

# Synthesis of 1,3-diamino-2,4,6-trinitrobenzene from trinitroresorcinol

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## Introduction

Modern secondary explosive should have high detonation parameters (VOD >7.5 km/s) and low sensitivity for impact (15J), friction (>360N), attack by bullet and jet projectile (no detonation). The other requirements for explosives are strongly related to the type of projected type of ammunition, in which the explosive will be used. E.g. for high-mass shells melt-cast explosives are preferred so melting point of explosive (or composition) can't exceed 100°C and should be stable in liquid phase (like TNT, DNAN). To small caliber missiles the explosives with low critical diameter are looking for. For some ammunition types when demilitarization is foreseen so in this case water or acetone soluble explosives are desired (e.g. NTO, RDX). The other but very important factor which is determining suitability of explosive is the production cost. If the production process requires high temperatures, long reaction times, complex reagents, synthesis is multistage and yields are low the explosive rather not find wider application. An example of explosive which is a some kind of low sensitivity standard is 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). For density 1.80 g/cm<sup>3</sup> the detonation velocity for TATB is equal 7.3 km/s and impact sensitivity 50 J [1] but due to relatively high production costs it use is limited to special purposes.

In some purposes an alternative for TATB is its homologue contain only two amino groups 1,3-diamino-2,4,6-trinitrobenzene (DATB). The lack of one amino group causes that DATB has better oxygen balance and lower critical diameter [1]. DATB has been synthesized for the first time by Noelting and Collin in reaction between 1,3-dioxy-2,4,6-trinitrobenzene and ammonia [2]. Pure DATB melts at 284–285°C [3, 4] and next undergoes exothermic decomposition above 300°C. Impact sensitivity ( $h_{50}$ ) is equal > 320 cm (for TNT 200 cm). At a density 1.82 g/cm<sup>3</sup> detonation velocity is equal 7.64 km/s and detonation pressure 25.1 GPa. Detonation critical diameter is approx. 0.5 mm [5].

All described DATB synthesis methods based on three strategies: (1) introduction amino groups with ammonia into halogen or alkoxy groups place in trinitrobenzene derivatives, (2) direct amination of nitrobenzene in vicarious nucleophilic substitution (VNS) conditions, (3) nitration of diaminobenzene. Scheme showing various methods DATB synthesis is shown in Figure 1.

Historically DATB second method was developed by Meisenheimer (after his name complex formed during nucleophilic substitution in aromatic compounds was named). He used hydroxylamine in a sodium methoxide environment for hydrogen substitution in trinitrobenzene [6]. The third original path described by Bell and Cohen was direct nitration of diaminobenzene [7]. Last discovered DATB synthesis methods apply gaseous ammonia and dichloro- or difluorotrinitrobenzene [8, 3]. In 2002, Bellamy et al. reported a original modification of

Noelting method, wherein dimethoxytrinitrobenzene is prepared in reaction of trinitroresorcinol with triethyl orthoformate [4]. The resulting precursor is then treated with ammonia in toluene and DATB is formed with yield 98% (of last step) and the product has melting point 285°C.

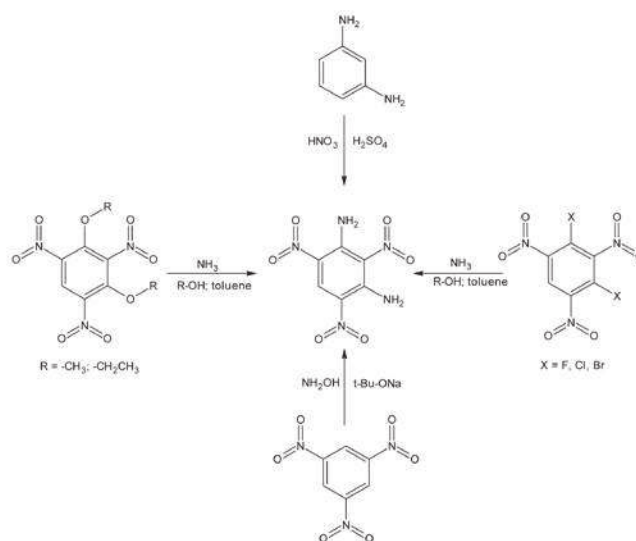


Fig. 1. Scheme showing various methods for DATB synthesis

The aim of this work was check whether it is possible to obtain DATB by using trinitroresorcinol (TNR) which in first step was ethoxylated with triethyl orthoformate and next aminated in autoclave with ammonia dissolved in toluene at overpressure 8 bar in room temperature.

