

Formation of the Sensitive Impurity 1,3,5-Triamino-2-chloro-4,6-dinitrobenzene in Pilot Plant TATB Production

A. K. Nandi,* S. M. Kasar, U. Thanigaivelan, A. K. Mandal, and R. K. Pandey

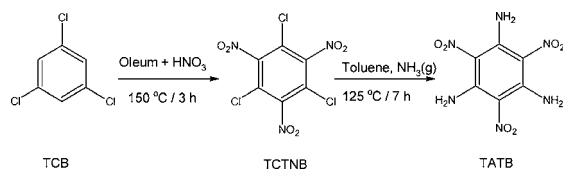
Chemical Engineering and Pilot Plant Division, High Energy Materials Research Laboratory, Sutarwadi, Pune-411021, India

ABSTRACT: A thermally stable, insensitive, high-explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is manufactured by amination of 1,3,5-trichloro-2,4,6-trinitrobenzene in toluene with NH₃ gas. An orange–red, sensitive impurity, 1,3,5-triamino-2-chloro-4,6-dinitrobenzene (TACDNB), was found forming with product TATB in the pilot-plant process. This impurity was isolated and characterized by single-crystal XRD, NMR, FTIR, DSC, and sensitivity test. The chemical reactivity of this impurity with aqueous sodium hydroxide solution was also studied. The process anomalies which led to the formation of this impurity with product TATB were investigated. This TACDNB impurity was formed due to amination of 1,3,5,6-tetrachloro-2,4-dinitrobenzene (T₄) when excess NH₃ gas was fed into the reactor.

INTRODUCTION

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) has generated considerable interest in the field of high explosives due to its excellent thermal stability and extreme insensitivity to impact and friction.¹ Although some alternate routes for TATB synthesis has been reported,² they are restricted to the development stage. The large-scale production of TATB is still an adaptation of the ‘Benziger route’ from starting raw material 1,3,5-trichlorobenzene (TCB) as shown in Scheme 1.³

Scheme 1. Synthesis route adopted for TATB in the pilot-plant process



TATB preparation involves two unit processes, viz., nitration and amination. TCB is first nitrated to 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB). Product TATB is synthesized in the second step by amination of the intermediate TCTNB in toluene with ammonia gas. TATB produced by this process is a yellow-coloured powdery material of purity ~99% with acceptable chloride impurity content (<1%, estimated by potentiometric titration of an acidified extract of TATB in a sodium hydroxide solution against a standard silver nitrate solution using an Ag/AgCl electrode). This process has been extensively studied by various authors. This laboratory has also established this process on pilot-plant scale.⁴

The pilot plant of this laboratory is presently in operation for regular production of TATB as well as collection of engineering data required to set up a large-scale production plant. Approximately 1–2% orange red particles (ORP) were found in few amination batches. These red particles are of larger size (>300 μm) and are easily distinguishable from yellow TATB particles (<100 μm). Initially, it was thought that the degradation of TATB during the amination reaction leads to

the formation of ORP. Foltz et al.⁵ obtained an orange-brown colour product during cooling recrystallisation of yellow TATB in DMSO from very high temperature.⁵ The colour change is due to degradation of TATB by radicals. Thus, introduction of radical scavengers (antioxidants) such as butylated hydroxytoluene (BHT), 1,4-naphthaquinone, etc. and removal of metallic surfaces during crystallization are found to be very effective at preventing the reaction. However, the authors did not disclose the reaction scheme and chemical structure of the compound responsible for the colour change. The colour change of canary yellow pristine TATB to green by exposure to ultraviolet light,⁶ electron irradiation,⁷ and γ radiation⁸ has been studied in detail by various authors. This colour change is a surface phenomenon and increases with penetration of radiation. The green TATB is slightly less thermally stable (by –10 K) than yellow TATB.⁸ It is proposed that this colour change from yellow to green is due to loss of oxygen from the nitro group, forming a nitroso derivative.⁹

However, the formation of ORP during TATB preparation remained unnoticed by previous authors. ORP are formed during the amination reaction and are a visible impurity in TATB. The impurities of TATB were previously isolated and characterized. NH₄Cl is found as a major inorganic impurity (<1%) in TATB¹⁰ along with various minor organic impurities, viz. chloronitrobenzenes and their aminated derivatives.¹¹ These minor organic impurities are soluble in toluene, acetone, etc. and are not visually distinguishable from TATB. They are generally detected/estimated by the analysis of the solvent extract of batch material. The ORP discussed herein is a toluene-insoluble material and appears as a visible impurity (~1–2%) in TATB due to its colour and larger particle size. This certainly raises some concern and issues to consider regarding the bulk properties of the material. Accordingly, a thorough study has been carried out to identify the red particles by characterization techniques such as single-crystal X-ray

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diffraction, NMR, FTIR, and chemical analysis. The thermal (DSC) and sensitivity (impact and friction) tests were also carried out on the isolated impurity. The process conditions which favor this impurity formation were also analysed.

