New Synthetic Methods for 4,4',5,5'-Tetranitro-2,2'-bi-1*H*-imidazole (TNBI)

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Abstract: Four new nitration methods for the synthesis of 4,4',5,5'-tetranitro-2,2'-bi-1*H*-imidazole (TNBI) were examined. TNBI was synthesized by nitration of 2,2'-bi-imidazole (BI) with the following mixtures: $(CH_3CO)_2O/HNO_3$, $(CF_3CO)_2O/HNO_3$, P_4O_{10}/HNO_3 and $H_3PO_4/P_4O_{10}/HNO_3$. Nitration of BI with a mixture of nitric acid and acetic anhydride leads to 4,4'-dinitro-bi-imidazole. The other nitrating conditions investigated gave TNBI in lower yields (6.0-22.4%). Crystallization of crude TNBI from wet ethanol/acetone gave TNBI as its dihydrate. The structures of BI and TNBI were characterized by ^1H, ^{13}C and ^{15}N NMR spectroscopy and elemental analysis. Friction and impact sensitivity, detonability and detonation velocity were determined for pure TNBI dihydrate.

Keywords: tetranitrobiimidazole, nitration, synthesis, explosive properties

1 Introduction

4,4',5,5'-Tetranitro-2,2'-bi-1*H*-imidazole (TNBI) was probably synthesized for the first time in 1933 by Lehmstedt [1] via the nitration of 2,2'-bi-imidazole (BI). However, at that time, high-precision structural analytical methods were not available and the author proposed the structure as the N-nitro derivative. In 1970 Novikov and co-workers [2] published the results of a systematic study of the nitration of imidazole and bi-imidazole with different nitration mixtures. Based on the quantity of nitration products obtained, they proved that the nitration of BI under harsh nitration conditions gives tetranitrobi-imidazole,

which is a C-nitro derivative [2]. Confirmation of the TNBI structure was proved by single crystal X-ray diffraction [3]. Moreover, the X-ray results showed that the product crystallized from water in the form of the dihydrate (TNBI·2H₂O). The mechanism of C-nitro imidazole formation is well known and includes the thermally induced sigmatropic rearrangement of an N-nitro derivative [4].

Cho and co-workers presented the results of a theoretical study of the energetic properties of TNBI in two papers [5, 6]. They recorded the ^{1}H and ^{13}C NMR spectra and measured the friction and impact sensitivity of TNBI from different sources. Its thermal stability was investigated using DSC, and its hygroscopicity in presence of sulfates was determined [5]. Density functional theories were used to predict the molecular structure, density and heat of formation of TNBI. Its detonation properties were calculated using the Cheetah thermochemical code. The theoretical detonation pressure in the C-J point of TNBI is comparable to that calculated for octogen, and its detonation velocity is similar to that of hexogen [6]. Recently, energetic salts of the TNBI dianion with guanidinium, aminoguanidinium and alkali metals cations were investigated by Klapötke [7] and Chavez [8].

In the present work we describe new nitration methods for the synthesis of TNBI. It is known that impurities (especially sulfates) increase the hygroscopicity of TNBI [5]. Based on this observation, we have chosen to produce TNBI by using nitrating mixtures without sulfuric acid. The structures of the products were characterized by NMR spectroscopy. Mechanical sensitivity, detonability and detonation velocity were determined for pure TNBI·2H₂O.

## 2   Experimental

2.1 Materials and methods

Glyoxal solution, ammonium acetate, fuming nitric acid, trifluoroacetic anhydride, phosphoric acid and phosphorus pentoxide, were of analytical grade (99%). Solvents like acetone, alcohols and water were of reagent grade (99.5%).

The ^{1}H,^{13}C and ^{15}N NMR spectra were recorded at room temperature with a Bruker DRX 500 spectrometer using TMS as the internal standard. Differential thermal analyses and thermal gravimetric analysis (DTA/TG) were carried out simultaneously using a LabSys-DTA-TG Setaram apparatus. Samples of the products of ca. 5 mg mass were heated from 25 to 400 °C at 5 K·min⁻¹ in a pure nitrogen atmosphere (flow rate ca. 50 cm³·min⁻¹). Elemental analyses were performed using a Perkin-Elmer CHNS/O 2400 analyzer.

The detonability was tested on a steel plate (thickness: 2 mm); the charge of pressed explosive was placed on the plate and initiated with a standard blasting cap. The values of the detonation velocity were measured for charges (unconfined) of 16.0 mm diameter, using short-circuit sensors and an electronic counter recorder.

