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# Green Synthetic Approach for High-Performance Energetic Nitramino Azoles

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Supporting Information

**ABSTRACT:** A mild and efficient strategy for the nitration of aminosubstituted pyrazoles/triazole employing a mixture of potassium nitrate and concentrated sulfuric acid  $(KNO_3/H_2SO_4)$  as a nitrating reagent proceeded smoothly to give nitramino-substituted products. These were treated with corresponding bases to give energetic salts 1– 10. The compounds were fully characterized, and single crystal X-ray diffraction studies were obtained for 1, 4, 6, and 10. The physical



properties and detonation performance were measured or calculated. Salts 1, 2, 6, 8, and 9 exhibited excellent detonation performance and acceptable sensitivities as well as good stabilities, which suggested that they have potential to be useful as high-performance explosives.

n the development of energetic materials, the synthetic L chemistry of novel energetic molecules grows slowly and faces many challenges.<sup>1,2</sup> Although many energetic compounds have been prepared, superior replacements are limited. Scientists are still focusing on the search for new candidates to replace traditional explosives ( $Pb(N_3)_2$  and RDX) to satisfy the requirement of energy, safety, and environmental issues.<sup>3–9</sup> Nitrogen-rich energetic salts are considered to be green explosives and have attracted significant attention due to their fascinating properties such as high nitrogen content, high density, high heat of formation, and good detonation performance.<sup>10-12</sup> Since those salts based on nitraminosubstituted nitrogen-rich heterocycles nearly always exhibit better performance than the corresponding nitro-substituted analogs, synthetic protocols for the introduction of the nitramino moiety have received considerable attention in past years.<sup>13,14</sup>

Direct nitration of amino-substituted reactants is an important process for preparation of nitramino products. Various nitration methods have been reported such as use of a mixture of concentrated sulfuric acid and nitric acid,<sup>15–17</sup> fuming (100%) nitric acid,<sup>15,18–20</sup> or  $HNO_3/Ac_2O/TFA.^{21-24}$  However, the reaction yields are often low or require quite low reaction temperatures and often large amounts of harmful waste acid result, which create serious environmental issues. Therefore, developing a green, mild, and efficient approach for the synthesis of nitramino-based compounds is highly desirable.

With these concepts in mind, we report an efficient nitration protocol for the synthesis of nitramino-substituted compounds by using a mixture of potassium nitrate and sulfuric acid  $(KNO_3/H_2SO_4)$  as the nitrating reagent. In comparison with mixed acid, potassium nitrate is more economical as it has a

longer shelf life and is less hazardous than nitric acid. This green protocol features mild conditions, short reaction time, simple operation, and good yields.<sup>25,26</sup>

The synthetic route to the new energetic salts 1-10 is shown in Scheme 1. 3,5-Diamino-4-nitropyrazole (I) was prepared according to the literature.<sup>27-29</sup> Many attempts to nitrate it have failed. By following a typical procedure on nitration of amino-substituted pyrazole derivatives,<sup>21,22</sup> the nitrating system (HNO<sub>3</sub>/Ac<sub>2</sub>O/TFA) was tried, and the dinitramino product (I') was isolated. However, the yield is low (10%), and the product is also quite sensitive to mechanical interactions. Therefore, we continued to search for a more efficient method to nitrate the amino-substituted compound (I) and found that it could be treated with a mixture of potassium nitrate and concentrate sulfuric acid to form the nitramino product (I'), which was extracted with ethyl acetate. Further reaction of nitramino product (I') in the ethyl acetate phase with bases gave the corresponding energetic salts 1-4 in high yields.

Use of such a protocol is reasonably safe since it is not necessary to isolate the extremely sensitive neutral dinitramino compound. Similarly, the nitrating system (HNO<sub>3</sub>/Ac<sub>2</sub>O/TFA) was used to nitrate compound II according to the literature,<sup>22</sup> but the yield was quite low and sometimes no product (II') was obtained. The nitrating mixture (KNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>) was then employed to introduce dinitramino groups into II, which were subsequently reacted with nitrogen-rich bases to form salts 5–7 in high yields.

