

High Nitrogen Energetic Salts of 4,4',5,5'-Tetranitro-2,2'-Biimidazole

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Received April 9, 2013, Accepted May 16, 2013**Key Words :** Nitrogen rich salts, Hygroscopic property, TNBI, Energetic material

The nitro group is known as a useful tool to provide high energy to a compound. However, nitro group is generally connected with carbon or nitrogen and consume oxygen linked to the carbon or nitrogen backbone of the molecule to release energy. Representatives of the compounds include 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-triazine (RDX). Current interest has focused on the development of high-energy-density materials (HEDMs) with higher performance and decreased sensitivity to thermal shock and friction.¹ There is currently considerable interest in high-nitrogen energetic materials (HNEMs) that are able to release energy using method other than those mentioned above. HNEMs are catching on as environmental materials that release N₂ gas and release high energy by changing the compound they are reacted with from a single- or double-bonded to a triple-bonded nitrogen compound. Nevertheless, the synthesis of these compounds consisting of only nitrogen is difficult. Accordingly, HNEMs are synthesized in the form of a salt compound.^{2,3}

High-nitrogen salt energetic materials have the characteristics described above, as well as low vapor pressure, high density, good thermal stability, and low solubility in water. Cromer reported 4,4'-5,5'-tetranitro-2,2'-biimidazole (TNBI) as a promising explosive expected to have good insensitivity and performance.⁴ Since first reporting TNBI, Cho *et al.* have improved the method of synthesis.⁵

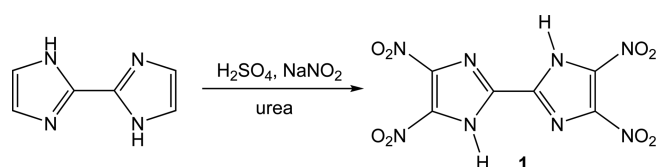
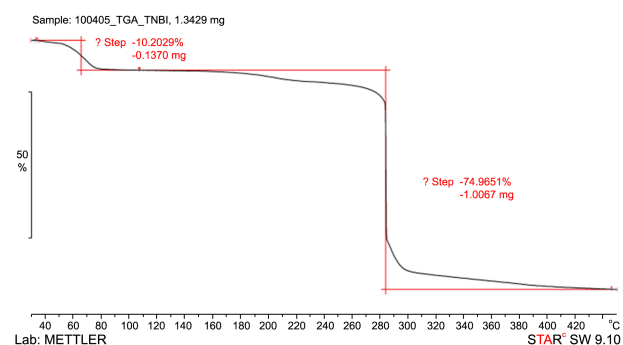
Nevertheless, TNBI synthesized using the improved method shows hygroscopicity owing to the acidic proton of -N-H and therefore cannot be used as explosives.

The purpose of this study is to synthesize high-nitrogen salt by substituting a high-nitrogen cation for the acidic hydrogen responsible for the hygroscopicity. Based on this method, we would like to produce an insensitive high-nitrogen salt TNBI.

Experimental & Results

TNBI is generally synthesized by nitration of biimidazole and is a good material for use as a high explosives (Scheme 1).

The TGA data of 4,4'-5,5'-tetranitrobiimidazole shown in Figure 1 reveal a loss of weight in the range of 60-100 °C. After drying the sample at 100 °C, no further weight loss was observed. However, weight loss was observed when the sample was exposed to the atmosphere. This finding suggests that the water absorbed by the acidic hydrogen in

**Scheme 1.** Synthesis of 4,4',5,5'-tetranitro-2,2'-biimidazole (1).**Figure 1.** TGA thermogram of TNBI (1).

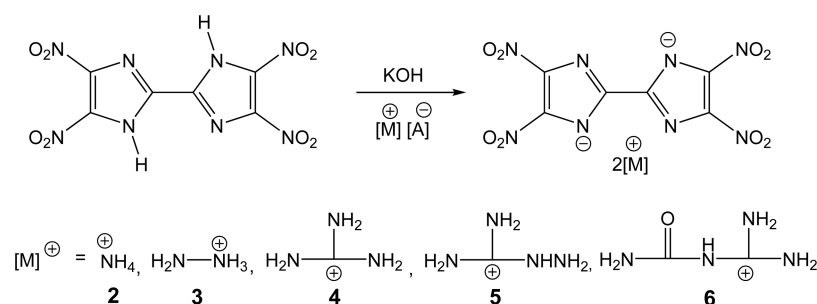
TNBI from the atmosphere was released, indicating that the molecule has a hygroscopic problem.