EXPERIMENTAL SECTION

Isolation, Purification and Single-Crystal Preparation of ORP. Orange–red particles were first isolated by mechanical sieving (+25-BSS) of contaminated batch material. It was purified by recrystallisation in DMSO. Powdered crude material was dissolved in hot DMSO (125 °C), and the solution was allowed to cool slowly. The crystals obtained were then isolated by filtration and washed several times with water and then vacuum-dried. The crystallized material was subjected to all characterization tests. One small crystal with well-developed faces was selected for single-crystal X-ray diffraction study.

Characterization. The crystallized material was subjected to different tests to evaluate its chemical structure and thermal and explosive properties. The IR spectrum was recorded in a Shimadzu Infrared Spectrometer (FTIR-8400) employing a KBr matrix. ¹H- and ¹³C NMR spectra were recorded utilising a Bruker 200 MHz instrument using DMSO-*d*₆ as the solvent and tetramethyl silane (TMS) as an internal standard. DSC was recorded on 1–2 mg of sample using a Perkin-Elmer DSC instrument (DSC-7). The sample was heated at a rate of 10 °C/min under N₂ atmosphere. The single-crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 25 °C. The X-ray generator was operated at 50 kV and 30 mA using Mo K α radiation. Data were collected with ω scan width of 0.3° and with three different settings of φ (0°, 90°, and 180°), keeping the sample-to-detector distance fixed at 6.145 cm and the detector position (2θ) fixed at –28°. The X-ray data collection was monitored by Bruker's SMART program (version 5.0. Bruker AXS Inc.: Madison, WI). All the data were corrected for Lorentzian, polarization, and absorption effects using Bruker's SAINT and SADABS programs [Bruker; SMART (v5.628), SAINT (v6.45a), Bruker AXS Inc.: Madison, WI, 2004]. XPREP was used to determine the space group. SHELX-97 was used for structure solution and full matrix least-squares refinement on F₂ (Sheldrick, G. M. SHELXS-97, SHELXL-97; University of Göttingen: Germany. 1997). Molecular diagrams were generated using XShell program embedded in SHELXTL. Geometrical calculations were done using SHELX-97. All the hydrogen atoms were treated as riding model and refined isotropically.

Impact sensitivity was determined by the drop hammer method using a 2-kg drop weight, and friction sensitivity was determined utilizing the Julius Peter apparatus by following standard methods.¹² The amino group was estimated in a modified Kjeldhal apparatus using a method described by Rigdon et al.¹³ The Cl[–] content in the sample was estimated by a method described by Mehilal et al.¹⁰

RESULTS AND DISCUSSION

Single Crystal X-ray Diffraction Study. The X-ray crystallographic study reveals the structure of the compound. The ORTEP view of the molecule is shown in Figure 1. It is 1,3,5-triamino-2-chloro-4,6-dinitrobenzene (TACDNB). The crystallographic data on unit cell and relevant information are summarized in Tables 1–4.

NMR Study. TACDNB is a symmetric molecule and belongs to the point group C_{2v}. Accordingly, ¹³C NMR of

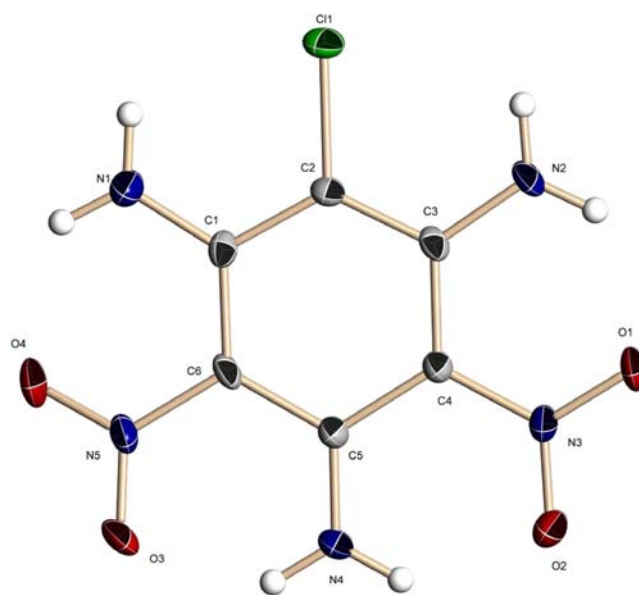


Figure 1. ORTEP view of 1,3,5-triamino-2-chloro-4,6-dinitrobenzene (TACDNB) drawn at 30% probability displacement ellipsoids.