2.2 Syntheses

All of the nitration products described below are explosive and all operations with them should be carried out by specially trained personnel. Warning! Mixtures of HNO_3 and acetic anhydride containing more than 50% by weight of HNO_3 can undergo spontaneous explosion. TNBI was prepared by direct nitration of BI with four different nitration systems. The synthesis of BI (substrate) is described below. The synthetic schemes for BI and TNBI are presented in Scheme 1.
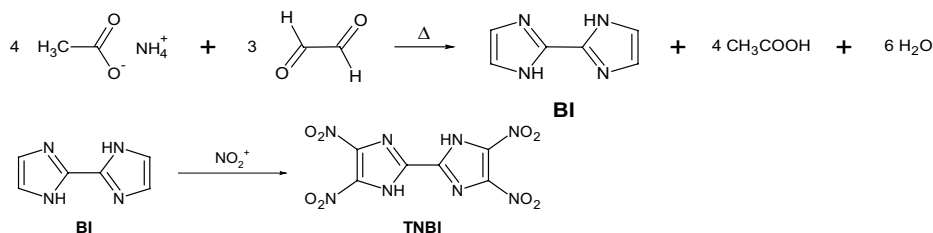
Scheme 1. Synthesis of 2,2'-bi-imidazole and 4,4',5,5'-tetranitro-2,2'-bi-imidazole.

2.2.1. Synthesis of 2,2'-bi-imidazole

BI was prepared by a modified Steffens method [9]. Ammonium acetate (801.6 g, 10.4 mol) was dissolved in distilled water (300 g). At a temperature of 40 °C, glyoxal solution (40%, 250 g, 1.7 mol) was added dropwise with constant stirring. The mixture was kept at 40 °C for 2 h. After that time, the solution was cooled to 10 °C, the solid brown precipitate was filtered off, and washed with water and acetone until the filtrate was neutral. After vacuum drying 36.0 g (47% yield) of BI was obtained. The product was thermally stable up to ca. 250 °C when sublimation commenced.

2.2.2. Nitration of 2,2'-bi-imidazole with $(CH_3CO)_2O/HNO_3$

Acetic anhydride (76.1 cm³, 0.8 mol) was added dropwise to fuming nitric acid (125.2 cm³, 3.0 mol) at a temperature below 5 °C. BI (20.1 g, 0.15 mol) was added in small portions at a temperature below 15 °C. The mixture was then kept at 10 °C for 2 h. The resulting solution was cooled to 0 °C and cold

water (300 cm^3) was added. The yellow precipitate was filtered off and washed with water until the filtrate was neutral. Finally, the product was washed with acetone and dried to give a yellow solid (6.6 g). Its decomposition temperature was 350 °C (DTA).

2.2.3. Nitration of 2,2'-bi-imidazole with (CF$_3$CO)$_2$O/HNO$_3$

Trifluoroacetic anhydride (452 cm^3, 3.2 mol) was added dropwise to fuming nitric acid (125.2 cm^3, 3.0 mol) at a temperature below 5 °C. BI (20.1 g, 0.15 mol) was added in small portions at a temperature below 15 °C. The mixture was then kept at 10 °C for 2 h. The resulting solution was cooled to 0 °C and cold water (300 cm^3) was added. The yellow precipitate was filtered off and washed with water until the filtrate was neutral. Finally, the product was washed with acetone and dried to give TNBI (10.5 g, 22.4% yield). Its decomposition temperature was 272 °C (DTA).

2.2.4. Nitration of 2,2'-bi-imidazole with P$_4$O$_{10}$/HNO$_3$

Phosphorus pentoxide (92.3 g, 0.33 mol) was added portion-wise to fuming nitric acid (125.2 cm^3, 3.0 mol) at a temperature below 10 °C. BI (20.1 g, 0.15 mol), at a temperature of 25-35 °C, was then added in small portions to the resulting solution. The mixture was then kept at 40 °C for 4 h. The resulting solution was cooled to 0 °C and cold water (300 cm^3) was added. The yellow precipitate was filtered off and washed with water and acetone. Vacuum drying gave the final product (2.8 g, 6.0% yield). Its decomposition temperature was 270 °C (DTA).