It is almost impossible to use TNBI in explosives owing to its hygroscopic problem; therefore high nitrogen salt compounds were newly synthesized with the substitution of a high-nitrogen cation. High nitrogen salt compounds were synthesized with the following cations: ammonium, hydrazinium, guanidinium, aminoguanidinium, and guanyl ureanium (Scheme 2). The thermal properties of each salt are listed in Table 1.

With the exception of di(guanylureanium) TNBI, the synthesized compounds no longer had a hygroscopic nature and showed improved thermal stabilities characterized by a decomposition pattern that did not indicate melting clearly.

The TGA data of di(aminoguanidinium)-4,4'-5,5'-tetranitro-2,2'-biimidazole, which are representative of the synthesized high nitrogen salts are shown in Figure 2. These data reveal that unlike TNBI, there was no decrease in weight in the range of 60-100 °C indicating that the hygroscopic problem had been solved. Moreover, the synthesized TNBI salts showed the same behavior as high energy explosives that are typically decomposed around 220 °C.

The structure of di(aminoguanidinium)-4,4'-5,5'-tetranitro-2,2'-biimidazole was investigated by X-ray crystal diffraction (Figure 3). The results revealed that the combination of



Scheme 2. Synthesis of the high nitrogen salts of TNBI.

Table 1. Thermal properties of high nitrogen salts of TNBI

No.	T_m^a (°C)	T_d^b (°C)	Hygroscopicity	ΔH_{cation} (KJ mol ⁻¹)
2	-	341	negative ^c	626.4
3	-	229	negative	770.0
4	-	320	negative	575.9
5	-	237	negative	667.4
6	-	190	positive ^d	518.3

^amelting point. ^bthermal decomposition temperature. ^cthere is not hygroscopic property in high nitrogen salts of TNBI. ^dthere is hygroscopic property in high nitrogen salts of TNBI.

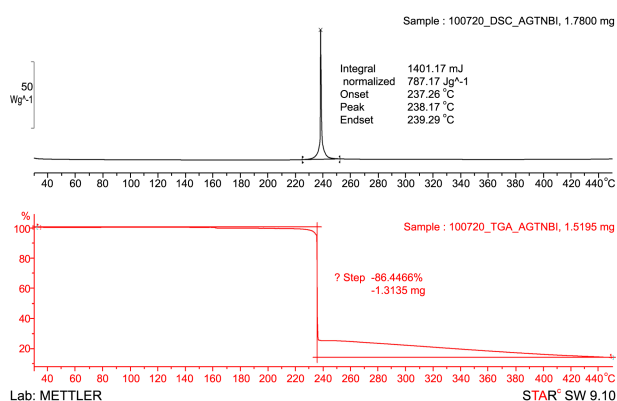


Figure 2. DSC and TGA thermogram of **5**.

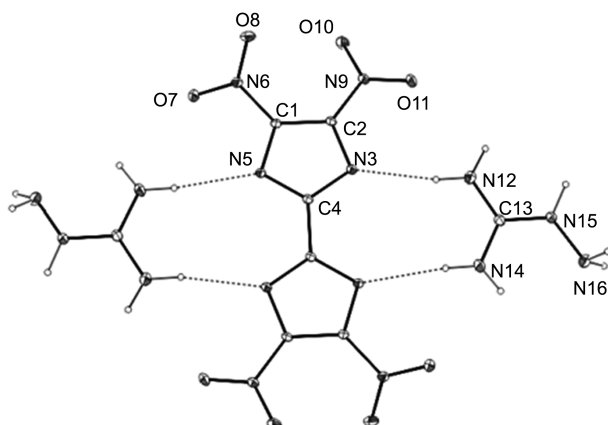


Figure 3. ORTEP drawing of molecular structure of **5**.

amino and nitro substituents provides inter- and intramolecular hydrogen bonds that may stabilize the molecule

Table 2. Test results of small scale sensitivity test

Test	explosives	value
Impact sensitivity	TNBI (dried)	5-6 J
	AGTNBI	> 79.4 J
Friction sensitivity	TNBI	351.1 N
	AGTNBI	> 352.8 N

and increase its crystal density and insensitivity.

