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4-Amino-3-Hydrazino-1,2,4-Triazolium 5-Nitrotetrazolate: A High-Density Energetic Materials

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Abstract: 4-Amino-3-hydrazino-1,2,4-triazolium 5-nitrotetrazolate (AHT·NT): an energetic nitrogen-rich salt was preparedand fully characterized by1H,13C NMR, and IR spectroscopy, differential scanning calorimetry (DSC), andelemental analysis. AHT·NT crystallizes in the triclinic crystal system in Monoclinic crystal system P2 (1) /c group. By including two molecular moieties in the unit cell, the calculated density is 1.789 g·cm-3. There are extensive hydrogen bonding interactions between the cation and the anion form acomplex 3D network.The heat of formationwas calculated with the Gaussian 03suite of programs. AHT·NT exhibit promising detonation performances (pressure: 31.0 GPa; velocity:8831 m·s-1; EXPLO 5.05) that exceedthose of conventional TNT. Impactsensitivity was also determined byhammer tests and resulted at4.5 J. AHT·NT exhibit reasonablephysical properties, such as good thermal (Td = 164.9°C), and reasonable impact sensitivities, making this salt potential energetic material.

Keywords: Energetic materials; Detonation performance; Nitrogen heterocycle.

1. Introduction

Nitrogen-rich energetic salts are of great interest because their properties can be changed by careful choice of the component ions.[1]By combining the appropriate backbones with the suitable functional groups, the energetic properties can be tuned and improved.[2]The nitrogenous heterocycles, such as triazole,[3] tetrazole,[4] triazine,[5] and tetrazine[6], provide good backbones for thediscovery of new energetic compounds. Such heterocycles are often modified by functional groups such as–NH_2, and –NH-NH_2 to act as cations.

The incorporation of hydrazino groups increases the heat of formation of the entire molecule and the density，and lowers the sensitivity.[4] Amino groups are often incorporated into azole heterocycles because their derivatives are easilyprotonated.[7,8] These traditions have led to many chemical advances. Various energetic cations derived from amino-substituted triazoles and tetrazoles, in which each cation pairs with a family of nitrogen-rich anion to form new energetic salts, have been well documented.[9] However, despite the number of basic groups (such as amino groups) introduced into the azole ring, the compounds were protonated only to form monovalent cations. [10-16]

A divalent cation can pair with two oxygen-enriched anions, which are useful in increasing the density and improving the detonation performance.[17] Because of the protonated groups of –NH2 and –NH-NH2, AHT may be protonated by strong mineral acids such as HNO3.[18]Here, we wish to report the synthesis of the highly impact sensitive 4-amino-3-hydrazino-1,2,4-triazolium 5-nitrotetrazolate (4). Compound 4 was fully characterizedwith NMR and IR spectra, DSC, elemental analysis, andtheX-ray determination.TheX-ray determination shows that the extensive hydrogen bonding interactions between the cations and anions form acomplex 3D network, which contributes greatly to thehighdensity of the4-amino-3-hydrazino-1,2,4-triazole salt.

2. Experimental section

***Caution*:**Although we experienced no difficulties in handling these materials, the high positive heats of formation can render the compounds unstable.