2.2.5. Nitration of 2,2'-bi-imidazole with H$_3$PO$_4$/P$_4$O$_{10}$/HNO$_3$

Phosphorus pentoxide (92.3 g, 0.33 mol) was added portion-wise to 85% phosphoric acid (103.7 g, 0.90 mol) at a temperature below 25 °C. Fuming nitric acid (125.2 cm^3, 3.0 mol) was added to the resulting solution. BI (20.1 g, 0.15 mol) was added to the nitrating mixture in small portions at a temperature of 25-35 °C. The reaction mixture was then kept at 35-40 °C for 4 h. The resulting solution was cooled to 0 °C and cold water (200 cm^3) was added. The yellow precipitate was filtered off and washed with water and acetone. Vacuum drying gave the product (19.7 g, 42.0% yield). Its decomposition ONSET temperature was 276 °C (DTA).

3   Results and Discussion

3.1 Elemental analysis

The results of the elemental analysis of the nitration products are shown in Table 1. All products with a decomposition temperature around 270-275 °C had elemental compositions similar to that calculated for TNBI·2H$_2$O and published by Klapötke [7]. The composition closest to the theoretical was for the sample obtained from the H$_3$PO$_4$/P$_4$O$_{10}$/HNO$_3$ system. The products after recrystallisation from wet solvents were the stable dihydrate. The composition of a sample had not changed significantly after several months of storage at room temperature.

Table 1.   Results of elemental analysis of the BI nitration products

Nitration mixture	HNO$_3$/BI, mole ratio	Reaction time, [h]	Decomp. [°C]	Elemental analysis, [%]		
				C	H	N
(CH$_3$CO)$_2$O/HNO$_3$		2	350	-	-	-
(CF$_3$CO)$_2$O/HNO$_3$	20.0	2	272	22.89	1.82	31.57
P$_4$O$_{10}$/HNO$_3$		4	270	23.06	1.81	30.52
H$_3$PO$_4$/P$_4$O$_{10}$/HNO$_3$		4	276	21.84	1.59	31.81
NaNO$_3$/H$_2$SO$_4$*	5.4	17	275	22.52	1.55	31.71
Theoretical composition of TNBI·2H$_2$O				20.58	1.73	32.00

* literature data [7]

It is well known that the formation of C-nitro derivatives of imidazole occurs by a thermally induced rearrangement of N-nitro compounds [10]. Our results suggest that this rearrangement occurs at 40 °C, with satisfactory yields. The yields of TNBI dihydrate (42%) obtained are slightly lower than the literature results for a NaNO$_3$/H$_2$SO$_4$ mixture (51%), but the reaction temperature was not as high and the reaction time was shorter (25%). Additionally, the product was free of sulfate, which is responsible for an increase in the hygroscopicity of TNBI.

3.2 NMR spectroscopy

The ^{1}H NMR spectrum of BI exhibited two singlets, at δ = 7.1 ppm (narrow) and 12.7 ppm (broad), with an intensity ratio of 2:1. The ^{13}C NMR (decoupled) spectrum exhibited only one signal at δ = 139.3 ppm. The proton signals were assigned to the four olefinic protons (7.1 ppm) and the two amino protons (12.7 ppm), respectively. The single ^{13}C NMR peak was assigned to the four sp^2 carbon atoms. The signal from the bridge carbons has a very low intensity and is not visible, as is typical for 3° and 4° carbon atoms in hydrocarbons [10].

The NMR analysis for TNBI samples was conducted only for samples prepared according to paragraph 2.2.5. The ^{1}H NMR spectrum of TNBI shows only one signal at $\delta = 5.1$ ppm. The chemical shift of the amino protons in TNBI is strongly dependent on the acidity of the solution; this effect was mentioned by Cho [5]. After a second recrystallisation of the product from ethanol/acetone, the chemical shift of the N-H protons in TNBI had a value of 5.1 ppm. In the ^{13}C NMR spectrum, two closely located signals were observed at $\delta = 138.7$ and 138.2 ppm. The proton signal was assigned to the two amino protons (5.1 ppm). Olefinic protons are absent, which confirms the complete substitution with nitro groups. The two signals, with almost identical chemical shifts, in the ^{13}C NMR spectrum were assigned to the four olefinic carbons. The presence of two signals from the four carbons suggests that the olefinic carbons in the two nitro-substituted imidazole rings are magnetically non-equivalent. The signal from the bridge carbons are of very low intensity and practically invisible in a classical NMR experiment. In the ^{15}N decoupled spectrum, two singlets were observed at $\delta = 236$ and 359 ppm. The first signal can be attributed to nitrogen atoms in the imidazole rings, whilst the second signal has a chemical shift characteristic of nitrogen atoms in C-nitro compounds. The ^{15}N NMR spectrum confirmed the structure of the TNBI skeleton. The information obtained from the NMR spectra is in good agreement with the literature [5, 7], however the ^{15}N NMR results are presented for the first time.