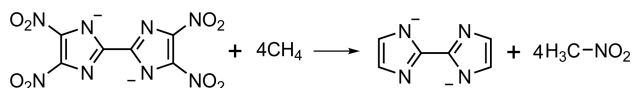
It is also very important to characterize sensitivities of explosives. We have tested small scale sensitivity test of TNBI and aminoguanidium TNBI samples. The test results are summarized in Table 2.

The impact sensitivity test was carried out using a Julius Peter's tester with 5 kg hammer. The friction sensitivity test was used a BAM large friction tester.

The 50% impact sensitivity criterion of AGTNBI (**5**) is 79.4J or more and friction sensitivity of **5** is 352.8N or more, which is much more insensitive than that of dried TNBI.

Physical Property. Heat of formation is one of the important characteristics for energetic salts which is directly related to the biimidazole system in an ionic species.⁹

All calculations were carried out using the program package Gaussian 03 (Revision D.01).¹⁰ The geometric optimization of the structures and frequency analyses was accomplished by using the B3LYP with the 6-31+G** basis set,¹¹ and single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-



Scheme 3. Isodesmic reaction of 4,4',5,5'-tetranitro-2,2'-biimidazole dianion.

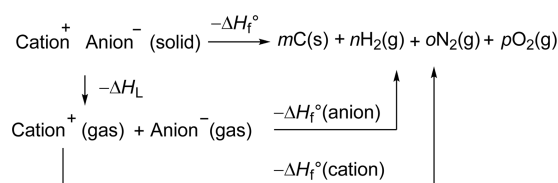


Figure 4. Born-Haber cycle for the formation of 4,4',5,5'-tetranitro-2,2'-biimidazole salts.

Table 3. Physical properties of TNBI salts

Compd.	density ^a [g cm ⁻³]	density ^b [g cm ⁻³]	H _L ^{o c} [kJ mol ⁻¹]	H _{cation} ^{o c} [kJ mol ⁻¹]	H _{anion} ^{o c} [kJ mol ⁻¹]	H _f ^{o c} [kJ mol ⁻¹]	H _f ^{o c} [kJ g ⁻¹]	P ^d [GPa]	vD ^e [m s ⁻¹]
2	1.774	-	1269.8	626.4	45.5	28.5	0.0819	29.00	8189
3	1.826	-	1244.2	770.0	45.5	341.3	0.902	33.63	8715
4	1.701	-	1150.9	575.9	45.5	46.3	0.107	24.33	7810
5	1.698	1.697	1120.9	667.4	45.5	259.4	0.561	25.65	8023
6	1.715	-	1076.7	518.3	45.5	-330	-0.637	24.78	7859

^aCalculated density. ^bX-ray density. ^cHeat of formation (calculated via Gaussian 03). ^dCalculated detonation pressure (EXPLO5 V5.05). ^eCalculated detonation velocity (EXPLO5 V5.05).

energy surface without imaginary frequencies. The remaining task is to determine the heats of formation of the cation and anion, which are computed by using the method ofisodesmic reactions (Scheme 3).

Based on Born-Haber energy cycles (Figure 4), the heats of formation of ionic salts can be simplified by the Eq. (1):

$$\Delta H_f^\circ (\text{ionic salt, 298 K}) = \Delta H_f^\circ (\text{cation, 298 K}) + \Delta H_f^\circ (\text{anion, 298 K}) - \Delta \text{HL} \quad (1)$$

The lattice potential energies (UPOT) and lattice enthalpies (ΔHL) were calculated according to the followed equations provided by Jenkins and are summarized¹² in which ΔHL is the lattice energy of the ionic salt. The ΔHL value can be predicted by the formula, Eq. (2),¹² where UPOT is the lattice potential energy, nM and nX depend on the nature of the ions Mp⁺ and Xq⁻, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

$$\Delta \text{HL} = \text{UPOT} + [p(nM/2-2) + q(nX/2-2)]RT \quad (2)$$

The equation for the lattice potential energy, UPOT, takes the form of Eq. (3),

$$\text{UPOT} (\text{kJ mol}^{-1}) = \gamma(\rho m / M m)1/3 + \delta \quad (3)$$

where ρm is the density (g cm⁻³), Mm is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol⁻¹ cm) and δ (kJ mol⁻¹) are assigned literature values.¹²