Table 1. Crystal data and structure refinement of TACDNB

empirical formula	C ₆ H ₆ ClN ₅ O ₄
formula weight	247.61
temperature/K	297(2)
wavelength/nm	0.071073
crystal system	monoclinic
<i>a</i> /nm	0.36421(19)
<i>b</i> /nm	0.8299(4)
<i>c</i> /nm	1.4419(8)
β /deg	95.259(9)
space group	P2 ₁
volume/nm ³	0.4340(4)
<i>Z</i>	2
calculated density/kg-m ⁻³	1.895
absorption coefficient/mm ⁻¹	0.451
<i>F</i> (000)	252
crystal size/mm ³	0.51 × 0.40 × 0.09
θ range for data collection/deg	1.42–25.00
limiting indices	–4 ≤ <i>h</i> ≤ 3, –9 ≤ <i>k</i> ≤ 9, –17 ≤ <i>l</i> ≤ 17
reflections collected/unique	2501/1441 [<i>R</i> (int) = 0.0380]
completeness to theta = 25.00	97.5%
absorption correction	semi-empirical from equivalents
max. and min transmission	0.9605 and 0.8029
refinement method	full-matrix least-squares on <i>F</i> ²
data/restraints/parameters	1441/1/145
goodness-of-fit on <i>F</i> ²	1.151

TACDNB shows four signals at δ (ppm): 89 (s, 1C, C–Cl), 113 (s, 2C, C–NO₂), 146 (s, 1C, C–NH₂), and 148 (s, 2C, C–NH₂). ¹H NMR of this compound shows two signal at δ (ppm): 7.99 (s, 4H, NH₂) and 10.17 (s, 2H, C₅–NH₂).

FTIR Study. FTIR spectra of both TATB and TACDNB were recorded and are shown in Figure 2. The vibrational spectrum of TATB was extensively studied by Towns.¹⁴ TATB shows IR absorption bands at 3319 and 3220 cm⁻¹ for asymmetric (ν_a) and symmetric (ν_s) stretching vibrations of NH₂, respectively. These bands are at slightly lower wavenumbers when compared with the corresponding values of aniline (3440 and 3360 cm⁻¹). This is due to the influence of

Table 2. Bond lengths [Å] for TACDNB

bond	length (Å)	bond	length (Å)
C(1)–N(1)	1.326(7)	C(6)–N(5)	1.409(6)
C(1)–C(2)	1.395(7)	N(1)–H(1A)	0.8600
C(1)–C(6)	1.418(7)	N(1)–H(1B)	0.8600
C(2)–C(3)	1.381(7)	N(2)–H(2A)	0.8600
C(2)–Cl(1)	1.731(5)	N(2)–H(2B)	0.8600
C(3)–N(2)	1.334(6)	N(3)–O(2)	1.228(6)
C(3)–C(4)	1.429(7)	N(3)–O(1)	1.233(6)
C(4)–N(3)	1.398(6)	N(4)–H(4A)	0.8600
C(4)–C(5)	1.436(7)	N(4)–H(4B)	0.8600
C(5)–N(4)	1.306(7)	N(5)–O(3)	1.224(6)
C(5)–C(6)	1.424(7)	N(5)–O(4)	1.233(6)

Table 3. Bond angles [deg] of TACDNB

bonds	angle (deg)	bonds	angle (deg)
N(1)–C(1)–C(2)	118.8(4)	N(5)–C(6)–C(1)	119.0(4)
N(1)–C(1)–C(6)	124.5(4)	N(5)–C(6)–C(5)	119.0(4)
C(2)–C(1)–C(6)	116.8(4)	C(1)–C(6)–C(5)	121.9(4)
C(3)–C(2)–C(1)	125.1(4)	C(1)–N(1)–H(1A)	120.0
C(3)–C(2)–Cl(1)	117.6(4)	C(1)–N(1)–H(1B)	120.0
C(1)–C(2)–Cl(1)	117.3(4)	H(1A)–N(1)–H(1B)	120.0
N(2)–C(3)–C(2)	119.4(4)	C(3)–N(2)–H(2A)	120.0
N(2)–C(3)–C(4)	123.0(5)	N(4)–C(5)–C(6)	121.1(4)
C(2)–C(3)–C(4)	117.6(4)	N(4)–C(5)–C(4)	120.9(5)
N(3)–C(4)–C(3)	119.7(4)	C(6)–C(5)–C(4)	118.0(4)
N(3)–C(4)–C(5)	119.7(4)	N(5)–C(6)–C(1)	119.0(4)
C(3)–C(4)–C(5)	120.5(4)	N(5)–C(6)–C(5)	119.0(4)
N(1)–C(1)–C(2)	118.8(4)	C(1)–C(6)–C(5)	121.9(4)
N(1)–C(1)–C(6)	124.5(4)	C(1)–N(1)–H(1A)	120.0
C(2)–C(1)–C(6)	116.8(4)	C(1)–N(1)–H(1B)	120.0
C(3)–C(2)–C(1)	125.1(4)	H(1A)–N(1)–H(1B)	120.0
C(3)–C(2)–Cl(1)	117.6(4)	C(3)–N(2)–H(2B)	120.0
C(1)–C(2)–Cl(1)	117.3(4)	H(2A)–N(2)–H(2B)	120.0
N(2)–C(3)–C(2)	119.4(4)	O(2)–N(3)–O(1)	117.8(4)
N(2)–C(3)–C(4)	123.0(5)	O(2)–N(3)–C(4)	121.7(4)
C(2)–C(3)–C(4)	117.6(4)	O(1)–N(3)–C(4)	120.5(4)
N(3)–C(4)–C(3)	119.7(4)	C(5)–N(4)–H(4A)	120.0
N(3)–C(4)–C(5)	119.7(4)	C(5)–N(4)–H(4B)	120.0
C(3)–C(4)–C(5)	120.5(4)	H(4A)–N(4)–H(4B)	120.0
N(2)–C(3)–C(2)	119.4(4)	O(3)–N(5)–O(4)	118.7(4)
N(2)–C(3)–C(4)	123.0(5)	O(3)–N(5)–C(6)	122.0(4)
N(4)–C(5)–C(6)	121.1(4)	O(4)–N(5)–C(6)	119.3(4)

