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# Bis[3-(5-nitroimino-1,2,4-triazolate)]-Based Energetic Salts: Synthesis and Promising Properties of a New Family of High-Density Insensitive Materials

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***Abstract:*** Bis[3-(5-nitroimino-1,2,4-triazolate)]-based energetic salts were synthesized in a simple, straightforward manner. They exhibit low solubility in available solvents, high hydrolytic stability, excellent thermal stability, high density, positive heat of formation, low shock sensitivity, and excellent detonation properties. The physical and energetic properties of some salts are similar and even superior to those of RDX.

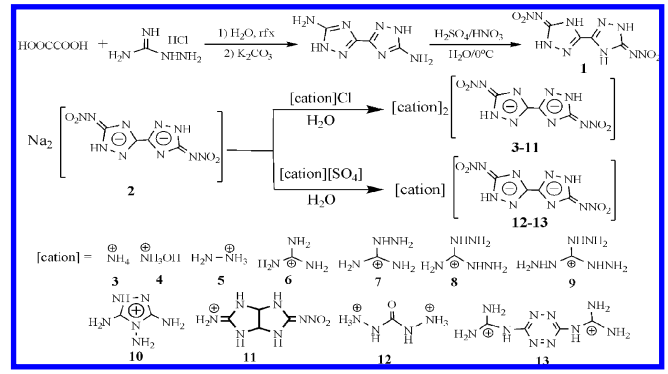
Energetic materials are extensively used for a variety of military purposes and industrial applications. Current interest has been focused on the development of high-energy-density materials (HEDMs) with higher performance and/or decreased sensitivity to thermal shock and friction.[1] However, the requirements of insensitivity and high energy are quite often contradictory to each other, making the development of new HEDMs a difficult and challenging problem. In the pursuit of new energetic materials, high-nitrogen heterocyclic compounds have attracted considerable attention.[2−4] Along with the development of ionic liquids and their applications in energetic fields,[3] nitrogen-containing heterocyclic halide-free energetic salts have gradually become a hot topic, as these salts possess intrinsically low volatility, high thermal stability, a simple synthesis process, and readily modified properties.[3−6] This provides a powerful methodology for the design and synthesis of HEDMs for specific purposes.

The N−$NO_2$ group is an important "explosophore" that is present in many energetic compounds. When the R−NH−$NO_2$ group is bonded to tetrazole[4b,6b] or at the 3(5)-position of 1,2,4-triazole,[5c,7] it is usually assigned as a nitroimine structure. The strong electron-withdrawing effect of the nitro group can deprotonate azoles to form energetic salts when paired with bases. However, it is not clear which structure is preferable in primary nitroamines and nitroimines when NH−$NO_2$ is bonded to azoles.

In our continuing effort to seek more powerful, less sensitive, eco-friendly explosives and propellants, we were interested in bis[3-(5-nitroimino-1,2,4-triazole)] ($H_2$BNT) because its monoanionic salt ($HBNT^-$) showed promising thermal stability (>200 °C) and poor solubility in organic solvents, water, and acids.[8] The structure of $H_2$BNT was (without proof) considered to be bis(3-nitroimine-1,2,4-triazole), which is different from the nitroamine-bonded 1,2,4-triazole analogues.[5c,7] Since the structure is a key point for exploration of energetic performance and applications, it was significant to unambiguously determine the structure of $H_2$BNT. Recently, the sensitivity of $H_2$BNT to thermal and mechanical initiation was reported.[9] Herein, we report the synthesis and characterization of BNT-based dianionic salts.

Although $HBNT^-$ and its monoanionic salts have been reported,[8] their synthetic procedures are tedious; also, the starting materials are expensive, and the overall yield is quite low. Two of the key requirements for practical application of an energetic compound are that its synthesis must be simple and the starting materials should be inexpensive. On the basis of the symmetric nature of $H_2$BNT, a much easier and more straightforward method for its synthesis was developed (Scheme 1). The condensation of inexpensive oxalic acid with aminoguanidine hydrochloride and subsequent cyclization gave rise to bis[3-(5-amino-1,2,4-triazolyl)],[10] and subsequent nitration with concentrated nitric acid and sulfuric acid afforded $H_2$BNT. $Na_2$BNT (**2**) was obtained by adding aqueous NaOH to a hot aqueous solution of $H_2$BNT (pH ∼10). $Na_2$BNT is soluble in hot water. The metathesis reactions of $Na_2$BNT with monocationic halides in hot water resulted in the formation of corresponding energetic salts **3**−**11**. Interestingly, the treatment of $Na_2$BNT with excesses of dicationic sulfates gave rise to **12** and **13** in high yields and purities.