3.3 Thermal analysis of products

DTA/TG analyses were carried out to identify the characteristic temperatures of the synthesized compounds and to preliminarily assess the purity of the reaction products. From the thermograms of BI, it follows that under the experimental conditions, the sample of BI is stable to ca. 250 °C, when sublimation commences (Figure 1). The maximum rate of sublimation occurred ca. 325 °C. After sublimation the product formed colorless crystals which were present in the crucible. The DTA curve increases slowly until sublimation commences and this behavior was repeated in all BI thermograms. These results indicate that low molecular weight by-products of the condensation decompose exothermically up to the sublimation point.

Samples prepared by nitrating BI with acetic anhydride/nitric acid mixture (paragraph 2.2.2) were thermally stable to 350 °C, when decomposition commenced. This decomposition temperature is too high for TNBI and suggests that 4,4'-dinitrobi-imidazole had been prepared [11]. Nitration of BI with $(CF_3CO)_2O/HNO_3$ and P_4O_{10}/HNO_3 mixtures lead to TNBI with different purity (by DTA). The yields did not exceed 22.4%. The use of a large excess of the

nitrating mixture based on trifluoroacetyl nitrate allowed TNBI to be obtained in satisfactory yield. Nevertheless, this method is unpromising due to the high price of trifluoroacetic anhydride.
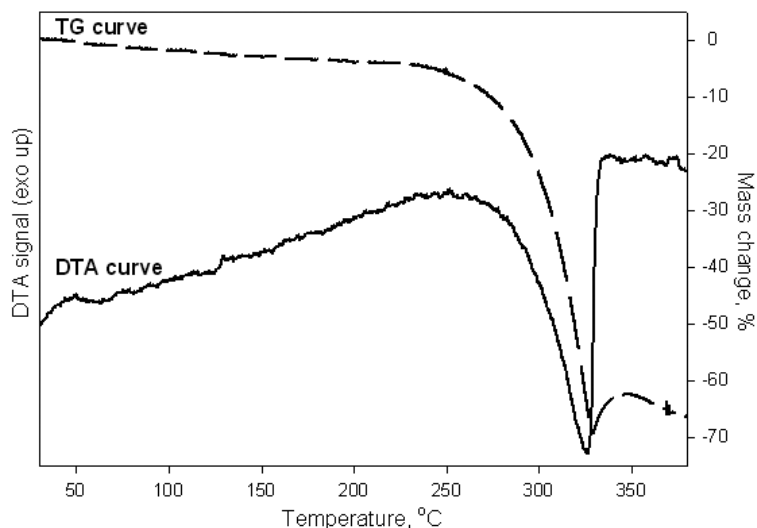

Figure 1. DTA/TG curves of BI obtained by the condensation of glyoxal solution with ammonium acetate (heating rate 5 K/min).

Thermal analysis was conducted for the TNBI sample synthesized according to the procedure described in paragraph 2.2.5. and the results are presented in Figure 2. The sample before analysis was crystallized from wet ethanol/acetone mixture and carefully dried (100 °C). The thermal curves are typical in shape for energetic materials. The DTA curve has two characteristic features whose temperatures correspond with steps in the TG curve. The first is an endothermic peak at 70 °C, and the second is an exothermic peak at 280 °C. The first peak can be attributed to complete evaporation of water absorbed from the air, but the peak shape (and length) indicates that it is not typical moisture but crystallization water. The second narrow peak with a relatively large height can be attributed to fast and exothermic decomposition of pure TNBI. The mass change which accompanied the dehydratation of sample allowed the stoichiometry of TNBI dihydrate to be calculated. The water mass which evaporated from the investigated sample indicated that after crystallization from wet ethanol/acetone, the TNBI was recovered as the dihydrate. The characteristic temperatures recorded for the synthesized TNBI·H_2O are in good agreement with literature data [5].
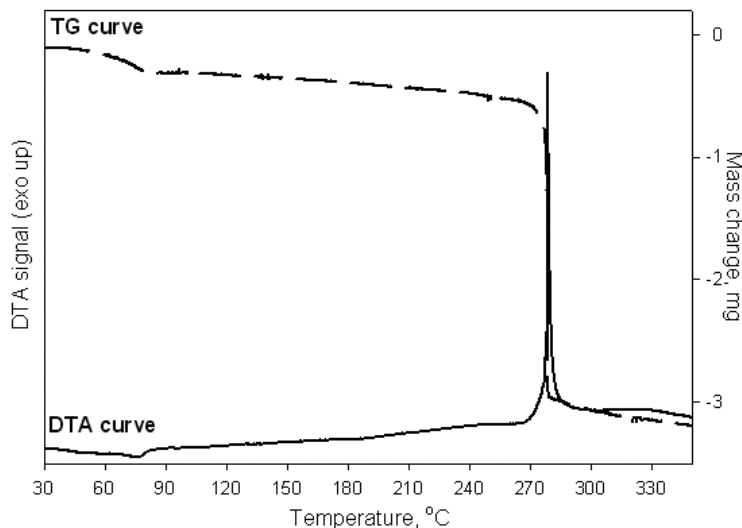
Figure 2. DTA/TG curves of TNBI dihydrate obtained from the nitration of BI with $H_3PO_4/P_4O_{10}/HNO_3$ (heating rate 5 K/min).