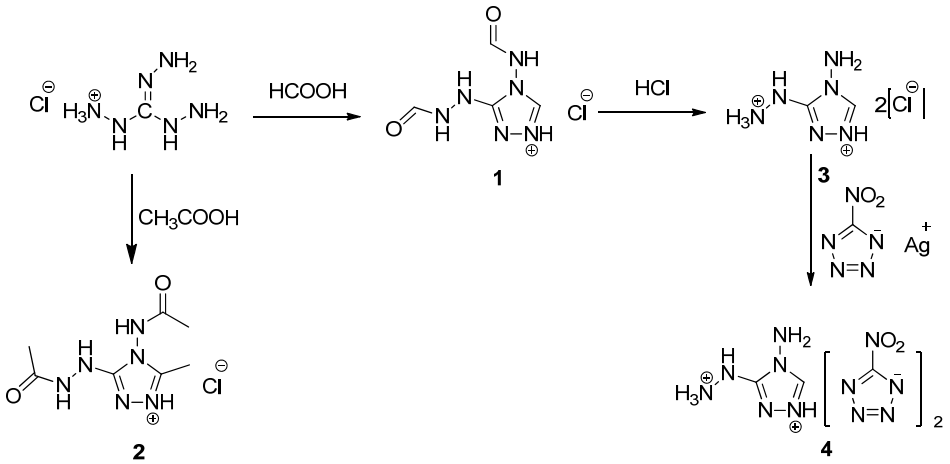
4-Amino-3-hydrazino-1,2,4-triazolium hydrochloride(3) : Triaminoguanidine hydrochloride (TAG•HCl) (2.81 g, 20 mmol) was added to 15 mL formic acid (b.p. 100.8 °C). The mixture was stirred and refluxed at 100–110 °C for 2 h. The excess volatile formic acid was removed under partial vacuum to recover a viscous, resinous residue. From this residue, 4-formamido-3-formhydrazino-1,2,4-triazole hydrochloride (**1**) was isolated in moderate yield. The viscous residue was dissolved and stirred vigorously in dilute hydrochloric acid at 80 °C. As the reaction progressed, white crystals of 4-amino-3-hydrazino-1,2,4-triazolium hydrochloride (**3**) precipitated. The product was filtered and washed with several aliquots (50 mL total) of ice water. The product was dried under high vacuum, resulting in a good yield (2.28 g, 61%) of **3**.MS m/z (ESI$^+$): 115.07, $[C_2H_7N_6]^+$; elemental analysis (%) Calc. for $C_2H_8N_6Cl_2$ (MW = 187.03 g·mol^{-1}): C, 12.83; H, 4.28; N, 44.92; found C, 12.80; H, 4.19; N, 45.12; IR (KBr): 3328, 3141, 2954, 2689, 1661, 1536, 1505, 1421, 1348, 1316, 1272, 1228, 1194, 1184, 1150, 1071, 1060, 1030, 951, 880, 772, 713, 663, 606, 558 cm^{-1}; ^{1}H NMR (D_2O) δ: 9.63, 9.19, 8.84, 7.63 ppm;^{13}C NMR (D_2O) δ: 154.28, 141.25 ppm; Impact sensitivity: >40 J.

4-Amino-3-hydrazino-1,2,4-triazolium 5-nitrotetrazolate (4): To obtain energetic salts **4,** solutions of silver 5-nitrotetrazolate (10 mmol) in distilled water (20 mL), in distilled water (10 mL) , were added dropwise to the solution of compound **3** (0.935 g, 5 mmol) in distilled water (20 mL). After stirring at room temperature for 1 h, the precipitate was filtered and rinsed with 10 mL distilled water. The solvent was evaporated in vacuum and the residue was recrystallized from methanol and dried in air to give the target product. Yield: 93%, pale yellow solid. MS m/z (ESI$^+$): 115.06 $[C_2H_7N_6]^+$; m/z (ESI$^-$): 114.0 $[CN_5O_2]^+$; elemental analysis (%) calcd for $C_4H_8N_{16}O_4$ (MW = 344.21 g·mol^{-1}): C 13.95, H 2.33, N 65.12; found C 14.06, H 2.42, N 64.81; IR(KBr): 3344, 3036, 2775, 2597, 1998, 1705, 1639, 1596, 1527, 1506, 1430, 1311, 1211, 1084, 1056, 939, 912, 853, 707, 608 cm^{-1}; ^{1}H NMR (D_2O) δ: 9.43, 8.18, 7.75 ppm; ^{13}C NMR (D_2O) δ: 167.43, 153.88, 142.05 ppm.

3. Results and discussion

3.1. Synthesis

Guanidine hydrochloride was refluxed in 3 equiv. of hydrazine hydrate at 110 °C for 2 h, yielding triaminoguanidine hydrochloride (TAG•HCl).[19-21] Refluxing TAG•HCl in formic acid and removal of the solvent produced a viscous residue. A moderate yield of4-formamido-3-acethydrazino-triazole hydrochloride 1 was isolatedfrom this residue. The residue was then hydrolyzed by hydrochloric acid and water (1:1 ratio) to form 4-amino-3-hydrazino-1,2,4-triazolium hydrochloride 3. Then,five energetic salts based on oxygen-rich anions and the AHT cation were synthesized (Scheme 1). Such salts would be expected to have relatively high oxygen contents. Compounds 4 were readily synthesized by anion exchange with silver 5-nitrotetrazolate with 3 in methanol or water.