***Scheme 1***



As shown in Table 1, all of the salts exhibit excellent thermal stability, which most likely can be attributed to the extensive and strong hydrogen-bonding interactions between cations and anions. The decomposition temperatures, which fall in the range 198−290 °C, are higher than that of $H_2$BNT (165 °C) and comparable to those of RDX (230 °C) and HMX (287 °C).

The densities of **3**−**13**, which are in the range 1.63−1.95 g/cm$^3$, are higher than those of the reported 3-nitroamino-1,2,4-triazole analogues.[5c,7] It should be noted that the densities of commonly used explosives such as TNT, TATB, RDX, and HMX are in this range. Interestingly, the densities of **3** and **12** fall in the range for new high-performance energetic materials (1.8−2.0 g/cm$^3$). Their high densities are ascribed to the extensive and strong hydrogen bonds between cations and $BNT^{2-}$. To the best of our knowledge, the density of **12** (1.95 g/cm$^3$) is the highest of the reported energetic salts.

Salts **5**−**13** possess much lower impact sensitivities than RDX and HMX (7.4 J), which suggests that they can serve as promising candidates for safer materials to replace RDX. The impact sensitivities

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***Table 1.*** Properties of Dianionic Energetic Salts

| compd | $T_m$ (°C)[a] | $T_d$ (°C)[b] | $d_{meas}$ (g/cm$^3$)[c] | OB[d] | IS (J)[e] | $\Delta_f H_{cation}$ (kJ/mol)[f] | $\Delta_f H_{lat}$ (kJ/mol)[g] | $\Delta_f H_{salt}$ (kJ/mol)[h] | $\Delta_f H_{salt}$ (kJ/g)[h] | $P$ (GPa)[i] | $v_D$ (m/s)[j] | $I_{sp}$ (s)[k] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3[l] | dec | 217 | 1.83 (1.89) | −49.6 | − | 626.4 | 1392.8 | 105.8 | 0.36 | 34.9 | 9407 | 200.8 |
| 4 | dec | 218 | 1.78 | −34.8 | − | 669.5 | 1309.3 | 275.5 | 0.86 | 32.4 | 8856 | 240.0 |
| 5 | dec | 220 | 1.63 | −50.0 | 11 | 770.0 | 1269.4 | 516.4 | 1.61 | 26.2 | 8455 | 227.1 |
| 6[l] | dec | 265 | 1.70 (1.77) | −64.1 | >40 | 575.9 | 1234.5 | 163.1 | 0.44 | 26.6 | 8634 | 191.3 |
| 7 | 242 | 248 | 1.71 | −63.3 | >40 | 667.4 | 1183.1 | 397.5 | 0.98 | 26.3 | 8603 | 202.3 |
| 8 | dec | 235 | 1.68 | −62.6 | 31 | 769 | 1143.4 | 640.4 | 1.47 | 27.0 | 8701 | 212.6 |
| 9 | 237 | 244 | 1.64 | −62.0 | 23 | *871.5* | 1104.1 | 884.7 | 1.91 | 27.0 | 8705 | 221.9 |
| 10[l] | 178 | 198 | 1.75 (1.78) | −66.1 | >40 | 842 | 1121.1 | 808.7 | 1.67 | 28.3 | 8792 | 207.8 |
| 11 | dec | 281 | 1.80 | −63.9 | >40 | 805.3 | 1019.4 | 837.0 | 1.34 | 27.3 | 8474 | 212.3 |
| 12 | 162 | 222 | 1.95 | −46.2 | 38 | 1764.6 | 1963.2 | 47.2 | 0.14 | 36.0 | 9399 | 194.7 |
| 13 | dec | 290 | 1.80 | −63.7 | 32 | 1903.6 | 1829.6 | 319.8 | 0.71 | 24.3 | 8267 | 182.8 |
| TNT | 81 | 295 | 1.65 | −74.0 | 15 | − | − | −67.0 | −0.30 | 19.5 | 6881 | − |
| TATB | 350 | ∼360 | 1.93 | −55.8 | 50 | − | − | −154.2 | −0.54 | 31.2 | 8114 | − |
| RDX | dec | 230 | 1.82 | −21.6 | 7.4 | − | − | 92.6 | 0.42 | 35.2 | 8977 | − |
| HMX | dec | 287 | 1.91 | −21.6 | 7.4 | − | − | 104.8 | 0.35 | 39.6 | 9320 | − |