Bellamy et al. in the paper [4] described alkylation of trinitroresorcinol only with trimethyl orthoformate, while in case of TATB synthesis he used orthoformate trimethyl-, triethyl and tripropyl [4]. In our work trinitroresorcinol was chosen for synthesis of DATB due to the mild conditions of its preparation. Thanks to dihydroxysubstitution of benzene ring, nitration is possible in mild conditions in contrast to nitration of di- and trichlorobenzene (TCB). Synthesis of trinitroderivative of TCB requires the temperatures 140–150°C and reaction time ca. 20h [9]. Additionally, trinitroresorcinol is the available substrate and relatively inexpensive due to the continued use lead trinitroresorcinate in ammunition igniters.

## Results and discussion

All chemicals like trinitroresorcinol, triethyl orthoformate, toluene and ammonia were analytical grade and obtained from commercial sources (Avantor, Sigma-Aldrich, Loba Chemie, Chempur, Multax). NMR experiments were conducted with a Bruker Avance III HD 500 MHz spectrometer (field 11.7 T). <sup>1</sup>H and <sup>13</sup>C spectra were referenced to tetramethylsilane (TMS) protons and carbons respectively. The <sup>15</sup>N spectra are proton decoupled

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and chemical shifts are referenced to liquid ammonia. Spectra of all pure samples were measured at room temperature. DTA/TG measurements to determine the decomposition temperatures of products were conducted in open  $\text{Al}_2\text{O}_3$  crucibles (50  $\mu\text{L}$  in volume) in argon flow atmosphere (50 mL/min) at constant heating rate (5 K/min) from 25 to 500°C. DTA/TG analyses were carried out with a LabSYS apparatus (Setaram).

Synthesis scheme for DATB is shown in Figure 2. In the first step triethyl orthoformate was heated with trinitroresorcinol. Next the ethylation product was treated with ammonia in toluene under pressure.



Fig. 2. Scheme showing synthesis of DATB from trinitroresorcinol

**Synthesis of 1,3-diethoxy-2,4,6-trinitrobenzene:** in a round bottom flask (100  $\text{cm}^3$  in volume) equipped with a thermocouple and condenser, 50  $\text{cm}^3$  of triethyl orthoformate was placed and next 3.0 g of trinitroresorcinol was added. The reaction setup was placed in an oil bath and heated at 100°C for 3h. Initially the solution has a yellow color and after reaching 100°C color was changed to brown but still transparent. Then the simple condenser was changed into Liebig condenser and started raising the temperature of bath to 140°C taking ca. 15  $\text{cm}^3$  of distillate after reaching 140°C. When the distillation was finished the mixture was cooled to 25°C and placed in a fridge (4°C) for 0.5h. The precipitated crystals were filtrated and recrystallized from 50  $\text{cm}^3$  of ethanol. The product was air dried at 100°C for 24h. Pale yellow crystals (2.5 g) was obtained with yield 69%, the product was subjected to structural analysis with NMR technique. In the proton NMR spectrum of TEtTNB there are characteristic signals as follows: triplet 1.30 ppm, quartet 4.25 ppm and singlet 8.97 ppm. Two multiplets correspond to ethyl groups in ethoxyl derivatives, singlet can be attributed to single proton in 5-position of benzene ring. The ratio of the signals integrals is equal 6:4:1 and corresponds to the expected structure of diethoxytrinitrobenzene. In  $^{13}\text{C}$  NMR spectrum there are characteristic groups of signals at aliphatic region (15.6 and 17.0 ppm) corresponds to ethyl groups. Due to the symmetry of the DEtTNB molecule only four signals are observed in aromatic region of the spectrum: 126.1 (C5); 137.5 (C2); 142.5 (C4, 6) and 149.6 (C1, 3) ppm. In  $^{15}\text{N}$  NMR spectrum there only two signals 361.0 ppm (nitro group in position 4 and 6), 361.7 ppm (nitro group in position 2).