3.4 Heat of combustion

Heat of combustion of TNBI dihydrate ($TNBI \cdot 2H_2O$) was determined experimentally using a standard water calorimeter (PRECYZJA-BIT, Bydgoszcz, Poland) equipped with a standard calorimetric bomb according to Polish Norm BN-66/6093-12:1966. Weighed, pressed samples (d = 1.50 $g \cdot cm^{-3}$) of the compound were placed in a quartz crucible and placed in the bomb. The reactor was then filled with pure oxygen at an initial pressure of 2.0 MPa. The reported heat of combustion is an average of three experimental runs; the measurement error was below 0.02 $kJ \cdot g^{-1}$.

The heat of combustion of $TNBI \cdot 2H_2O$ was found to be 8.8 $kJ \cdot g^{-1}$. This value is close to that of octogen (9.3 $kJ \cdot g^{-1}$) [12], which suggests that $TNBI \cdot 2H_2O$ may be used as a high-energy ingredient of explosive and pyrotechnics compositions.

3.5 Explosive properties

The friction and impact sensitivity tests were carried out according to BAM methods using a standard Peters apparatus and a Kast Fallhammer. TNBI dihydrate, after recrystallisation from acetone/ethanol, is insensitive to friction up to 360 N. Its impact sensitivity was found to be equal to 11 J. These values are typical for secondary explosives with reduced sensitivity, such as 1,1-diamino-

2,2-dinitroethene (DADNE with crystal size ca. 250-350 μm).

The detonability was determined by initiation of pressed pellets of TNBI dihydrate with a standard blasting cap (without booster). A pellet (16.0 mm, density 1.73 g·cm^{-3}) was placed on a steel plate of dimensions 80×150×2 mm. The plate after the test had been punctured and the hole was the same diameter as the tested charge. These test results demonstrate that TNBI·2H$_2$O of 16.0 mm diameter can be detonated.

For measurement of the detonation velocity (VOD), TNBI·2H$_2$O was cold pressed into cylindrical pellets. The pellets were fragile and after pressing, weighing and measurement of their dimensions, the lateral surfaces of the pellets were protected with elastic tape. The density of tested charges pressed from pure TNBI dihydrate was ca. 1.73 g·cm^{-3}. VOD was found to be 7950 ± 50 m·s^{-1}. The theoretical VOD computed with the CHEETAH [13, 14] code for the same density was 8182 m·s^{-1}. The difference between the experimental result and the calculated value may be due to the diameter of the tested charges, which are undoubtedly over the critical diameter, but probably smaller than the diameter at which the VOD no longer increases. The experimental detonation velocity of TNBI·2H$_2$O is similar to that of 3-nitro-1,2,4-triazol-5-one. The theoretical detonation velocities for pure TNBI computed for 97% of the theoretical density are higher (8685-8803 m·s^{-1}) [6].

4   Conclusion

The nitration of BI with fuming nitric acid in the presence of acetic anhydride probably leads to 4,4'-dinitrobi-imidazole [11], a product with high thermal stability. When the nitration was conducted in the presence of trifluoroacetic anhydride, TNBI is formed. The nitration of BI with mixtures of fuming nitric acid/phosphorus pentoxide and phosphoric acid/phosphorus pentoxide are new routes to TNBI. After crystallization of the crude product from wet ethanol/ acetone mixture, a stable TNBI dihydrate is formed. The use of nitrating mixtures without sulfuric acid allows stable TNBI dihydrate to be obtained. The investigation of the explosive properties of TNBI dihydrate shows that this compound is able to detonate at 16.0 mm diameter and the detonation velocity is equal to 7950 ± 50 m·s^{-1}. The impact and friction sensitivity of TNBI dihydrate are similar to those of other typical explosives with reduced sensitivity (*e.g.* DADNE).

Acknowledgements

5 References

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