[a] Melting point. [b] Thermal degradation temperature. [c] Measured density. Values in parentheses were corrected by subtracting the volume of a water molecule [$V(H_2O) = 25$ Å$^3$]. [d] Oxygen balance. [e] Impact sensitivity. [f] Calculated molar heat of formation of the cation. [g] Calculated molar lattice energy. [h] Calculated heat of formation of the salt. [i] Calculated detonation pressure. [j] Calculated detonation velocity. [k] Calculated specific impulse in seconds. [l] Calculations were performed using the corrected density.

of **6**, **7**, **10**, and **11** are greater than 40 J, so they can be classified as insensitive materials.[11]

The calculated heat of formation of $BNT^{2-}$ (245.8 kJ/mol) is much more positive than that of monoanionic 3-nitroimino-1,2,4-triazolate (−13.5 kJ/mol).[5c] Thus, it is not surprising that **6** and **7** exhibit much higher heats of formation than their monoanionic guanidinium (0.27 kJ/g) and aminoguanidinium (0.78 kJ/g) analogues.[5c] All of the salts possess positive heats of formation that fall in the range 0.14−1.91 kJ/g. As anticipated, the calculated heats of formation increase with increasing nitrogen content in the guanidinium-derivatized salts **6**−**9**.

The calculated detonation pressures of **3**−**13**, which lie in the range 24.3−36.0 GPa, are higher than that of TNT (19.53 GPa) and comparable to those of TATB (31.15 GPa) and RDX (35.2 GPa). Detonation velocities ($v_D$) were found in to be the range 8267−9407 m/s; they are higher than those of TNT (6881 m/s) and TATB (8114 m/s) and comparable to those of RDX (8977 m/s) and HMX (9320 m/s). All of the salts have specific impulse values ranging between 182.8 and 240.0 s. The promising performance suggests potential applications of $BNT^{2-}$ salts as ingredients in explosives and propellants. This is especially the case for **3**, **4**, and **12**, as their energetic performance values are very similar and even superior to those of RDX.

Single-crystal X-ray diffraction analysis confirmed the structure of $H_2BNT$ to be a nitroimine (Figure S1 in the Supporting Information). The strong intramolecular and intermolecular hydrogen bonds link the discrete $H_2BNT$ molecules into a 2D layer (Figures S2 and S3). Structure optimization calculations on $H_2BNT$ further suggested that the nitroimine is the more stable form, as it has a lower total energy (the threshold value between the two stable isomers is 12.55 kcal/mol; Figure S4).

To define the structure of $BNT^{2-}$, four possible models of $BNT^{2-}$ are provided (Figure S5). The differences in binding energy and binding enthalpy between the models and $H_2BNT$ were calculated. The 1-positioned protons of 1,2,4-triazole in $H_2BNT$ form intramolecular hydrogen bonds with the nearest nitroimine oxygen atoms. The hydrogen bonds were kept in model 1, and the binding energy of model 1 was the lowest (Table S1). Thus, the 4-positioned protons of 1,2,4-triazole in $H_2BNT$ are easily lost during the reaction.

In summary, a simple and straightforward approach for the synthesis of bis[3-(5-nitroimino-1,2,4-triazole)] has been developed. The structure of $H_2BNT$ was confirmed as an *N*-nitroimine rather than a primary *N*-nitroamine. Its salts, which can be easily synthesized and safely handled, exhibit promising physical properties, such as low solubility in common solvents, excellent thermal stability, high density, positive heats of formation, and low shock sensitivity. The densities of some salts fall in the range for new high-performance energetic materials (1.8−2.0 g/cm$^3$). One dicationic salt possesses the highest density of the reported energetic salts (1.95 g/cm$^3$). The calculated detonation velocities and detonation pressures of the salts are higher than those of conventionally used TNT and TATB. Interestingly, the properties of ammonium, hydroxyammonium, and carbonic dihydrazidinium salts are similar and even superior to that of RDX, which suggests that they may serve as a series of promising alternatives to RDX.

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**Supporting Information Available:** Experimental details for the syntheses and characterization of all compounds; descriptions, figures, and a CIF file of the crystal structure; details of the calculations; and description of and figure showing the charge distributions of $H_2BNT$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) According to the U.N. Recommendations on the Transport of Dangerous Goods, impact sensitivity is defined as follows: insensitive, >40 J; less sensitive, ≥35 J; sensitive, ≥4 J; very sensitive, ≥3 J.

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