DTA/TG curves obtained for DEtTNB are shown in Figure 3. On DTA curve two peaks was observed, first endothermic with maximum at 121°C, which can be attributed to the melting of the sample and second exothermic with max. at 281°C which can be assigned to exothermic decomposition of the sample. TG curve analysis shown that sample is stable up to ca. 170°C when it begins to slow mass loss. The maximum rate of mass loss is observed at 280°C and this effect is well corresponding with exothermic peak observed on DTA curve. Small and broad exothermic peak with max. ca. 320°C is observed and can be assigned to changes running in solid decomposition products. DTA/TG analysis of the 1,3-diethoxy-2,4,6-trinitrobenzene sample shows that the compounds has a high-energetic properties and can be considered as an explosive.

**Synthesis of 1,3-diamino-2,4,6-trinitrobenzene:** 100  $\text{cm}^3$  of toluene was placed in an autoclave (vol. 300  $\text{cm}^3$ ) and reactor was cooled with solid  $\text{CO}_2$  bath to -40°C. Next gaseous ammonia was passed through the toluene for 15 min. After completion of saturation of toluene, in one portion 1.5 g of DEtTNB was added. The autoclave

was closed and magnetic stirrer was started. The mixture was allowed to warm naturally to ambient temperature (20°C), resulting ammonia pressure inside was ca. 8 bar. Under these conditions the system was mixed for 24h. Then pressure was reduced to atmospheric and autoclave was opened. Resulting suspension of yellow crystals in toluene was filtered, washed with cold toluene and methanol. Product was air dried at 100°C for 24h. Finally 1.1 g of yellow crystals was obtained ( $\alpha = 91\%$ ).

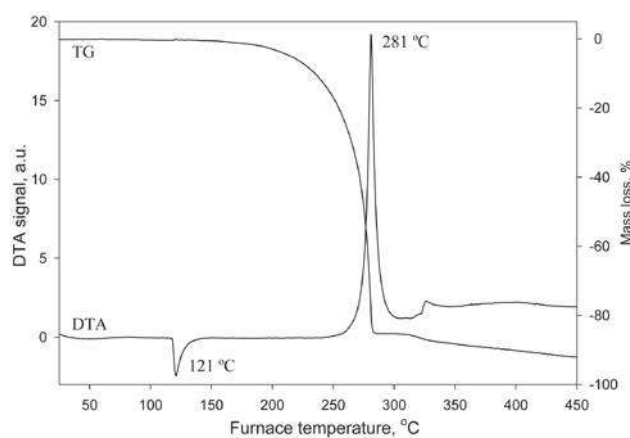


Fig. 3. DTA/TG curves obtained for 1,3-diethoxy-2,4,6-trinitrobenzene sample

Due to the low solubility of DATB in most organic solvents [10], the NMR spectra with satisfactory resolution can be obtained only with polar aprotic solvents like DMSO, DMF or NMP. Presented NMR spectra of DATB was registered in  $\text{DMSO}-d_6$ . In the proton NMR spectrum a singlet 9.12 ppm is observed which can be attributed to aromatic proton in position 5 of ring. The protons of amino groups have a very similar chemical shift to C-H proton and signals overlaps each other. The proton spectrum recorded with 500 MHz spectrometer allow to see small peak asymmetry and make deconvolution. Another method to obtain the signal from protons of amino groups is to register the  $^1\text{H}-^{15}\text{N}$  HSQC spectrum and therefore chemical shift of the  $-\text{NH}_2$  protons appears approx. 9.1 ppm. Due to the symmetry of DATB molecule on  $^{13}\text{C}$  NMR spectrum (Fig. 5) four signals are appeared with chemical shifts: 121.4; 122.9; 132.1 and 146.4 ppm. The first signal can be attributed to carbon which is connected to nitro group in position 2, next signal is from carbons in position 4 and 6 of the ring, signal 132.1 ppm can be assigned to carbon which is connected with proton (intensity is enhanced by Overhauser effect (NOE)). The last peak corresponds to carbons in positions 1 and 3 in the benzene ring. The nitro groups in DATB gives two signals in  $^{15}\text{N}$  NMR spectrum (Fig. 6) with chemical shifts: 366.9 ppm (position 4 and 6) and 368.3 ppm (position 2). The nitrogens in amino groups are represented by signal 95.0 ppm.