intra- and intermolecular hydrogen bonding associated with the NO₂ group. An amino group interacts with the ortho nitro groups of the same benzene ring and with a nitro group on a nearest neighbour TATB molecule to form infinite planar sheets of TATB that are bonded intermolecularly and intramolecularly by strong hydrogen bonds.¹⁵

TACDNB shows four bands (3442, 3323, 3269, 3224 cm⁻¹) in this region (Figure 2) which indicate the presence of two kinds of NH₂ groups in the molecule. Indeed the molecule has two kinds of NH₂ groups due to its symmetrical structure (Figure 3). The hydrogen atoms of the amino group at the C₅ position are completely intramolecularly hydrogen bonded with the oxygen atom of adjacent nitro groups. The hydrogen atoms of other amino groups (C₁ and C₃) are both inter- and intramolecularly hydrogen bonded similar to the TATB molecule. Thus ν_a and ν_s of intra- and intermolecularly hydrogen-bonded NH₂ appear at 3319 and 3220 cm⁻¹,

respectively, whereas the completely intramolecularly hydrogen-bonded NH₂ group shows these bands at 3442 and 3269 cm⁻¹. The band at 1030 cm⁻¹ is assigned as the stretching vibration for C–Cl.

Study of Base Hydrolysis Process. The purity of TATB was determined by amino groups estimation method in a modified Kjeldhal apparatus.¹³ The sample was digested in a steam bath with an aqueous NaOH solution in the presence of DMSO. The evolved NH₃ gas was absorbed in 0.1 N H₂SO₄ solution and the concentration estimated by back-titration. Each TATB molecule was converted to tri-nitro-phloroglucinol with evolution of three molecules of NH₃ gas as shown in the reaction in Scheme 2.¹³ TACDNB was also subjected to this analysis, and evolved NH₃ gas was estimated. TACDNB shows ~33% less NH₃ gas evolution compared to TATB. The ratio of NH₃ gas evolved is found as TACDNB/TATB = 2:3. Though TACDNB has three amino groups, only two are replaced by ⁻OH in the base hydrolysis process.

An attempt has been made to derive the reaction scheme and mechanism for base hydrolysis of TACDNB. The presence of the strong electron-withdrawing substituent NO₂ makes the compound susceptible to nucleophilic attack, and the reaction proceeds stepwise. The possible reaction mechanism is proposed based on the basic theory of nucleophilic attack on aromatic species¹⁶ and is shown in Scheme 3. The most significant canonical state of the anionic species (Wheland intermediate) is that in which the negative charge is accommodated and stabilised by an oxygen atom of the nitro group. This can only occur if the attacking ⁻OH enters into C₅ followed by C₁ or C₃ position and corresponding Wheland intermediates I and II are stabilised by the nitro group. The third ⁻OH attack does not take place, as there is no nitro group to stabilise Wheland intermediate III, and the reaction does not proceed further. The electron-withdrawing inductive (*-I*) effect of Cl is not sufficient for stabilisation of the intermediate anion. Thus, TACDNB liberates only two molecules of NH₃ during base hydrolysis.