We also examined the nitration of 5-(5-amino-2H-1,2,3-triazol-4-yl)tetrazole  $(III)^{30,31}$  with the same reagent (KNO<sub>3</sub>/

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Scheme 1. Synthesis of Energetic Salts 1-10



 $H_2SO_4$ ). Previously, it was shown that nitration of III by using a mixture of sulfuric acid and nitric acid gave a zwitterionic salt instead of the nitramino product (III').<sup>32</sup> Also, because of the strong oxidizing and nitrating properties of  $HNO_3/H_2SO_4$ , unexpected products often resulted. When a mixture of potassium nitrate and sulfuric acid was employed to nitrate III, followed by reaction of the ethyl acetate extract with bases, energetic salts 8–10 were obtained successfully.

The <sup>15</sup>N NMR spectra of selected compounds 1, 4, 5, and 8 were recorded in  $d_6$ -DMSO, and chemical shifts are given with respect to CH<sub>3</sub>NO<sub>2</sub> as the external standard (Figure 1). The



assignments were made by comparison with reported structures.<sup>30,33</sup> There are four signals in the spectrum of 1 (top), the signals for the nitro groups (N1 and N4) are observed at low field, while the signal for the hydroxylammonium cation (NH<sub>3</sub>OH<sup>+</sup>) appears at high field,  $\delta = -292.4$  ppm. However, due to the fast proton exchange and the conjugatated system, only one signal ( $\delta = -144.9$  ppm) was observed for N2 and N3. Similarly, there are only three signals observed in the spectrum of potassium salt (4). The signal ( $\delta = -140.3$  ppm) for N2/N3 is downfield relative to 1. In the

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spectrum of **5**, the signals for the nitro groups also appear as expected at low field ( $\delta = -14.3$  and -18.2 ppm). Only one signal ( $\delta = -142.5$  ppm) was observed for the nitrogen atoms N2/N3/N4. The spectrum of **8** has seven signals at -3.2 (N7/N8), -19.3 (N1), -42.3 (N3/N5), -44.1 (N4), -84.0 (N6/N9), -149.2 (N2), and -294.9 ppm (NH<sub>3</sub>OH<sup>+</sup>).

Dihydroxylammonium 3,5-dinitramino-4-nitropyrazolate (1) crystallizes from water in the triclinic space group P-1 with a high crystal density of 1.936 g cm<sup>-3</sup> at 20 °C and two molecules in the unit cell. The molecular structure is shown in Figure 2a. Deprotonation occurred at the nitramino groups leaving a hydrogen atom on the nitrogen atom (N15) on the pyrazole ring. The nitramino moieties and the nitro group are almost planar with the pyrazole ring with the torsion angles of  $O(1)-N(3)-N(4)-C(5) = 2.3(3)^\circ$ ,  $C(10)-N(11)-N(12)-O(13) = -179.25(17)^\circ$ , and C(5)-C(6)-N(7)-O(9) =



Figure 2. (a) Single-crystal X-ray structure of 1; (b) single-crystal X-ray structure of 4; (b) single-crystal X-ray structure of 6; (b) single-crystal X-ray structure of 10.

Table 1. Physicochemical and Energetic Properties of 1-10

	$ ho^a$	$Dv^{b}$	$P^{c}$	$\Delta H_{f}^{\ d}$	$T_{\rm dec}^{\ e}$	IS <sup>f</sup>	$FS^{\mathbf{g}}$
compds	g cm <sup>-3</sup>	m s <sup>-1</sup>	GPa	kJ g <sup>-1</sup>	°C	J	Ν
1	1.90	9394	40.0	0.32	155	6	120
2	1.87	9581	38.5	1.01	194	12	160
3	1.80	8842	32.6	-0.08	192	15	240
4	2.12	7640	26.4	-0.91	232	2	120
5·H <sub>2</sub> O	1.80	8745	33.8	0.21	183	15	160
6	1.85	9118	35.2	1.22	174	10	120
7•3H <sub>2</sub> O	1.71	8262	27.1	-1.04	210	20	240
8	1.82	9285	34.8	1.65	194	15	160
9	1.71	9022	30.1	2.54	183	10	160
10·2H <sub>2</sub> O	1.55	7774	20.5	-0.17	202	22	240
$Pb(N_3)_2$	4.80	5877	33.4	1.55	315	2.5-4	0.1-1
RDX	1.80	8795	34.9	0.32	204	7.4	120

<sup>*a*</sup>Density (measured with a gas pycnometer at 25 °C). <sup>*b*</sup>Detonation velocity calculated with EXPLO5 v6.01. <sup>*c*</sup>Detonation pressure calculated with EXPLO5 v6.01. <sup>*d*</sup>Heat of formation. <sup>*c*</sup>Decomposition temperature (onset temperature at a heating rate of 5 °C min<sup>-1</sup>). <sup>*f*</sup>Impact sensitivity. <sup>*g*</sup>Friction sensitivity.