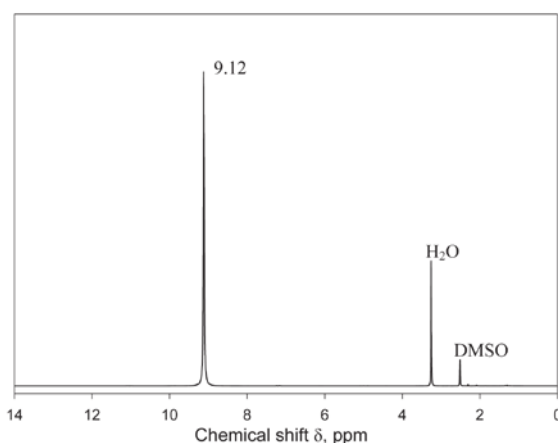


Fig. 4.  $^1\text{H}$  NMR spectrum of 1,3-diamino-2,4,6-trinitrobenzene

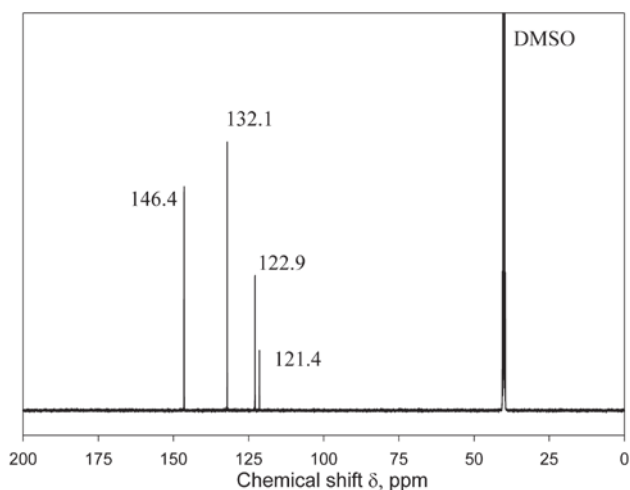


Fig. 5.  $^{13}\text{C}$  NMR spectrum of 1,3-diamino-2,4,6-trinitrobenzene

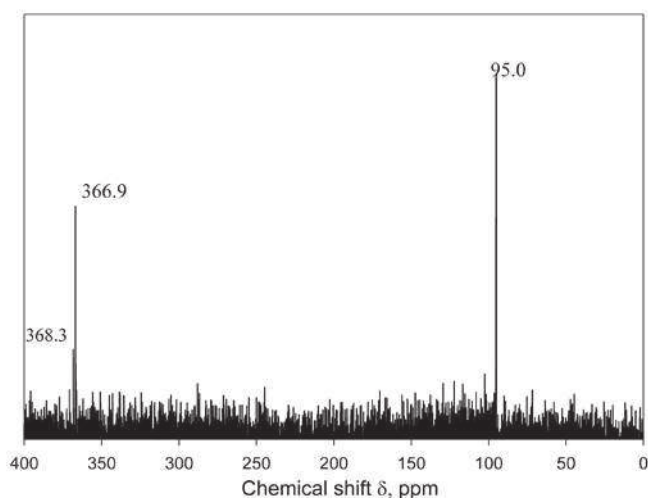


Fig. 6.  $^{15}\text{N}$  NMR spectrum of 1,3-diamino-2,4,6-trinitrobenzene

DTA/TG curves obtained for DATB are shown in Figure 7. On DTA curve two endothermic peaks with different intensity was observed: 229°C (wide and low intensity) and 284°C (sharp). For first DTA signal loss of weight was not accompanied so it can be interpreted as the polymorphic phase change [4]. Second endothermic signal corresponds to the melting of the sample and is accompanied by small mass loss, which means that the melting takes place with a partial decomposition of the sample. The maximum decomposition rate occurs at 325°C but maximum of exothermic decomposition peak is observed at 366°C. This difference can be explained by intramolecular condensation of amino and nitro groups, which is endothermic process. This process is characteristic for aromatic amino- nitrocompounds having these groups in the *ortho* position. The condensation process is accompanied by the water release which is observed on the TG curve as a slow mass loss [11]. The broad exothermic peaks with low intensity which are occurred after main decomposition peak can be attributed to oxidation of solid decomposition products. Analysis of DTA/TG curves obtained for DATB can classify it as a high-energetic material, which is confirming the published literature data [1].

