

Synthesis, characterization and evaluation of 1,2-bis(2,4,6-trinitrophenyl) hydrazine: A key precursor for the synthesis of high performance energetic materials

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ABSTRACT

1,2-Bis(2,4,6-trinitrophenyl) hydrazine (**3**) is one of the precursors in the synthesis of an important energetic material viz., hexanitrazobenzene. The simple and convenient lab scale synthesis of title compound (**3**) was carried out by the condensation of picryl chloride (**2**) with hydrazine hydrate at 30–50 °C in methanol based on the lines of scanty literature reports. Picryl chloride was synthesized by the reaction of picric acid (**1**) with phosphorous oxychloride based on the lines of reported method. The synthesized compound (**3**) was characterized by IR and ¹H NMR spectral data. Some of the energetic properties of the synthesized compound have also been studied. The theoretically computed energetic properties of the title compound (**3**) indicated the superior performance in comparison to tetranitrodibenzotetraazapentalene (TACOT) and hexanitrostilbene (HNS) in terms of velocity of detonation.

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1. Introduction

The nitro alkyl and aryl derivatives of hydrazine have also been reported to possess good high-energy properties such as explosive and rocket propellant. The hydrazine and its alkylated derivatives burn rapidly and completely in air with a considerable evolution of heat [1]. It has been suggested that [2]; the thermal stability of a molecule could be achieved by introduction of amino group into aromatic ring, condensation [3] of picryl chloride into appropriate moiety or through the introduction of conjugation. In general, the explosive performance [4] of synthesized compound could also be evaluated by determining various explosive parameters [5] such as oxygen balance, velocity of detonation [6], density and heat of formation.

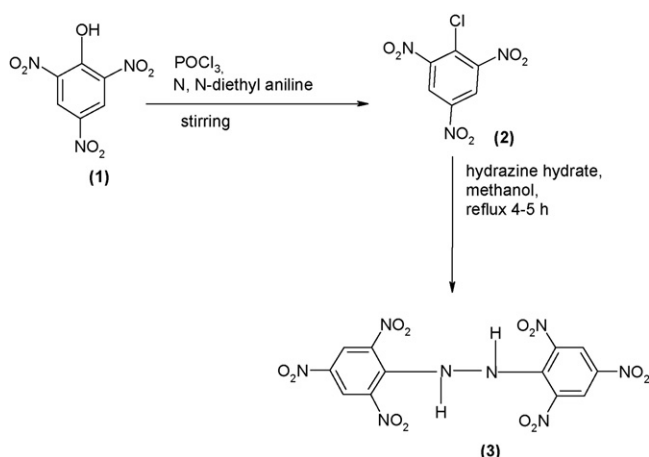
A number of research papers and books which describe their chemistry, synthesis, properties and other salient features are openly available in the literature [7–9]. Of course, higher performance has always been a prime requirement in the field of energetic materials but, more recently, a combination of properties has become desirable. In addition to a combination of safety, reliability and stability, some specific examples are (a) heat-resistant explosives for warheads of high speed missiles and perforation of

oil and gas wells, (b) high performance explosives, (c) insensitive high explosives (IHEs) for low-vulnerability munitions, and (d) melt castable explosives or explosive binders for better performance.

One of the important thermally stable energetic materials reported in the literature is hexanitrostilbene (HNS). The synthesis of HNS has been reported by Shipp [10] of the American Naval Ordnance Laboratory (NOL) in 1964. The ultra-fine HNS (1,3,5-trinitro-2-[(E)-2-(2,4,6-trinitrophenyl)vinyl]benzene) with desired properties is needed for military and civilian applications because of its reliable threshold energy to short impulse shock waves and its excellent thermal and shock stability [11]. HNS has also been reported for use in achieving stage separation in space rockets. Similar to HNS, conjugation exists in hexanitroazobenzene (HNAB) and hexanitro tetrachloroazo benzene (HNTCAB) [12]. They are interesting explosives from the point of view of thermal stability [13]. HNAB is of interest because of its melting point and relative insensitivity compared with pentaerythritol tetranitrate (PETN) and HNS [14]. One of the scanty reported [15] method of obtaining HNAB involves the treatment of picryl chloride with hydrazine, to obtain hexanitrohydrazobenzene. The hexanitrohydrazobenzene is further oxidized by nitric acid or nitrogen oxide gas in a glacial acetic acid solution to obtain HNAB. HNAB is reported as a very powerful and brisant high explosive. At a density of 1.77 g/cm³, the detonation velocity is 7250 m s⁻¹. The synthesis of key precursor hexanitrohydrazobenzene has been reported at 20 kg/batch [16]. The synthesis and characterization of 4-picryl amino-2,6-dinitro toluene as a new insensitive explosive possessing better thermal