Chlorine Content Analysis. The TACDNB was also subjected to Cl⁻ content analysis by a method reported in literature.¹⁵ The sample was digested in concentrated NaOH solution (10M) in the presence of cosolvent DMSO. TATB is converted to trinitrophenol and the inorganic chloride (present in the form of NH₄Cl) and organic chloride (present in the form of chloronitrobenzenes mainly TCTNB) are liberated to the solution. It was estimated by titration against dilute AgNO₃ solution (0.02 M) using Ag/AgCl electrode (DG141) in the Mettler autotitrator (model: DL55). The chloride content value for TACDNB is found to be ~0.05% as against its theoretical value, 14.35%. This indicates that the chloride in the compound does not get liberated by this method. The chloride is in the meta position of the nitro group in the benzene ring and shows reluctance for nucleophilic attack. The nitro group directs the nucleophilic attack in the ortho and para positions only.

Thermal Analysis. The thermal properties of TATB have been extensively studied and reported in literature.¹⁷ In our laboratory, thermal analysis of TACDNB was carried out using DSC. The DSC profile of both TACDNB and TATB are shown in Figure 4. The DSC profile of TACDNB shows a small endothermic peak at ~211 °C and a strong exothermic peak at ~328 °C. TACDNB is less thermally stable than TATB (decomposition temp. ~384 °C). Unlike TATB, TACDNB shows two stage decomposition. The heat release value for

Table 4. Torsion angles (deg) of TACDNB^a

bonds	angle (deg)	bonds	angle (deg)
N(1)–C(1)–C(2)–C(3)	179.4 (5)	N(1)–C(1)–C(6)–N(5)	0.8 (8)
C(6)–C(1)–C(2)–C(3)	0.3 (8)	C(2)–C(1)–C(6)–N(5)	179.9 (5)
N(1)–C(1)–C(2)–Cl(1)	–1.6 (7)	N(1)–C(1)–C(6)–C(5)	–179.9 (5)
C(6)–C(1)–C(2)–Cl(1)	179.2 (4)	C(2)–C(1)–C(6)–C(5)	–0.8 (7)
C(1)–C(2)–C(3)–N(2)	179.9 (5)	N(4)–C(5)–C(6)–N(5)	0.4 (8)
Cl(1)–C(2)–C(3)–N(2)	0.9 (7)	C(4)–C(5)–C(6)–N(5)	–179.1 (4)
C(1)–C(2)–C(3)–C(4)	–0.5 (8)	N(4)–C(5)–C(6)–C(1)	–178.9 (5)
Cl(1)–C(2)–C(3)–C(4)	179.5 (4)	C(4)–C(5)–C(6)–C(1)	1.6 (7)
N(2)–C(3)–C(4)–N(3)	1.0 (8)	C(3)–C(4)–N(3)–O(2)	–178.8 (5)
C(2)–C(3)–C(4)–N(3)	–178.5 (4)	C(5)–C(4)–N(3)–O(2)	1.3 (8)
N(2)–C(3)–C(4)–C(5)	–179.1 (5)	C(3)–C(4)–N(3)–O(1)	3.3 (8)
C(2)–C(3)–C(4)–C(5)	1.3 (7)	C(5)–C(4)–N(3)–O(1)	–176.5 (5)
N(3)–C(4)–C(5)–N(4)	–1.5 (8)	C(1)–C(6)–N(5)–O(3)	–166.7 (5)
C(3)–C(4)–C(5)–N(4)	178.7 (5)	C(5)–C(6)–N(5)–O(3)	14.1 (8)
N(3)–C(4)–C(5)–C(6)	178.0 (5)	C(1)–C(6)–N(5)–O(4)	11.7 (7)
C(3)–C(4)–C(5)–C(6)	–1.9 (7)	C(5)–C(6)–N(5)–O(4)	–167.5 (5)

^aSymmetry transformations used to generate equivalent atoms.

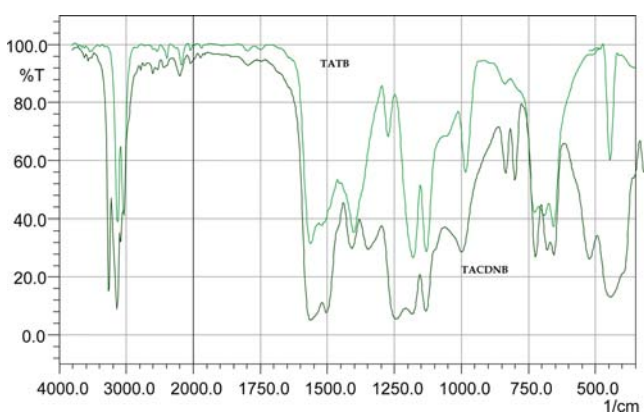


Figure 2. FTIR spectra of TATB and TACDNB.