DTAB which is energetic material with reduced sensitivity can be relatively easily obtained from available trinitroresorcinol. This means that explosive with desired properties can be prepared by using other explosive with much higher sensitivity. Trinitroresorcinol used to DATB synthesis may also come from demilitarization of artillery detonators and igniters which would have important ecological aspect. The use of recovered trinitroresorcinol to DATB synthesis can be alternative to the destruction of detonators by burning, which would also reduce the amount of toxic lead introduced to the environment.

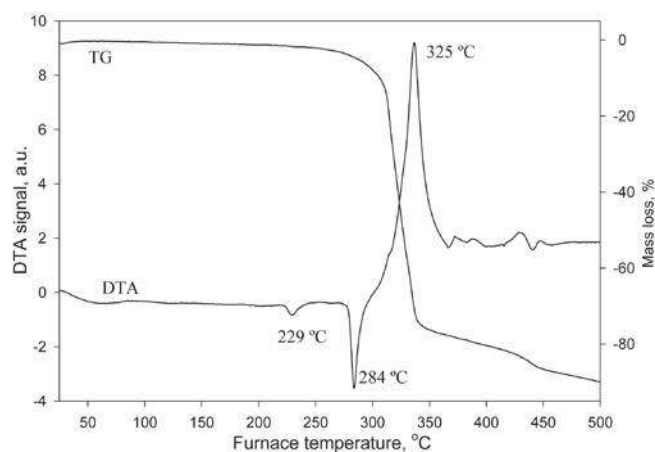


Fig. 7. DTA/TG curves for 1,3-diamino-2,4,6-trinitrobenzene

## Conclusion

Based on the experimental results analysis it can draw the following conclusions:

1. In reaction between trinitroresorcinol and triethyl orthoformate the 1,3-diethoxy-2,4,6-trinitrobenzene can be obtained which is a useful substrate for DATB synthesis. The precursor can be classified as explosive and due to the relatively low melting point may be used as component of melt cast explosives.
2. Substitution of ethoxyl groups in DETNB by using ammonia in toluene proceeds with high yield. Applied relatively long time for complete substitution may be shortened in particular thanks to the use of ammonia overpressure in autoclave.
3. DATB decompositions starts just after it has melted so elaboration in liquid phase of DATB is impossible. The volume change accompanying phase change (229°C) in solid phase is unknown. It is necessary to perform quantitative studies of this phenomenon to estimate the maximum safe temperature for use of formulations contain DATB.

## Acknowledgments

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## Aktualności z firm

### News from the Companies

*Dokończenie ze strony 54*

#### Muzeum sztuki i wzornictwa w Brukseli

W grudniu 2015 w Brukseli otwarte zostało muzeum współczesnej sztuki i wzornictwa ADAM (Art and Design Atomium Museum), mieszczące się w centrum biznesowym Brussels Trade Mart w parku wystawowym Heysel Exhibition Park. W muzeum można zwiedzić „Plasticarium” – jedyną na świecie stałą wystawę poświęconą sztuce i wyrobom użytkowym wykonanym z tworzyw sztucznych. Wystawa została stworzona przez Philippe Decelle, prawdziwego entuzjastę, któremu udało się zgromadzić kilka tysięcy eksponatów – począwszy od „złotej ery” tworzyw we wczesnych latach 60. XX w. *pop art* i postmodernizm. (kk)

(<http://www.plasticseurope.pl/>, 4.01.2016)

#### Laboratorium informatyki biomedycznej we Wrocławiu

Na Politechnice Wrocławskiej powstało laboratorium informatyki biomedycznej, w którym będą prowadzone badania m.in. nad wykorzystaniem wirtualnej rzeczywistości w szkoleniu lekarzy i we wczesnym diagnozowaniu choroby Alzheimera. Uruchomienie nowoczesnego laboratorium wiąże się z otwarciem nowego kierunku studiów na Politechnice Wrocławskiej – informatyki medycznej. Jak poinformował w poniedziałek PAP Michał Ciepelski z biura prasowego wrocławskiej uczelni, Politechnika Wroclawska zdecydowała się na uruchomienie nowego kierunku studiów, ponieważ informatyka zaczyna odgrywać coraz większą rolę w medycynie.

