**N,N′-Bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′, 3,3′, 5,5′, 6,6′-octanitroazo-benzene (BTDAONAB): A new thermally stable insensitive high explosive**

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**N,N′-Bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′, 3,3′, 5,5′, 6,6′-octanitroazo-benzene (BTDAONAB) has been synthesized by condensing 4,4′-dichloro-2,2′, 3,3′, 5,5′, 6,6′-octanitroazo-benzene (DCONAB) with 3-amino-1,2,4-triazole in methanol. The title compound has been characterized by elemental analysis and spectral data (IR and NMR). Some thermal and explosive properties of the compound have also been studied and the data indicate that the BTDAONAB possesses remarkable thermal stability and is, at the same time, safe for handling, transportation and storage.**

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There is a requirement of explosive compositions which are safe, reliable and stable at elevated temperatures and this has given birth to the development of two approaches in case of modern explosive compositions, i.e., (i) synthesis of thermally stable insensitive high explosives and (ii) development of plastic bonded explosives (PBXs). The thermal stability as well as invulnerability of explosive molecules can be achieved by the introduction of amino groups into nitro aromatic ring, condensation of nitro aryl halides with amino triazole, introduction of conjugation between two nitroaryl compounds or through the introduction of furoxan group to nitroaryl compound followed by amino groups. Further, with the use of concept of introduction of amino groups, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) has been synthesized whose high thermal stability and impact and friction insensitivity are well known. This compound is also often regarded as a benchmark for comparison of thermally stable and insensitive explosives. These remarkable characteristics of TATB favour its use for military and civilian applications where thermal stability and insensitivity are considered of prime importance. Furthermore, with the use of concept of introduction of triazole ring to enhance thermal stability, 3-picrylamino-1,2,4-triazole (PATO) and 1,3-bis (1,2,4-triazol-3-yl-amino)-2,4,6-trinitro-benzene (BTATNB) have also been synthesized and reported in the literature.

With this in mind, a new explosive molecule, N,N′-bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′, 3,3′, 5,5′, 6,6′-octanitroazo-benzene (BTDAONAB) was conceived, designed and synthesized.

**Experimental Procedure**

**Methods and Materials**

The melting points were determined in open capillaries and are uncorrected. The density was determined experimentally using Archimedes principle. The IR spectra were recorded on a Perkin-Elmer infrared (IR) spectrophotometer using KBr matrix. 1H-NMR and 13C-NMR spectra were recorded on Bruker 90 MHz instrument. Chemical shifts were recorded in ppm with reference to tetramethyl silane (TMS) as an internal standard. Elemental analyses were performed on a Carlo-Erba EA 1108 elemental analyzer.

Deflagration temperature was determined by heating 0.02 g of sample in a glass test tube in a Wood’s metal bath at a heating rate of 5°C/min and the temperature at which sample got ignited/decomposed was recorded as a deflagration temperature.

Differential thermal analysis (DTA) was recorded using DTA Apparatus at a heating rate of 10°C/min with 10 mg of a sample in the presence of static air. The activation energy of decomposition was determined by Ozawa and Kissinger methods after recording DTA at four different heating rates, i.e., 5, 10, 15 and 20°C/min.
The impact sensitivity was determined by “Fall Hammer Method” using 2.0 kg drop-weight, and friction sensitivity was determined on a “Julius Peters Apparatus” by following standard methods\textsuperscript{15}. The velocity of detonation (VOD) was calculated theoretically with the help of the expressions proposed by Rothestein and Hutchinson\textsuperscript{16}. A simple empirical relationship between the detonation velocity (VOD) at a theoretical maximum density and a factor $F$ that is dependent solely upon the chemical composition and structure, postulated for a gamut of ideal explosives, is expressed by the following linear equations

$$D = \frac{F - 0.26}{0.55}$$

where, $D$ is velocity of detonation and $F$ is factor which is calculated as follows:

$$F = \frac{100}{MW} \left[ n(O) + n(N) - \frac{n(H)}{2n(O)} - \frac{n(B)}{3} - \frac{n(C)}{1.75} - \frac{n(D)}{2.5} - \frac{n(E)}{4} - \frac{n(F)}{5} \right] G$$

where, $G = 0.4$ for liquid explosives and $G = 0$ for solid explosives. $A = 1.0$ if the compound is aromatic, otherwise $A = 0$, $MW$ is molecular weight, $n(O)$ is number of oxygen atoms, $n(N)$ is number of nitrogen atoms, $n(H)$ is number of hydrogen atoms, $n(B)$ is number of oxygen atoms in excess of those already available to form $CO_2$ and $H_2O$, $n(C)$ is number of oxygen atoms double bonded to carbon as in $C=O$, $n(D)$ is number of oxygen atoms singly bonded directly to carbon as in $C-O-R$ linkage where $R=H,-NH_4$ or $-C$ and $n(E)$ is number of nitrate groups either as nitrate esters or nitrate salts.

