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Synthesis and characterisation of 4-picrylamino-2,6-dinitrotoluene (PADNT): a new insensitive explosive

Mehilal, R.B. Salunke, A.K. Sikder, J.P. Agrawal*

High Energy Materials Research Laboratory, Ministry of Defence, Sutarwadi, Pune 411 021, Maharashtra, India

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Abstract

A chemoselective reductive method has been achieved for the preparation of 4-picrylamino-2,6-dinitrotoluene (PADNT), a new insensitive energetic material which has been characterised by spectral data and elemental analysis. Some explosive properties of the compound have also been determined and the results indicate that PANDT is quite safe to impact and friction.

Keywords: Reduction; 4-Amino-2,6-dinitrotoluene (ADNT); PADNT; Insensitiveness; Impact and friction sensitivity

1. Introduction

In order to increase the performance level of conventional warheads, it is necessary to increase the energy output of the explosives which are used for their fillings. Two approaches have emerged out successfully in this direction involving melt-cast explosives and/or plastic bonded explosives (PBXs).

2,4,6-Trinitrotoluene (TNT) has been used traditionally as only the melt-cast explosive. Of course a very few of such explosives are of recent origin. The set point of pure TNT is 80.8°C, much lower than its decomposition temperature (300°C). Hence, it can be safely melted using steam. The TNT is an unique explosives which has been used alone or in combination with RDX, HMX or aluminium in different munitions or modern warheads/shells [1]. It has also been used as a starting material for synthesis of two most com-

* Corresponding author. Tel.: +91-212-389-263; fax: +91-212-381-316.
E-mail address: jpa@vsnl.com (J.P. Agrawal).

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monly used thermally stable explosives, i.e. 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) [2] and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [3], a high melting explosive that has been applied in situations where a combination of insensitivity to impact as well as heat, is important.

To exploit the advantage of amino group in order to enhance thermal stability of explosives [4–6] and facile reduction of TNT selectively [7–11], we have synthesised and characterised 4-picrylamino-2,6-dinitrotoluene (PADNT) with a good yield and high purity. This method is reliable, since the process is less complicated and consists of only three steps. The results obtained from preliminary evaluations on explosive and thermal behaviour of the compound are incorporated here.

2. Experimental

The melting points were recorded on open capillaries and are uncorrected. FTIR (in KBr disc) and ^{1}H NMR were recorded on Perkin-Elmer FTIR Spectrophotomer, Model-1600 and Bruker 90 MHz Model WG-90, respectively. Chemical shifts (δ units) are reported in parts per million (ppm) downfield from tetramethylsilane. The elemental analysis were performed on Elemental Analyser, Model Carlo-Erba EA 1108.

Deflagration temperature [12] was determined by heating 0.02 g of the sample in a glass tube of a Wood's metal bath at a heating rate of 5°C/min and the temperature of ignition of sample was recorded as deflagration temperature. Differential thermal analysis (DTA) was recorded on DTA apparatus by heating 10 mg of sample at a rate of 10°C/min in the presence of static air.

The impact sensitivity was determined by Fall Hammer Method using 2 kg drop weight and friction sensitivity was assessed on "Julius Peter's Apparatus" by following standard methods [13]. The velocity of detonation (VOD) [14] and detonation pressure (Dp) [15] were calculated by methods reported in the literature.

3. Materials

The *p*-1,4-dioxane, methanol and concentrated ammonium hydroxide (NH_4OH) were procured from Qualigens Fine Chemicals, Mumbai. The TNT of high purity (set point 80.8°C) and picric acid were obtained from "High Explosives Factory", Pune. Hydrogen sulfide (H_2S), generated from ferrous sulphide and dilute hydrochloric acid in Kipp's apparatus, and thus, dried over calcium chloride, was used as a reducing agent.

3.1. Synthesis

The synthesis of 4-picrylamino-2,6-dinitrotoluene involves two steps:

1. synthesis of 4-amino-2,6-dinitrotoluene (ANDT);
2. synthesis of 4-picrylamino-2, 6-dinitrotoluene (PADNT).

3.1.1. 4-Amino-2,6-dinitrotoluene (ADNT), ***1***

The ADNT was prepared by adopting the method of Prasad et al. [16]. Yield ∼60%, mp 169–171°C.

IR (KBr), ν cm^{-1}: 3478 and 3380 (–NH_2 str.), 3096 (Ar–H), 2990 and 2934 (–CH_3 str.), 1658 (–C=N and –NH def.), 1536 and 1352 (–NO_2 asym. and sym. str.), 1434 (aromatic skeletal), 1094 (–N → O str.).

^{1}H NMR (DMSO-d_6/TMS) δ ppm: 7.50 (Ar–H), 5.65 (br–NH_2), 2.24 (s, CH_3).

Analysis for $C_7H_7N_3O_4$ (Mol. wt. 197). Calculated (%): C 42.63, H 3.55, N 21.32; found (%): C 42.39, H 3.41, N 21.09.

3.1.2. 4-Picrylamino-2,6-dinitrotoluene (PADNT), ***2***

To a 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer and reflux condenser, 4-amino-2,6-dinitrotoluene (1.97 g, 0.01 mol) and picryl chloride (2.47 g, 0.01 mol) were transferred carefully. Methyl alcohol (50 ml) was added subsequently into the flask and the reaction mixture was then refluxed for 3 h. After the reflux, the reaction mixture was allowed to cool at ambient temperature and ultimately poured into crushed ice. The yellow precipitate, thus, obtained, was filtered, washed thoroughly with distilled water and finally recrystalised from ethyl acetate. Yield, 3.5 g (∼85%), mp 198–200°C; DTA, 201°C (endo.) and 299°C (exo.).