179.6(2)°. In the structure of 1, the bond length of N3–N4 (1.2984 (19) Å) is shorter than the bond length of N11–N12 (1.3292 (19) Å). In Figure S1 (Supporting Information), the molecular layers are stacked in two kinds of  $\pi$ – $\pi$  interactions with distances of 3.11 and 3.25 Å, respectively. In addition, the molecules were stabilized by many hydrogen bonds. In the ac plane (Figure S2, Supporting Information), several hydrogen bonds involving N(15)–H(15)…O(14), N(15)–H(15)…O(8), N(17)–H(17B)…O(9), O(18)–H(18)…O(9), O(18)–H(18)…N(11), N(19)–H(19A)…N(4), and O(20)–H(20)…O(2) are observed.

Dipotassium 3,5-dinitramino-4-nitropyrazolate  $(4 \cdot 2H_2O)$  crystallizes as a dihydrate from water in the orthorhombic space group *Pnma* with a calculated density of 2.044 g cm<sup>-3</sup> at 20 °C in spite of having four molecules of water and eight molecules in the unit cell. The molecular structure is shown in Figure 2b. The bond lengths and bond angles are comparable to those in 1. The bond length of N(3)–N(4) is 1.315(3) Å, while that of N(11)–N(12) is 1.313(2) Å. The potassium atoms are coordinated irregularly by either all the oxygen atoms in the nitro groups and water molecules or the nitrogen atoms (N4/N11/N15). In addition, the atoms in the anion are nearly planar. Thus, the planar anions result in a buildup of layer–layer stackings along the *c* axis, which is stabilized by the complex coordination environment (Figure S3, Supporting Information).

Dihydrazinium (4,4'-dinitro-1H,1'H-[3,3'-bipyrazole]-5,5'diyl)bis(nitroamide) (6) crystallizes from water in the monoclinic space group C2/c with a calculated density of 1.871 g cm<sup>-3</sup> at 20  $^{\circ}$ C and four molecules in the unit cell. The molecular structure is given in Figure 2c. The bond length of C12-C12' (1.477(3) Å) is slightly longer than that of the parent molecule (1.466 Å).<sup>34</sup> The bond length of N6-N7 is 1.323(2) Å. In a half molecule, the nitro and nitramino moieties are coplanar with the pyrazole ring with torsion angles of  $C(5)-N(6)-N(7)-O(8) = 176.98(17)^{\circ}$  and O(2)- $N(3)-C(4)-C(12) = 1.6(3)^{\circ}$ . However, the two pyrazole rings in the anion are not planar having a dihedral angle between the two rings at 56.75°. The structure is dominated by an extensive hydrogen bonding network involving N(10)- $H(10)\cdots O(9), N(14)-H(14A)\cdots O(1), N(14)-H(14B)\cdots$ N(6), N(13)-H(13B)····O(8), and N(13)-H(13C)····N(11).

The diammonium salt  $(10.2H_2O)$  crystallizes as a dihydrate in the monoclinic space group P21 with a crystal density of 1.568 g cm<sup>-3</sup> at 20 °C and two formula units in the unit cell. Its molecular structure is given in Figure 2d. The proton is located on the nitrogen atom (N6) of the triazole rather than the center nitrogen atom (N7). The parameters including bond lengths and bond angles in 10 are comparable to those in reported structures.<sup>30,31</sup> The bond length of N(3)-N(4) is 1.3042(19) Å, which is shorter than those observed in 1, 4, and 6. The bond lengths of N(11)-N(12) = 1.344(2) Å, N(12)-N(13) = 1.311(2) Å, and N(13)-N(14) = 1.347(2) Å in the tetrazole ring indicate that N12-N13 approaches a N=N double bond. The triazole ring and the tetrazole ring are twisted at an angle of  $30^{\circ}$  ( $\angle N(8) - C(9) - C(10) - N(14) =$ 149.99(17)°). The nitramino group is slightly twisted out of the triazole ring  $(\angle N(3) - N(4) - C(5) - N(6) = -7.4(3)^{\circ})$ . Each hydrogen atom of the ammonium cations forms hydrogen bonds with the nitrogen atoms of the tetrazole/ triazole rings or the oxygen atoms (O17 and O18) of water molecules and the oxygen atom (O1) of nitro groups (N(15)- $H(15D)\cdots O(1)$ ). In addition, the water molecules (O17 and O18) also form hydrogen bonds with nitrogen atom (N12) and oxygen atoms (O1 and O2) in the anion.