The detonation pressure (DP) was calculated\textsuperscript{17} by using the following equation.

$$DP = \delta \frac{D^2}{4}$$

where, $\delta$ is density of the compound and $D$ is velocity of detonation.

4-Chlorobenzoic acid, m.p. 240-42°C, a starting compound for the preparation of 4,4’-dichloro-2,2’, 3,3’, 5,5’, 6,6’-octanitrozobenzene, was procured from the trade. Also, 3-amino-1,2,4-triazole, m.p. 154-56°C and sodium azide(purity $>99\%$) were obtained from E Merck, Mumbai and SD Fine Chemicals, Mumbai respectively. Methyl alcohol, chloroform and ethyl acetate, used as solvents, were also procured from trade, i.e., Qualigens, Mumbai.

**Synthesis**

**4-Chloro-3,5-dinitrobenzoic acid, 1**

40 mL of oleum (25%) was transferred carefully to a 250 mL three-necked round-bottomed flask fitted with a mechanical stirrer, dropping funnel and reflux condenser and 36 mL of fuming nitric acid was added drop-wise under stirring and maintaining the temperature $\approx 25-30°C$ (ice bath cooling). To this nitrating mixture, 4-chlorobenzoic acid (10 g, 63.9 mmol) was added slowly with continuous stirring. After the addition, reaction mixture was heated on a water bath to achieve a temperature of 92-95°C which was maintained for 4 h under continuous stirring. The reaction mixture was allowed to cool to ambient temperature followed by pouring into the crushed-ice. The pale yellow compound, thus obtained, was filtered and washed thoroughly with cold water till it is acid-free. The product was crystallized from ethyl acetate. The yield was 12.8 g (81.2%) and m.p. was 162-63°C. IR (KBr) cm$^{-1}$: 3438 (m, O-H Str.), 3082 (m, Ar-H Str.), 1708 (s, C=O Str), 1612 (m, C=C Str), 1546 and 1350 (s, NO$_2$ Asym and Sym Str), 1466 (w, C-O Str), 1270 (s, O-H deformation, out of plane), 748 (s, C-Cl Str). $^1$H-NMR (acetone-$d_6$/TMS) $\delta$ ppm: 1.1 (s, COOH proton), 8.2 (s, 2H aromatic protons). Anal. for C$_7$H$_3$N$_2$O$_6$Cl (mol. wt. 246); Calcd: C-34.07, H-1.21, N-11.35, Cl-14.40%; Found: C-33.86, H-0.91, N-11.16, Cl-14.21%.

**4-Chloro-3,5-dinitroaniline, 2**

20 mL of oleum (25%) was carefully transferred to a three-necked round-bottomed flask fitted with a mechanical stirrer, reflux condenser and dropping funnel followed by the drop-wise addition of 4 mL of concentrated sulfuric acid (98%). To this, 4-chloro-3,5-dinitrobenzoic acid (10 g, 40.56 mmol) was added slowly under continuous stirring. After complete dissolution, 40 mL of chloroform was also added through a dropping funnel and the temperature of the reaction mixture was raised to 35-40°C. Sodium azide (4 g, 61.5 mmol) was added in small portions under vigorous stirring followed by reflux for 4 h. The reaction mixture was allowed to cool and then poured into the crushed ice. The dark yellow product thus obtained was filtered and washed with water till it is...
acid-free. The product was crystallized from ethyl acetate. The yield was 7.4 g (~84%) with a m.p. of 188-190°C. IR (KBr) cm⁻¹: 3476 and 3378 (m, NH₂ Asym and Sym Str), 3090 (m, Ar-H Str), 1636 (N-H deformation), 1536 and 1344 (s, NO₂ Asym and Sym Str), 1312 (s, C=N Str), 754 (s, C-Cl Str). ¹H-NMR (acetone-d₆/TMS) δ: 7.7 (s, 2H, aromatic proton), 5.6 (br, 2H, NH₂). Anal. for C₆H₄N₃O₄Cl (mol. wt. 217); Calcd: C-33.10, H-1.83, N-19.31, Cl-16.32%; Found: C-32.76, H-0.89, N-18.99, Cl-16.11%.