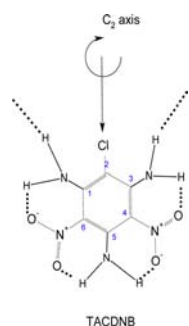
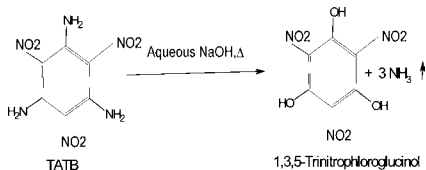


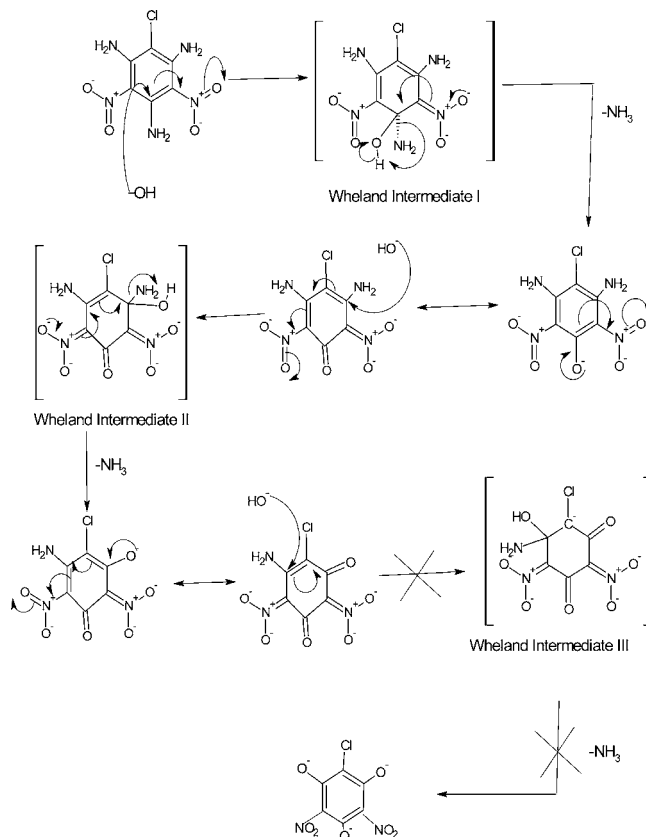
Figure 3. Structural representation of hydrogen bonds present in TACDNB.

Scheme 2. Base hydrolysis reaction for TATB



decomposition of TACDNB ($\Delta H = -687$ J/g) is found less than that of TATB ($\Delta H = -932$ J/g). The small endo peak at 211 °C ($\Delta H = 24.3$ J/g) for TACDNB may be due to

Scheme 3. Reaction mechanism showing base hydrolysis of TACDNB



crystallographic phase change rather than melting. Like TATB, TACDNB also does not have an observable melting point.

Sensitivity Test. Friction and impact sensitivity data of TATB, TACDNB, and contaminated TATB sample are shown in Table 5. All samples were found to be friction insensitive up to 36 kg (upper limit of the instrument). However, there is a substantial difference in impact sensitivity. TACDNB is more sensitive to impact compared to TATB. The height of 50% explosion (H_{50}) was reduced from a range of 150–170 cm to 50–58 cm. Thus, the TACDNB-contaminated TATB sample is