All of the new compounds are potential energetic materials; thus, the physicochemical and energetic properties were either determined experimentally or calculated. The data are summarized in Table 1. The thermal behavior of salts 1-10 was determined using differential scanning calorimetric (DSC) measurements at a heating rate of 5 °C min<sup>-1</sup>. All of these nitrogen-rich compounds show good decomposition temperatures ( $T_d \ge 150$  °C). Among them, the potassium salt (4) exhibits the highest decomposition temperature at 232 °C. The ammonium salts (7 and 10) also decompose at more than 200 °C. The heats of formation were calculated by using Gaussion 03 software.<sup>35</sup> The densities were measured by using a gas pycnometer at room temperature. As expected, the potassium salt (4) shows a high density of 2.12 g  $cm^{-3}$ . Some other salts also exhibit high densities (1, 1.90 g cm<sup>-3</sup>; 2, 1.87 g cm<sup>-3</sup>; and 6, 1.85 g cm<sup>-3</sup>).

Calculation of the detonation performance was performed with the EXPLO5 (version 6.01) program package<sup>36</sup> by using the calculated heats of formation and measured densities. Compound 2 exhibits the highest value detonation velocity  $(D\nu = 9581 \text{ m s}^{-1})$ . Additionally, **1**, **6**, **8**, and **9** also show excellent detonation velocities (**1**, 9347 m s<sup>-1</sup>; **6**, 9118 m s<sup>-1</sup>; **8**, 9285 m s<sup>-1</sup>; and **9**, 9022 m s<sup>-1</sup>). The calculated detonation pressures for **1**, **2**, **6**, and **8** are also promising (**1**, 40.0 GPa; **2**, 38.5 GPa; **6**, 35.2 GPa; and **8**, 34.8 GPa).

Considering safety issues, the impact and friction sensitivities were tested according to standard BAM technology.<sup>37</sup> The potassium salt 4 is sensitive to impact (IS = 2 J) and its friction sensitivity is 120 N. The impact sensitivities of energetic salts **1–3** based on 3,5-dinitramino-4-nitropyrazole are 6, 12, and 15 J, which are acceptable. For salts **5–10**, the impact sensitivities vary from 10 to 22 J. All the compounds have friction sensitivities between 120 and 240 N.

In summary, we have developed a mild, convenient, and lowcost process for the synthesis of high performance energetic salts 1–10. The method employs very mild reaction condition and environmentally friendly nitrating mixture (KNO<sub>3</sub>/ H<sub>2</sub>SO<sub>4</sub>). The energetic salts were isolated in high yields. All the compounds have been fully characterized, and salts 1, 4, 6, and 10 were confirmed by single crystal X-ray diffraction analysis. The results of physicochemical and detonation properties indicated that these compounds have potential applications in the field of energetic materials. Among them, 2 shows promising properties with a high density of  $1.87 \text{ g cm}^{-3}$ , a decomposition temperature of 194 °C, a detonation velocity of 9581 m s<sup>-1</sup>, and a detonation pressure of 38.5 GPa as well as acceptable sensitivities. Compounds 1, 6, 8, and 9 also exhibit much higher detonation performance than the current secondary explosive (RDX). Overall, this study offers a promising prospect for the preparation of energetic nitramino salts with a green and economic pathway.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b00589.

Synthesis, calculation detail, crystal refinements, NMR spectra (PDF)

### Accession Codes

CCDC 1895157–1895159 and 1895162 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/ cif, or by e-mailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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The authors declare no competing financial interest.

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(b) 13.4.2 Test 3 (a)(ii) BAM Fallhammer, p 75. (c) 13.5.1 Test 3 (b) (i): BAM friction apparatus, p 104.