4,4'-Dichloro-2,2', 3,3', 5,5', 6,6'-octanitroazobenzene, 3

To a 500 mL three-necked round-bottomed flask fitted with a mechanical stirrer, thermometer pocket and dropping funnel 250 mL of concentrated sulfuric acid (98%) was carefully transferred followed by drop-wise addition of 15 mL fuming nitric acid (98%) under vigorous stirring at 25-30°C (in an ice bath). 4-chloro-3,5-dinitroaniline (10 g. 45.97 mmol) was slowly added to this nitrating mixture while maintaining the same temperature. The temperature of reaction mixture was slowly raised to 85-90°C and 4-chlorobenzoic acid, which on nitration followed by Schmidt reaction produces compound 3. The oxidation of substituted aniline to azobenzene is a well known procedure¹⁰. Similarly, amino group of water and dried in a water jacketed oven at 60°C. The compound was further washed with acetone to remove any impurities and finally air dried to yield 3.6 g (64%) and DTA exotherm at 550°C. IR (KBr) cm⁻¹: 3322 (m, NH Str), 3130 (m, C-CH-N Str), 1550 and 1338 (s, NO₂ Asym and Sym Str), 1226 (m, N-N Str), 870 (m, NO₂ out of plane wagging), 700 (w, CH bending vibration). ¹H-NMR (DMSO-d₆/TMS) δ ppm: 9.4 (br, NH proton) 8.1 (s, =CH proton of triazole ring). ¹³C-NMR (DMSO-d₆/TMS) δ ppm: 158, 155, 136, 132, 139, 135; Anal. for C₁₆H₁₈N₁₈O₁₆ (mol wt. 706); Calcd: C-27.19, H-0.84, N-35.69%; Found: C-26.76, H-0.89, N-35.41%.

Results and Discussion

Synthesis and structural aspects

The synthesis of 4,4'-dichloro-2,2', 3,3', 5,5', 6,6'-octanitroazobenzene (DCONAB), 3, was carried out from 4-chlorobenzoic acid as a starting material which on condensation with 3-amino-1,2,4-triazole produces the title compound. The reaction involves during the synthesis of BTDAONAB is depicted in Fig. 1. Compound 3 was prepared¹⁸ from 4-chlorobenzoic acid, which on nitration followed by Schmidt reaction produces 4-chloro-3,5-dinitroaniline, 2 which on further nitration produces compound 3. The synthesis of 4,4'-dichloro-2,2', 3,3', 5,5', 6,6'-octanitroazobenzene (BTDAONAB), 4

In a three-necked round-bottomed flask fitted with a reflux condenser and additional funnel 4,4'-dichloro-2,2', 3,3', 5,5', 6,6'-octanitroazobenzene (5 g, 8.18 mmol) was transferred followed by addition of 100 mL of methanol. 3-amino-1,2,4-triazole (3, 5 g, 41.66 mmol) was added to this slowly with occasional swirling. The reaction mixture was refluxed for 5 h followed by cooling to ambient temperature and pouring into the ice-cooled water. The resulting brown precipitate was allowed to settle overnight. The product was filtered, washed thoroughly with distilled

Fig. 1—Scheme of Synthesis
3,5-dichloroaniline is selectively oxidized to an azo group in addition to aromatic ring being trinitrated. This occurs in strong sulfuric acid or potassium nitrate medium acting both as an oxidizing agent as well as a nitrating agent to give 3,3′, 5,5′-tetrachloro 2,2′, 4,4′, 6,6′-hexinitrozabenzen (TCHNAB), a heat resistant explosive (m.p. 309-314°C). In addition, it is a useful intermediate for the synthesis of other high explosives of this class. The nitrated compound 2 gives compound 3 by selectively oxidizing –NH₂ to N=N group and simultaneous introduction of nitro groups in the aromatic rings. The compound is obtained in good yield and melts at 340°C (decomp). The compound 3 was condensed successfully with 3-amino-1,2,4-triazole resulting in compound 4 in good yield coupled with high purity. The scheme of synthesis of compound 4 is given in Fig. 1. The compound 4 is a dark brown powder possessing a decomposition temperature of 550°C. This compound has been characterized by elemental analysis and spectral data (IR, NMR).