The enthalpy of an isodesmic reaction ($\Delta H_r(298^\circ)$) is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). Thus, the heats of formation of the cations and anions being investigated can be extracted readily (Table 4). With the values of the heats of formation and density of the energetic salts, the detonation pressures (P) and detonation velocities (D) were calculated using the program EXPLO5 V5.05.¹³

In Table 4 it is shown that all 4,4',5,5'-tetranitro-2,2'-biimidazole salts are endothermic compounds except Gu-TNBI (**6**). The enthalpies of energetic materials are controlled by the molecular structure of the compounds. Consequently, heterocycles with high nitrogen content show high heats of formation. The compounds of Am-TNBI (**2**), Hy-TNBI (**3**), Gua-TNBI (**4**), and AG-TNBI (**5**) exhibit positive heats of formation ranging between 28.5 and 341.3 kJ mol⁻¹.

Density is one of the most important factors determining

the performance of energetic compounds. The densities were estimated by employing tabulated volume parameters,¹⁴ which agree reasonably well with the X-ray values. The densities of TNBI salts are in the range of 1.698-1.826 g cm⁻³.

By using the calculated values of the heats of formation and the calculated values for the densities of the highly energetic TNBI salts **2-6**. The calculated detonation pressures of TNBI salts lie in the range between P = 24.33 and P = 33.63 GPa (comparable⁸ to TATB = 31.15, RDX = 35.17 GPa). Detonation velocities lie between D = 7810 and D = 8715 m s⁻¹ (comparable¹⁵ to TATB = 8114, RDX = 8977 m s⁻¹).

Conclusion

We synthesized a high-nitrogen salt energetic material with a combination of TNBI and nitrogen rich cations through the replacement of acidic hydrogen with high-nitrogen salt to remove the hygroscopic problem of the compound. Moreover, the insensitivity of TNBI were also improved by using high-nitrogen salts. The salts of TNBI that were newly synthesized are expected to be high-energy-density materials (HEDMs) characterized by a low vapor pressure, high density and good thermal stability. The physical properties of these energetic salts were calculated using the program package Gaussian 03 (Revision D.01) and EXPLO5 V5.05. The calculated detonation pressures of TNBI salts lie in the range between P = 24.33 and P = 33.63 GPa and detonation velocities lie between D = 7810 and D = 8715 m s⁻¹. Characterization revealed that, di(aminoguanidium)-4,4',5,5'-tetranitro-2,2'-biimidazole is a promising compound for the next generation of nitrogen-rich energetic materials.

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- Typical Procedure for synthesis of TNBI: Add 24.0 mL (98%, 427.7 mmol, 26 eq. (excess)) sulfuric acid and 2.2 g (16.5 mmol, 1.0 eq.) biimidazole to a round flask and agitate for 1 h. After dissolving the biimidazole, add 0.1 g (0.1 eq.) of urea as a catalyst and then slowly add 8.3 g (97.7 mmol, 1.5 eq.) of sodium nitrate at 20-30 °C. The addition of sodium nitrate results in the production of dark brown NOx gas. After adding the sodium nitrate, allow the

reaction to proceed for 5 h at 80 °C. Next, cool the reaction solution to 20 °C and slowly pour it into 1 L of ice water. Collect the precipitate product, 4,4'-5,5'-tetra-nitro-2,2'-biimidazole, and wash it with cold water three times to remove the acid. This process gives 8.4 g of 4,4'-5,5'-tetranitro-2,2'-biimidazole (yield: 60%) We confirmed it by ¹H-NMR, ¹³C-NMR and EA (elemental analysis).

¹H-NMR (CDCl₃) δ 10.58 (br, 2H), ¹³C-NMR (CDCl₃) δ 138.63, 138.24, IR (NaCl) 3600.9, 3542.1, 1537.1, 1484.2, 1413.7, 1372.5, 1325.5. Anal. Calcd. for C₆H₂N₈O₈: C 22.9, H 0.6, N 35.7. Found: C 22.5, H 0.7, N 35.0.

