitivity to temperature, °C	360	318	350	260
DTA (exotherm), °C	360	353 [16]	550	275
DSC (exotherm), °C	371 [15]	350 [16]	-	268
Oxygen balance (CO), %	-18.6	-17.8	-6.8	-5.9
Impact sensitivity (50% explosion), N·m	50 [14]	5	21	21
Friction sensitivity (insensitive up to), N	>353 [14]	240	353	362
Velocity of detonation (calc.), km/s [9]	7.9	7 .6	8.6	8.7
Detonation pressure (calc.), kbar [7]	273	244	341	354
Heat of detonation [H$_2$O(g)] (calc.), kJ/mol [7]	2.03	3.12	3.59	3.91
Adiabatic exponent (calc.) [10]	3.10	2.95	3.12	3.13
Gurney velocity (calc.), km/s [11]	2.79	2.40	2.71	2.80
I$_{SP}$, (calc.), N·s/g [13]	2.102	2.224	2.311	2.336

Conclusions

We have developed an efficient and straightforward procedure for the synthesis of BTeDAONAB. BTeDAONAB is a new and powerful explosive with favorable properties of moderate density, good thermal stability and low sensitivity. BTeDAONAB has been prepared via a four-step synthetic route and characterized by instrumental techniques including spectral methods. The study of the thermal, sensitivity and performance properties of BTeDAONAB suggests that (1) it has favorable thermal stability, (2) its performance is higher than those of HNS, TATB and BTDAONAB, and (3) its sensitivity is relatively good. Furthermore, the ease with which BTeDAONAB can be prepared from commercially available starting material suggests that it would be economically valuable to synthesize on a large scale for application in propellant and explosive formulations. Moreover, scale-up of the synthesis of this compound was also examined.

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