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Scheme 1. Synthesis of 1,2-bis(2,4,6-trinitrophenyl) hydrazine (3).

stability have also been reported [17]. The potassium salt of aromatic compounds with nitro groups is more stable and less impact sensitive than the parent compound. Potassium energetic materials are emphasized for no heavy metal pollution and their explosion capacity [18]. In present work we report the synthesis and characterization of 1,2-bis(2,4,6-trinitrophenyl) hydrazine an analogue of hexyl, and its evaluation for energetic applications. The synthesis of 1,2-bis(2,4,6-trinitrophenyl) hydrazine was carried out by the condensation of picryl chloride with hydrazine hydrate (Scheme 1).

2. Experimental procedures

2.1. Materials and methods

The starting materials used in the present study were of AR grade and used directly as purchased from the trade. The completion of reaction and purity of products were checked by silica gel TLC. The melting point of the synthesized compounds was measured using Thomas Hoover capillary melting point apparatus. The IR spectra were determined as nujol mull on a Shimadzu FTIR-8400 spectrophotometer. Proton NMR spectra were recorded on Varian 300 MHz spectrometer with tetramethyl silane as an internal standard. The sensitivity to impact stimuli was determined by applying standard staircase method using a 2-kg drop weight and the results are reported in terms of height for 50% probability of explosion ($h_{50\%}$) of the sample [19]. Figure of insensitivity (F of I) was computed by using tetryl (Composition Exploding—CE), as reference. The friction sensitivity of the compound was determined on a Julius Peter's apparatus till there was no explosion/ignition in five consecutive test samples at that weight. The results obtained for impact and friction sensitivity were within the uncertainty limits of ± 5 cm and ± 0.2 kg, respectively. The explosive properties of the synthesized compounds have been computed using Linear Output Thermodynamic User friendly Software for Energetic Systems (LOTUSES) code [20]. The results are compared with the well-known HEMs.

2.2. Synthesis of 1,2-bis(2,4,6-trinitrophenyl) hydrazine (3)

The synthesis of the title compound (3) involved the following steps.

2.2.1. Synthesis of picryl chloride

Picric acid (5 g, 0.022 mmol) was dissolved in 50 ml of phosphorous oxychloride and then (3.8 g, 0.025 mmol) of N,N'-diethyl aniline was added dropwise with continuous stirring. The resulting brown reaction mixture was allowed to stand for 15 min at room

temperature and then poured into 500 ml of ice-cold water with vigorously stirring to hydrolyze the phosphorous oxychloride. During hydrolysis the reaction mixture was kept in ice bath and the temperature was not allowed to increase beyond 40–50 °C. Then the resulting product was filtered and washed with water to afford the fine yellowish colored product (2) 92%, m.p. 83 °C (lit. m.p. 83 °C) [17].

2.2.2. Synthesis of 1,2-bis(2,4,6-trinitrophenyl) hydrazine

Picryl chloride (5.94 g, 2 mmol) dissolved in methanol (10 ml) was then added dropwise with continuous stirring to the hydrazine hydrate (0.60 ml, 1 mmol). The reaction mixture was then refluxed on water bath for 4–5 h at 40–50 °C. The progress of reaction was monitored by silica gel TLC technique. The obtained product was filtered, washed with methanol and dried. The crude product was recrystallized from methanol to afford fine crystals of 1,2-bis(2,4,6-trinitro) phenyl hydrazine] (3), 88%, m.p. 235–237 °C.