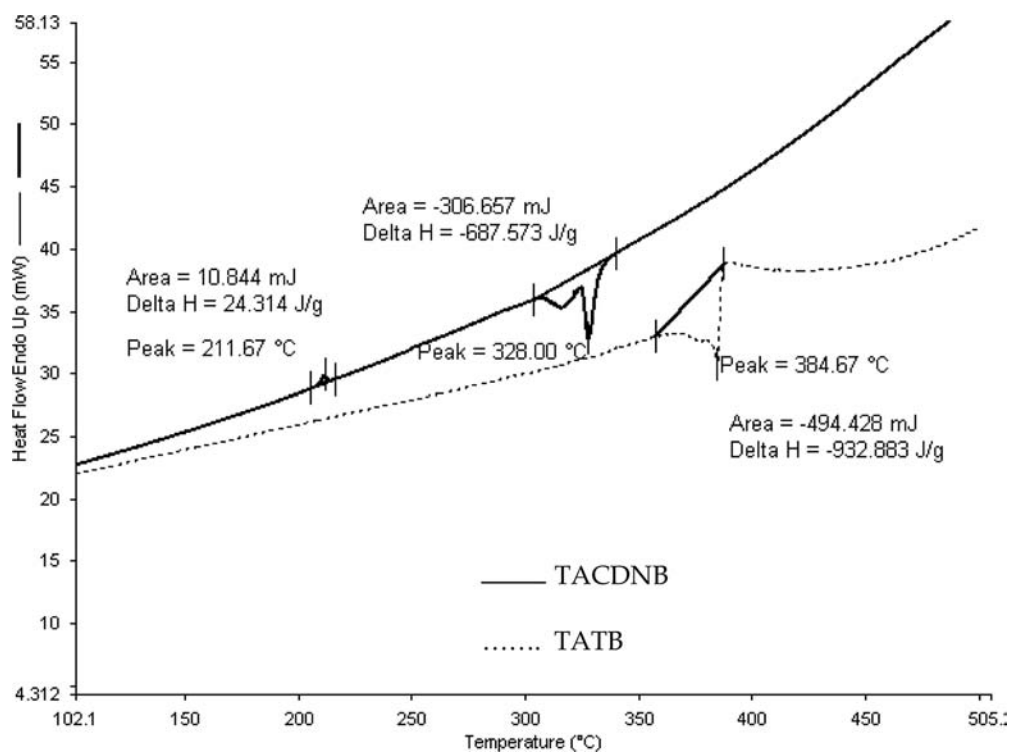


Figure 4. DSC profile of TACDNB and TATB.

Table 5. Impact and friction sensitivity data

sample code	impact test ^a		insensitive to friction ^b (kg)
	H_{50} (cm)	F of I	
TACDNB	50–58	56–64	36
TATB	150–170	170–224	36
TACDNB (2.5%) contaminated TATB	75–80	83–89	36

^a H_{50} , height of 50% explosion with 2 kg drop wt. ; F of I (Figure of Insensitivity) w.r.t standard CE(tetryl)(H_{50} = 57 cm); relative humidity = 45%, temp. 33 °C. ^b36 kg is the upper limit of the instrument

found to be more impact sensitive compared to the normal batch sample (Table 5). The basic properties of TACDNB were compared with TATB and are shown in Table 6.

Investigation on Process Conditions Attributed to Orange–Red Impurity Formation. An attempt was made to investigate the process conditions which lead to the formation of TACDNB in the amination reaction. It is already mentioned that this impurity formation was occasionally observed and occurred with few batch experiments. On analysis of process

conditions of the failed batches, it is revealed that excess ammonia (40–50% in excess of stoichiometric requirement) was fed into the reactor during amination. Generally 5–10% excess ammonia is required to be fed into the system to ensure complete amination. Inadequate ammonia feeding causes incomplete amination and results in low reaction yield.

As already discussed, TATB is prepared in two step processes, *viz.*, nitration and amination. The nitration process gives intermediated crude TCTNB which contains two predominant impurities 1,3,5,6-tetrachloro-2,4-dinitrobenzene (T_4 , 7–9%) and 1,3,5-trichloro-2,4-dinitrobenzene (T_3 , 2–3%).¹⁸ The reaction mechanism which leads to the formation of these two impurities in the nitration process was well reported in literature and it is beyond the scope of this paper.¹⁹ These impurities are not reactive to the weak nucleophile ammonia ($-R$ effect of two nitro groups does not activate the aromatic ring for nucleophilic attack), and hence crude precursor can be used in the amination process with out further purification. However, if excess ammonia is fed into the system, NH_3 reacts with T_4 , and compound TACDNB is formed which is precipitated out due to its poor solubility in toluene. Only the Cl groups which are in the ortho and para

Table 6. Comparison of properties of TACDNB and TATB

properties	TACDNB	TATB
state	solid	solid
colour	orange red	yellow
solubility	insoluble in most common solvents and soluble in DMSO	insoluble in most common solvents and sparingly soluble in DMSO
melting point (°C)	no observable mp	no observable mp
DSC (dec peak temp. °C)	322	380
impact sensitivity (H_{50} , m)	50–58	150–170
insensitive to friction (kg) ^a	36	36

^a36 kg is the upper limit of the instrument.

positions are replaced as nitro group directs ortho and para positions for nucleophilic attack. Chlorine at the meta position remains unchanged. T_3 also reacts with excess ammonia and forms 1,3,5-triamino-2,4-dinitrobenzene (TADNB). However, TADNB has good solubility in toluene, and hence, it does not precipitate out as TACDNB does.

It is also observed that the particle size of the impurity TACDNB is much larger than TATB. Higher particle size is favored by crystal growth.²⁰ The low concentration of T_4 in toluene and its poor reactivity with NH_3 keeps the formation rate very slow. Thus, the nucleation rate of the TACDNB crystallisation process is very slow compared to that of TATB resulting in formation of bigger particles. To demonstrate the proof that the TACDNB is formed from T_4 and also to understand the process conditions which favor the formation of this sensitive impurity, we have studied the amination of the T_4 in a small-scale (2 L) Parr pressure reactor (model 4532M). T_4 was isolated from the toluene-rich amination effluent (generated in the pilot-plant process) by distilling out the toluene. The yellow-coloured effluent toluene contains dissolved solids, chloronitrobenzenes mainly T_4 (~88%) and T_3 (~10%) along with unreacted TCTNB (<1%) and aminated chloronitrobenzenes (<1%). The isolated solid was purified by recrystallization using dichloromethane solvent. The GC analysis (Varian, model: CP-3800; capillary column BPX-50, length 30 m, ID 0.32 mm, film thickness 0.25 μm ; split capillary injector: split ratio 1:20, temp. 220 $^{\circ}C$; oven: isothermal, 200 $^{\circ}C$; ECD, 300 $^{\circ}C$; carrier gas ultrahigh pure (UHP) nitrogen; column flow 5 cc/min, makeup flow 25 cc/min; injection volume 0.1 μL ; sample concentration 30 mg/L; internal standard (2,5-dinitrotoluene) of recrystallized solid indicates the presence of T_4 ~95% along with T_3 ~5%. This recrystallized product was taken as the starting material for the study without further purification.