The IR spectrum of compound 3 shows absence of the characteristic absorption bands of =NH₂ group at 3476 and 3378 cm⁻¹ indicating conversion of =NH₂ group to azo group. Further, absence of aromatic stretching at 3090 cm⁻¹ reveals nitration of the aromatic ring. Similarly, compound 4 shows characteristic absorption bands for =NH₂ group at 3322 cm⁻¹ which supports the condensation of compound 3 with 3-amino-1,2,4-triazole. As regards ¹H-NMR, compound 3 does not show chemical shifts for =NH₂ and aromatic protons which further confirms the absence of NH₂ frequency in the IR spectrum. The ¹³C-NMR of compound 3 resonate four different types of carbon i.e. δ 159, 155, 137 and 124 for 2,2′, 6,6′ (4C) 3,3′, 5,5′ (4C), 1,1′ (2C) and 4,4′(2C), respectively.

The ¹H-NMR of compound 4 reveals a broad peak at δ 9.4 for =NH proton and a singlet at δ 8.1 for –CH protons.

<table>
<thead>
<tr>
<th>Properties</th>
<th>DCONAB (3)</th>
<th>BTDAONAB (4)</th>
<th>TATB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density, g/cm³</td>
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<td>1.97</td>
<td>1.94</td>
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<td>Deflagration temperature, °C</td>
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<tr>
<td>DTA, (exotherm), °C</td>
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<td>Friction sensitivity (Insensitive up to), kg</td>
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<td>36</td>
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<td>Velocity of detonation (calcd), m/s</td>
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<tr>
<td>Detonation pressure (calcd), kbar</td>
<td>196</td>
<td>341</td>
<td>300</td>
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</table>

Table 1—Comparative data on thermal and explosive properties of DCONAB, BTDAONAB and TATB

The thermal and explosive properties of compounds 3 and 4 were evaluated and results obtained are presented in Table 1. The Compound 3 deflagrates at 338°C as rationalized by the DTA thermogram of corresponding exotherm at 340°C. Thus, it is evident from the data that the thermal stability of compound 3 has increased to 340°C due to introduction of –N==N-bond which subsequently enhances conjugation of the molecule. In the same way, thermal stability of compound 4 has increased to 550°C due to introduction of amino triazole rings supporting the basic concept of increasing thermal stability as proposed by Agrawal. Thus, compound 4 has a unique distinction of being most thermally stable explosive reported so far, when compared to well-established thermally stable explosives like TATB (360°C); tetrinitrodibenzo-1,3a,4,4a-tetraaza-pentalene (TACOT) m.p. 410°C; 2,2′, 2′′, 4,4′,4″, 6,6′,6″-nonanitrophenyl (NONA), m.p. 440-450°C and 2,6-bispicrylamino-3,5-dinitropyridine (PYX)², m.p. 460°C.

The activation energy of decomposition (Ea) of the title compound 4 was determined by Ozawa and Kissinger methods and is found to be 65.40 kcal/mol and 64.95 kcal/mol, respectively. These values are in excellent agreement with each other and is higher than the well established thermally stable explosives, TATB (59 kcal/mol). The study of the explosive properties of compounds 3 and 4 (Table 1) reveals that compounds are safe towards impact and friction.
The calculated performance parameters such as velocity of detonation (VOD) and detonation pressure (DP) of compounds 3 and 4 are in the increasing order. In addition, the overall performance of compound 4 is better than a most thermally stable explosive, TATB (VOD 7866 m/s) which has been successfully used in stage separation of missiles and nuclear warheads. Further, experimentally determined high density (1.97 g/cm³) of Compound 4 and insensitivity to impact and friction coupled with improved velocity of detonation (8321 as against 7866 for TATB) make this compound more interesting for investigation in propellant and explosive formulations.

Conclusions

N-N′-Bis(1,2,4-triazol-3-yl)-4,4′-diamino-2,2′, 3,3′, 5,5′, 6,6′-octanitroazo-benzene (BTDAONAB) has been synthesized and characterized. The data suggests that its thermal stability is better than a most thermally stable explosive TATB and also its VOD is superior to TATB. Furthermore, the ease with which the title compound can be prepared from commercially available starting material suggests that the title compound would be economically viable to synthesize on a large scale for application in propellant and explosive formulations.

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