3. Results and discussion

3.1. Structural aspects

The incorporation of picryl amino groups into the molecule increases the energetics of the parent compounds, whereas incorporation of nitro groups' aromatic ring increases density and thermal stability as well as energetics of the molecule due to the better oxygen balance. The introduction of amino group in the aromatic ring also increases the insensitivity of the compound towards mechanical stimuli. The potassium salt of aromatic compounds with nitro groups is more stable and less impact sensitive than the parent compound. The compound 1,2-bis(2,4,6-trinitrophenyl) hydrazine (3) has two acidic hydrogen atoms, it is source of producing the potassium salts of compound (3). Since, the potassium salt of aromatic compounds with nitro groups is more stable and less impact sensitive than the parent compound. So the potassium salts of compound (3) might be used as primers. Considering these aspects, a systematic study was undertaken for the laboratory synthesis of (3). The melting point determination of the compound (3) confirmed its exothermic decomposition nature. The compound underwent decomposition at 235–237 °C. 1,2-Bis(2,4,6-trinitrophenyl) hydrazine (3) was characterized by spectroscopic techniques such as FTIR (KBr, ν cm⁻¹) and ¹H NMR (CDCl₃ + DMSO-d₆). The IR spectrum of product (3) showed major absorption bands at 3030 cm⁻¹ [aromatic (C–H)], 1600 cm⁻¹ [aromatic (C=C)], 3400–3200 cm⁻¹ [(N–H)] and 1350 and 1550 cm⁻¹ (symmetric NO₂ group). The ¹H NMR spectrum of compound (3) showed two sharp signals appeared at δ 7.65 and δ 8.76 corresponding to amino protons and aromatic protons of picryl ring (highly deshielded due to the presence of symmetric nitro groups), respectively.

3.2. Explosive properties

The sensitivity test results brought out that 1,2-bis(2,4,6-trinitrophenyl) hydrazine is impact insensitive up to 90 cm ($h_{50\%}$ explosion) and it is friction insensitive up to load of >36 kg. These trends suggest its overall low vulnerability to mechanical stimuli compared to that of other nitramine explosives such as RDX and HMX ($h_{50\%}$ friction insensitive up to 16 and 19 kg), respectively. The addition of amino group to polynitro aromatic system increases the density and thermal stability and thus decreases the sensitivity. Beside this, an introduction of picryl group in the hydrazine helps to increase the oxygen balance as well as velocity of detonation.

The performance parameters of 1,2-bis(2,4,6-trinitrophenyl) hydrazine theoretically predicted by applying Linear Output Thermodynamic User friendly Software for Energetic Systems (LOTUSES) code are given in Table 1. The theoretically predicted

Table 1
Theoretical performance properties of 1,2-bis(2,4,6-trinitrophenyl) hydrazine with other energetic material.