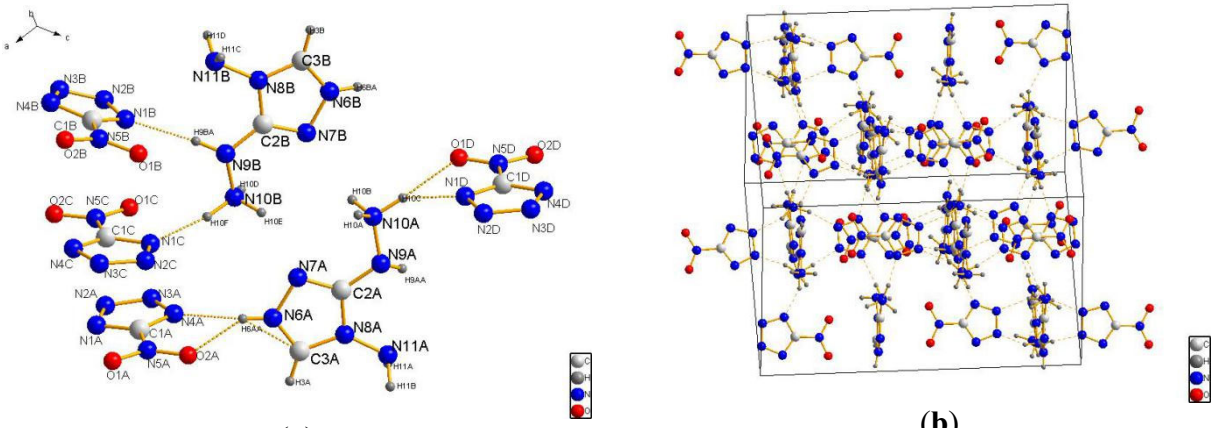


Scheme 1. Synthesis of the 4-amino-3-hydrazino-1,2,4-triazolium based salts.

3.1. X-ray crystallography

Crystals of**4**were determined by single-crystal X-ray diffraction. The structures of **4** is shown in Figure 1. Salt **4** crystallizes in a Monoclinic crystal system (space group *P2 (1) /c*)) (Figure 2a), and has a calculated density of 1.789 g·cm^{-3} (296(2) K). The main change observed are the N6 and N10 nitrogen atoms, which undergo protonation in 4-amino-3-hydrazino-1,2,4-triazole. Protonation results in a lengthening of the N6-N7 distances (1.433 Å), which are longer than N-N single bond (1.398 Å). The hydrazino and amino unit lie in the plane of the triazole ring. (torsion angle N11-N12-N13-N15 -177.43° , N13-N12-N11-C5 179.27°).

As can be seen from figure 1 b, there exist many hydrogen bonds between the cations and the anions of salt **4**. Figure 1b shows that the proton of the 1,2,4-triazole ring of **4** forms a strong hydrogen bond with the nitrotetrazole anion [N(11d)–H(10c)..O(1d), 2.521(378); N(11d)–H(10c)..N(1d), 1.898(378); N(6a)–H(6a)..C(3a), 1.903(425); N(6a)–H(6a)..N(4a), 2.001(493); N(10b)–H(10f)..N(1c), 1.8426 (431).



(**a**) (**b**)

Figure 1. (**a**) View of the molecular unit of **4**; (**b**) Unit cell packing of **4** (4-Amino-3-hydrazino-1,2,4-triazolium 5-nitrotetrazolate)

A selected bond lengths and angles of compounds **4** is given in Table 1. As expected and found in several selected structures discussed in this work, the 1,2,4-triazole ring is nearly planar, building an aromatic system, which can be seen at the torsion angle of 1,2,4-triazole ring is between -0.833(128)° and 0.785(125)°. The N-N bond lengths in 1,2,4-triazole ring of all structures of these compounds lie between 1.264(6) and 1.378(2) Å.

Table1:Selected bond lengths /Å and bond angles /° of compound **4**.