IR (KBr), ν cm^{-1}: 3310 (–NH str.), 3090 (Ar–H, str.) 2934, 2858 (–CH_3 str.), 1616 (–NH def. and –C=C– str.), 15324, 1340 (NO_2 asym. and sym.), 1170 and 1082 (C–N vibration).

^{1}H NMR (DMSO-d_6/TMS) δ: 10.4 (–NH proton), 9.06 (s, 2H, picryl), 8.03 (s, 2H, toluene) and 2.4 (–CH_3 protons).

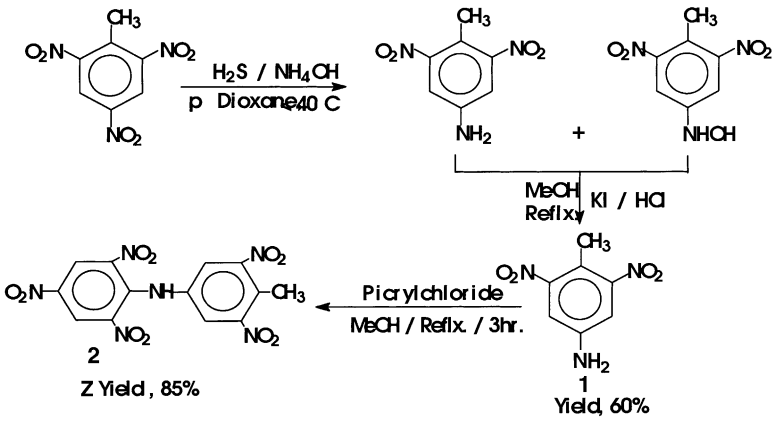
Analysis for $C_{13}H_8N_6O_{10}$ (Mol. wt. 408). Calculated (%): C, 38.24; H 1.96; N 20.59; found (%): C 38.08; H 1.89; N 20.36.

4. Results and discussion

The parent compound picryl chloride was obtained from picric acid by treatment with pyridine and phosphorus oxychloride [17] with high yield and excellent purity. 4-Picrylamino-2,6-dinitrotoluene (**2**) was synthesised by condensing picryl chloride with 4-amino-2,6-dinitrotoluene(**1**) which in turn, was prepared by selective reduction of TNT in the presence of hydrogen sulfide and concentrated ammonium hydroxide in 1,4-dioxane. The steps involved during the synthesis of the title compound are outlined in Scheme 1.

This method of selective reduction of TNT is a temperature and alkali dependent, and hence, during the course of reaction, the temperature was not allowed to increase beyond 40°C. Also the addition of conc. NH_4OH was not done in one instalment and the quantity of NH_4OH was gradually increased in subsequent instalments and this was experienced earlier by many authors [7,10]. Again the use of KI/HCl promptly converts 4-hydroxylamine-2,6-dinitrotoluene into 4-amino-2,6-dinitro toluene (**1**), thus, increases in the percent yield of PADNT. The method followed for the preparation of PADNT is simple, less expensive and reliable.

The PADNT is a yellow crystalline compound which melts at 198–200°C. The compound was characterised by spectral data (IR and ^{1}H NMR) and elemental analysis. The



Scheme 1.

IR spectrum of the compound shows intense absorption band at 3310 cm^{-1} corresponds to –NH stretching. The bands at 3090, 2934 and 2858 cm^{-1} are due to aryl- and alkyl-CH– stretchings. The –NH band as well as the –C=C stretching frequency appear to merge at 1616 cm^{-1}. The characteristic intense peak of asymmetric and symmetric stretchings of $–NO_2$ groups are observed at 1534 and 1340 cm^{-1}, respectively. The ^1H NMR of **2** shows the presence of –NH proton at 10.4δ and the chemical shift of aromatic protons of trinitrophenyl and dinitrotoluene resonate at 8.03δ and 8.03δ. The protons of $–CH_3$ group attached to dinitrophenyl group appear at 2.4δ. The observed elemental analysis data for C, H and N is in excellent agreement with the calculated values.

The PADNT was also evaluated for thermal and explosive properties and the data generated are given in Table 1. The compound deflagrates at 294°C, whereas DTA shows an

Table 1
Some explosive and thermal properties of PADNT

Melting point (°C)	198–201
Density (g/cm^3)	1.85
Deflagration temperature (°C)	294
Differential thermal analysis	
Endotherm (°C)	201
Exotherm (°C)	299
Impact sensitivity (cm) (50% explosion height)	135
Friction sensitivity (kg) (insensitive upto)	36
Velocity of detonation (m/s)	6628
Detonation pressure, (kbar)	203.17
Oxygen balance (%) (co-balance)[a,b]	−27.45

[a] Calculated values.

[b] OB represents the compounds lack or excess of oxygen needed to produce the most stable products and it has been calculated as per the formulae given in [14].

endotherm at 201°C due to melting followed by an exotherm at 299°C showing its decomposition and suggesting its good thermal stability. PADNT is a molecule with high density, 1.85 g/cm^3 (TNT, $d = 1.60$ g/cm^3), determined by of density bottle method and possesses somewhat Co and water balanced oxygen deficiency but unlike TNT which is heavily oxygen deficient (∼74%) and seriously affect the overall performance.

The explosive properties of **2** (PADNT) reveals that the compound is safe towards impact and friction (Table 1) and is reasonably powerful high explosive whose thermal and shock stability is considerably greater than that of many other known explosives of comparable energy.

5. Conclusion

A selective reduction method has been demonstrated for the preparation of 4-picrylamino-2,6-dinitrotoluene (PADNT) with a high yield and excellent purity. Based on the thermal and explosive properties, it may be concluded that the compound is safe, reliable and possesses a good thermal stability. This can also be an attractive option as a new energetic ingredient and safe for the development of insensitive explosive and propellant compositions.

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