7. Typical Procedure for synthesis of nitrogen rich salts: Add 10.0 g (0.032 mol) of 4,4'-5,5'-tetranitro-2,2'-biimidazole and 200 mL of methanol to a 500 mL round flask and set the solution temperature to 60 °C. Wait until all of the 4,4'-5,5'-tetranitro-2,2'-biimidazole dissolves. Next, dissolve 7.7 g of KOH (0.070 mol, 2.2 eq.) in 100 mL of water and add this to the 4,4'-5,5'-tetranitro-2,2'-biimidazole solution. After mixing this solution, it will turn into a dark yellowish suspension. Next, add 8.0 g (0.070 mol, 2.2 eq.) of aminoguanidium hydrochloride to this mixture. This produces an ion exchange reaction that causes the solution to gradually turn dark orange. Allow the reaction to 3-4 h until completion. Next, cool the solution to 25 °C, filter it, and then wash the filtrate with ice water. After drying, 13.1 g of di(aminoguanidium)-4,4'-5,5'-tetranitro-2,2'-biimidazole (5) was obtained (yield: 73%). IR (neat): ν 3423, 3395, 3289, 3096, 1666, 1592, 1520, 1466, 1373, 1303, 1191, 1110, 911, 856, 810, 751. ¹H NMR (300 MHz, DMSO-*d*₆) δ 8.9 (bs, 1H), 7.16 (bs, 4H), 4.72 (bs, 2H); ¹³C NMR (75 MHz, DMSO-*d*₆) δ 158.91, 143.84, 140.41. Anal. Calcd. for C₈H₁₅N₁₆O₈: C 20.7, H 3.3, N 48.4. Found: C 21.0, H 3.5, N 48.0. Diammonium-4,4'-5,5'-tetranitro-2,2'-biimidazole (2) Yield: 88%, IR (neat): ν 3278, 1495, 1480, 1442, 1391, 1368, 1307, 1245, 855, 811. ¹³C NMR (75 MHz, DMSO-*d*₆) δ 140.2, 143.8. Anal. Calcd. for C₆H₈N₁₀O₈: C 20.7, H 2.3, N 40.2. Found: C 21.2, H 2.5, N 39.8.

Dihydrazium-4,4'-5,5'-tetranitro-2,2'-biimidazole (3) Yield: 84%, IR (neat): ν 3320, 3200, 1511, 1477, 1368, 1314, 1257, 1087, 931, 852. ¹³C NMR (75 MHz, DMSO-*d*₆) δ 138.9, 139.9. Anal. Calcd. for C₆H₁₀N₁₂O₈: C 19.1, H 2.7, N 44.4. Found: C 19.5, H 2.4, N 45.0.

Diguanium-4,4'-5,5'-tetranitro-2,2'-biimidazole (4) Yield: 85%, IR (neat): ν 3430, 3356, 3176, 1663, 1487, 1465, 1387, 1306, 1200, 1111, 1014, 857, 813. ¹³C NMR (75 MHz, DMSO-*d*₆) δ 138.1, 146.6, 160.0. Anal. Calcd. for C₈H₁₂N₁₄O₈: C 22.2, H 2.8, N 45.4. Found: C 22.5, H 2.5, N 45.0.

Diguanylureanium-4,4'-5,5'-tetranitro-2,2'-biimidazole (6) Yield: 78%, IR (neat): ν 3462, 3356, 3052, 1733, 1698, 1595, 1529, 1466, 1377, 1345, 1309, 1261, 1188, 1110, 810. ¹³C NMR (75 MHz, DMSO-*d*₆) δ 155.8, 155.0, 143.7, 140.5. Anal. Calcd. for C₁₀H₁₄N₁₆O₁₀: C 23.2, H 2.7, N 43.2. Found: C 22.7, H 3.0, N 43.8.

8. Crystal data for di(aminoguanidium)-4,4'-5,5'-tetranitro-2,2'-biimidazole (5): crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-839299). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/per/catreq.cgi> or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.
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