Bond lengths			
C(2)-N(7)	1.292(6)	C(3)-N(8)	1.341(6)
C(2)-N(8)	1.337(6)	N(6)-N(7)	1.369(5)
C(2)-N(9)	1.346(5)	N(8)-N(11)	1.380（5）
C(3)-N(6)	1.264(6)	N(9)-N(10)	1.393（5）
Bond angles			
N(7)-C(2)-N(8)	113.0(4)	C(2)-N(7)-N(6)	101.7(4)
N(7)-C(2)-N(9)	126.2(5)	C(2)-N(8)-C(3)	105.2(5)
N(8)-C(2)-N(9)	120.7(5)	C(2)-N(8)-N(11)	123.0(4)
N(6)-C(3)-N(8)	107.0(5)	C(3)-N(8)-N(11)	131.7(5)
C(3)-N(6)-N(7)	113.0(4)	C(2)-N(9)-N(10)	115.9(4)

3.2. Physicochemical properties

Compound **4** has high nitrogen content reaching as high as 65.1%. The high nitrogen content results in high densities, and the low percentage of carbon and hydrogen always leads to a good oxygen balance (**4** has negative oxygen balances of -18.6). In the past several years, a large number of salts with the high nitrogen content were reported. Compared with such compounds, however, **4** has superior thermal and stabilities. One of the most important physical properties of a solid energetic material is its density. The crystal density of **4** is 1.789 $g \cdot cm^{-3}$. Heat of formation is another important parameter in evaluating the performance of energetic salts. This property of the salts can be calculated with good accuracy (including the heat of formation of the cation and anion, and the lattice energy of salts). The calculated heat of formation of the 5-hydrazinotetrazolium cation is 2033.5 $kJ \cdot mol^{-1}$. Salt **4** exhibit positive heats of formation with 730.1 $kJ \cdot mol^{-1}$(2.12 $kJ \cdot g^{-1}$) (RDX: 0.42 $kJ \cdot g^{-1}$; HMX: 0.38$kJ \cdot g^{-1}$). With the value of the heats of formation and density of the energetic salts, the detonation pressures (P) and detonation velocities (D) values of **4** was calculated with EXPLO program (version 5.05). As can be seen from Table 2, Salt **4** possesses a moderate heat of formation, high density, and the good oxygen balance among, which guarantees its high detonation performance, with a detonation pressure of 31.0 GPa and a detonation velocity of 8831 $m \cdot s^{-1}$ which are super than that of trinitrotoluene (TNT; P: 19.5 GPa; D: 6881 $m \cdot s^{-1}$). In the present study, impact sensitivity measurements were made using Bruceton method on a type 12 tooling.**4** is sensitive with impact sensitivities of 4.5 J.

Table 2. The physicochemical properties of related energetic salts compared with RDX and HMX.

Salt	T_d[1]	T_{sd}[2]	d_c[3]/d_m[4]	$\Delta H°_L$[5]	$\Delta H°_f$[6]/$\Delta H°_f$[7]	P[8]	D[9]	IS[10]
4	164.9	231.4	1.72/1.789	1529.0	730.1/2.12	31.0	8831	4.5
RDX [11]	204.1	230	1.82	-	83.8/0.38	35.2	8977	7.4
HMX [12]	276	287	1.91	-	105/0.361	39.6	9320	7.4

[1]Decomposition temperature [°C]. [2] Secondary Decomposition temperature [°C]. [3] Calculate Density [$g \cdot cm^{-3}$].[4] Measured Density [$g \cdot cm^{-3}$]. Using ULTRAPYC 1200, Automatic Density Analyzer.[5] Lattice energy [$kJ \cdot mol^{-1}$]. [6] Molar enthalpy of the formation of salt [$kJ \cdot mol^{-1}$]. [7] Enthalpy of the formation of ionic salts in per gram [$kJ \cdot g^{-1}$]. [8] Detonation pressure [GPa]. [9] Detonation [$m \cdot s^{-1}$]. [10] Impact sensitivety [J]. [11] Data from ref .

4. Conclusions

A nitrogen-rich energetic salt based on 4-Amino-3-hydrazino-1,2,4-triazole was prepared, and fully characterized with NMR and IR spectra, DSC, and elemental analysis. There are extensive hydrogen bonding interactions between the cation and the anion form a complex 3D network. The heat of formation was calculated with the Gaussian 03 suite of programs. The calculated density is 1.789 $g \cdot cm^{-3}$ which places it in a class of relatively dense compounds. AHT·NT exhibit promising detonation performances (pressure: 31.0 GPa; velocity: 8831 $m \cdot s^{-1}$; EXPLO 5.05) that exceed those of conventional TNT. Impact sensitivity was also determined by hammer tests and resulted at 4.5 J. AHT·NT exhibit reasonable physical properties, such as good thermal (Td = 164.9 °C), reasonable impact sensitivities, and excellent specific impulses, making this salt potential energetic material.

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