| HEM | Elemental composition (%) | | | | O.B. (%) | ρ (g/cm ³) | DF | ΔH_f (kJ/m) | VOD (km/s) | C–J P (GPa) | RS | SI (db) | HOE kJ/kg | PI (%) | ET (K) | VDP (l/kg) |
|---|---------------------------|-------|------|-------|----------|-----------------------------|------|---------------------|------------|-------------|-----|---------|-----------|--------|--------|------------|
| | MW | C | H | N | | | | | | | | | | | | |
| HNBH C ₁₂ H ₆ N ₆ O ₁₂ | 454 | 31.72 | 1.33 | 24.67 | 42.26 | 1.75 | 4.61 | +11 | 7.36 | 25.26 | 101 | 309 | 2827 | 103 | 2870 | 972 |
| PYX C ₁₇ H ₇ N ₁₁ O ₁₆ | 621 | 32.86 | 1.13 | 24.80 | 41.20 | 1.75 | 4.36 | 80 | 7.497 | 25.186 | 106 | 308 | 3006 | 110 | 3100 | 989 |
| TACOT C ₁₂ H ₄ N ₈ O ₈ | 388 | 37.12 | 1.03 | 28.86 | 32.96 | 1.81 | 4.14 | +459 | 7.05 | 23.15 | 135 | 298 | 3487 | 141 | 3900 | 1095 |
| HNS C ₁₄ H ₆ N ₆ O ₁₂ | 450 | 37.34 | 1.34 | 18.66 | 42.64 | 1.74 | 4.01 | +78 | 6.82 | 21.05 | 117 | 286 | 3153 | 123 | 3300 | 1050 |
| DIPAM C ₁₂ H ₆ N ₈ O ₁₂ | 454 | 31.72 | 1.33 | 24.67 | 42.26 | 1.79 | 4.42 | -28.84 | 7.56 | 26.36 | 102 | 313 | 2890 | 105 | 2900 | 988 |
| TATB C ₆ H ₆ N ₆ O ₆ | 258 | 27.9 | 2.34 | 32.56 | 37.18 | 1.93 | 4.58 | -139 | 7.86 | 28.46 | 80 | 322 | 2057 | 84 | 2100 | 1098 |
| NTO C ₂ H ₂ N ₄ O ₃ | 130. | 18.47 | 1.55 | 43.08 | 36.90 | 1.93 | 5.38 | -112 | 8.752 | 37.46 | 88 | 356 | 2719 | 91 | 2700 | 908 |
| RDX C ₃ H ₆ N ₆ O ₆ | 222 | 16.22 | 2.72 | 37.84 | 43.21 | 1.81 | 5.17 | +71 | 8.93 | 36.48 | 174 | 353 | 5098 | 181 | 4400 | 957 |
| HMX C ₄ H ₈ N ₈ O ₈ | 296 | 16.22 | 2.72 | 37.84 | 43.21 | 1.91 | 5.23 | +87 | 9.04 | 39.49 | 173 | 355 | 5073 | 180 | 4400 | 957 |

HEM: high energy material; MW: molecular weight; OB: oxygen balance; ρ : density; ΔH_f : heat of formation; DF: detonation factor; VOD: velocity of detonation; CJP: Chapman–Jouget pressure; SI: sound intensity; RS: relative strength; HOE: heat of explosion; PI: power index; ET: explosion temperature; VDP: volume of detonation products; HNBH: hexanitrohydrazobenzene or 1,2-bis(2,4,6-trinitrophenyl) hydrazine; PYX: 2,6-bis(2,4,6-trinitrophenylamino)-3,5-dinitropropidine; DIPAM: 2,2',4,4',6,6'-hexanitro-1,1'-biphenyl-3,3'-diamine; TACOT Z: 1,3,7,9-tetraazolo[1,2,3]benzotriazole-5,11-dium-6,12-diide, TATB: 2,4,6-triamino-2,4,6-trinitrobenzene; NTO: 5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one; RDX: 1,3,5-trinitro-1,3,5-triazine; HMX: 1,3,5,7-tetraamino-1,3,5,7-tetrazocane.

velocity of detonation (VOD), relative strength (RS) and sound intensity (SI) of 1,2-bis(2,4,6-trinitrophenyl) hydrazine was found superior in comparison to TACOT and HNS. This study warrants the further in depth studies on the experimental determination of velocity of detonation and other parameters to confirm the performance of the materials synthesized in the present study. The theoretical calculation of high energy compound promises its explosive properties, with higher value of velocity of detonation 7920 m s⁻¹, which is greater than that of TACOT and HNS. Therefore, compound (3) may be used as an energetic filler application.

4. Conclusions

The present study establishes the laboratory scale synthesis of versatile key precursor viz., 1,2-bis(2,4,6-trinitrophenyl) hydrazine for the synthesis of advanced energetic materials. The compounds were synthesized and characterized by instrumental techniques including spectral method. The DTA data indicated the exothermic nature of the compound. The predicted performance parameters and thermal as well as sensitivity studies give an indication of the potential of these compounds for applications wherein higher thermal stability coupled with low vulnerability are the main criteria. The data presented in this paper enriches the existing scanty data on 1,2-bis(2,4,6-trinitrophenyl) hydrazine. The stability and performance studies on compound 3 in thermally stable explosive formulation may be undertaken to assess its effect on the performance of the formulation.

The work reported in this paper warrants further in depth studies on 1,2-bis(2,4,6-trinitrophenyl) hydrazine in terms of its performance parameters which are interesting and important from the point of safety during its use as an intermediate for the synthesis of advanced energetic materials or its use as an energetic filler in the formulations.

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