Amination of this recrystallized product was carried out in toluene (50 g solid dissolved in 600 mL toluene) at two different temperatures viz. 125 and 150 $^{\circ}C$ (the present amination reaction temperature practiced in the pilot plant process of this laboratory is 125 $^{\circ}C$). Ammonia gas was fed into the reactor from a cylinder source to realize the intended reactor pressure (2, 3, 5, 7, 9, and 10 bar), and the reactor was sealed. The consumption of ammonia gas was monitored by observing the pressure drop of the reaction vessel upon standing for 1 h. The T_4 solution in toluene was first heated to 90 $^{\circ}C$, and the inert nitrogen gas present inside the reactor was vented off by opening the reactor pressure-releasing valve. The reactor was then heated to realize the desired reaction temperature. The observed reactor pressures were ~1.5 bar and ~2.5 bar at temperatures 125 and 150 $^{\circ}C$, respectively, which is due to toluene vapour pressure (boiling point of toluene is 109 $^{\circ}C$). Ammonia gas was fed into the reactor to realize the desired reactor pressure, and an initial rapid pressure drop (~0.25 bar) was observed due to dissolution of NH_3 gas in toluene which was compensated by further ammonia feeding, and the reactor was sealed. The consumption of the fed ammonia gas by the amination reaction with the dissolved solids (T_4 and T_3) was observed by noticing the reactor pressure upon standing for 1 h.

A set of experiments was carried out at reaction temperature 125 $^{\circ}C$. We did not observe any substantial drop in the reactor pressure (consumption of ammonia) from the reactor sealing pressure up to 5 bar. Moreover, there was also no precipitation of solid in the reaction mixture. However, a significant pressure

drop was observed when the reactor was sealed at 7, 9, and 11 bar. Upon standing, the reactor pressure was observed to get stabilized at ~5 bar. An orange-red precipitate (finer particles) was found in the reaction mixture. The precipitated solid was first isolated by decantation of toluene. It was then boiled in hot water (to remove by-product NH_4Cl), and the slurry was filtered, washed (with hot water), and dried. The orange-red solid was characterized by FTIR and DSC. The vibrational spectrum and the DSC profile match that of TACDNB. Thus, it may be concluded that the formation of TACDNB takes place at higher partial pressure of NH_3 gas (>3.5 bar, i.e. 5–1.5 bar exerted by toluene vapour) in the amination process at reaction temperature 125 $^{\circ}C$. However, at higher reaction temperature (150 $^{\circ}C$), TACDNB starts forming at a lower partial pressure of NH_3 (~1.5 bar, i.e., 4.0–2.5 bar exerted by toluene vapour).

As already discussed, the reactivity of the intermediate TCTNB with ammonia gas is higher than that of T_4 and T_3 . Hence, under a competitive environment, TCTNB gets aminated first. In the pilot-plant process of this laboratory, the ammonia gas is fed into the reactor at a constant rate from a cylinder source, and the reactor pressure is maintained at 4 bar. Towards the completion of reaction, i.e. after consumption of available TCTNB, a slow rise in reactor pressure (>4 bar) was observed due to accumulation of unreacted ammonia gas in the reaction vessel. Formation of TACDNB is taking place during this period. Accordingly, in the pilot-plant process, the ammonia feeding rate is controlled towards the end of the reaction which does not allow the reactor pressure to reach more than 5 bar which favors the formation of TACDNB.

CONCLUSION

The orange-red visible impurity, TACDNB, is formed in the amination process of crude TCTNB in the presence of excess ammonia. This is due to the amination of T_4 , a predominant impurity present in crude TCTNB. TACDNB is an objectionable impurity in the product TATB as it affects the impact sensitivity. The formation of this impurity can be avoided by feeding the appropriate quantity of NH_3 gas into the reactor and maintaining the reactor pressure <5 bar. TACDNB exhibits some explosive properties and needs further evaluation.

AUTHOR INFORMATION

Corresponding Author

*Fax: +91-020-25869031. E-mail: nandi.ak@hemrl.drdo.in.

Notes

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