W nowym laboratorium ma być realizowany m.in. projekt z zakresu zastosowania wirtualnej rzeczywistości w kształceniu lekarzy neurochirurgów i wczesnej diagnostyki choroby Alzheimera. Badania mają dotyczyć zaburzeń równowagi u pacjentów, u których tę chorobę zdiagnozowano. Wykorzystywane w nich będą urządzenia 3D oraz platforma posturograficzna, za pomocą której sprawdzana jest dynamika środka ciężkości. W projekty prowadzone przez wrocławską uczelnię zaangażowane są ośrodki medyczne z Wrocławia i Opola. (kk)

(<http://naukawpolsce.pap.pl/>, 15.12.2015)

#### OCHRONA ŚRODOWISKA

##### PCC Rokita zmniejsza emisję pyłów

Spółka PCC Rokita zainstalowała w elektrociepłowni najnowszej generacji elektrofiltr zmniejszający stężenie emitowanych pyłów. Pomimo że obniżone unijne normy, zgodnie z uczestnictwem

firmy w Przejściowym Planie Krajowym, obowiązywać będą dopiero w 2020 r., firma już teraz zmniejszyła stężenie z 50 na 20 mg/m<sup>3</sup>. Obecna norma jest znacznie wyższa i wynosi 100 mg/m<sup>3</sup>. Inwestycja kosztowała 7 mln PLN. (kk)

(<http://www.plastech.pl/>, 13.01.2016)

##### ICENIL odpowiedzią na zmiany klimatu i przemysłowe zagrożenia chemiczne

Konsorcjum ICENIL zajmie się wdrażaniem przyjaznych środowisku technologii energetycznych oraz zmniejszeniem zagrożeń chemicznych, wynikających ze złego zarządzania substancjami toksycznymi i odpadami przez zakłady przemysłowe. W skład konsorcjum wchodzi Międzynarodowe Centrum Bezpieczeństwa Chemicznego (ICCSS), Norweski Instytut Ochrony Powietrza (NILU) i NILU Polska, oraz Centrum Energetyki Akademii Górniczo-Hutniczej. ICENIL łączy międzynarodowe doświadczenie instytucji, tworząc specjalistyczną platformę analityczno-naukową. W badaniach wykorzystywane będą pionierskie techniki badawcze i obliczeniowe m.in. analiza zanieczyszczeń środowiska z kosmosu (obserwacja satelitarna) oraz modelowanie numeryczne klimatu i pogody, a także nowoczesna aparatura laboratoryjna. (kk)

więcej na [www miesiecznikchemik.pl](http://www miesiecznikchemik.pl)

(Komunikat prasowy Targi Kielce SA, 8.01.2016)

##### Bydgoszcz z czystszyim powietrzem dzięki inwestycji PGE

W Zespole Elektrociepłowni Bydgoszcz, po niespełna roku intensywnych prac, uruchomiona została instalacja odsiarczania spalin (IOS), która nawet 7-okrotnie obniży emisję dwutlenku siarki. Zakończony właśnie projekt o wartości 65 mln PLN jest częścią wartego kilkanaście mld PLN programu modernizacji aktywów Grupy PGE, którego celem jest wydłużenie zdolności wytwórczych bloków energetycznych poprzez dostosowanie ich do coraz ostrzejszych wymagań środowiskowych. Uruchomiona w Bydgoszczy instalacja zredukuje roczną emisję pyłu o ok. 13 ton oraz zmniejszy emisję dwutlenku siarki o ok. 1380 ton rocznie, co pozwoli dostosować urządzenia wytwórcze w ZEC Bydgoszcz do nowych wymagań środowiskowych UE. Dzięki temu PGE będzie mogła produkować ciepło dla mieszkańców Bydgoszczy, zapewniając pokrycie bilansu ciepła dla odbiorców komunalnych i przemysłowych w mieście po 2015 r. (kk)

(<http://www.gkpg.pl/>, 8.12.2015)

*Dokończenie na stronie 63*