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# 4-(1-Amino-5-aminotetrazolyl)methyleneimino-3methylfuroxan and Its Derivatives: Synthesis, Characterization, and Energetic Properties

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The condensation reaction of 4-formyl-3-methylfuroxan with 1,5-diaminotetrazole led to 4-(1-amino-5-aminotetrazolyl)methyleneimino-3-methylfuroxan (1) in high yield. Its structure was confirmed by an X-ray diffraction study. 4-(1-Amino-5-nitriminotetrazolyl)methyleneimino-3-methylfuroxan (2) was obtained through the nitration of 1 with 100 % HNO<sub>3</sub>. The nitrogen-rich salts of 2 with bases such as 1amino-1,2,3-triazole (3), 4-amino-1,2,4-triazole (4), and 3amino-1,2,4-triazole (5) were synthesized and characterized

# Introduction

The development of new high-energy-density materials (HEDM) continues to focus on the synthesis of the highnitrogen compounds. High-nitrogen materials are increasingly being tested as green replacements for traditional explosives, which are toxic and carcinogenic.<sup>[1]</sup> Many highnitrogen heterocycles such as furazan,<sup>[2]</sup> 1,2,3,4-tetrazine,<sup>[3]</sup> tetrazole,<sup>[4]</sup> and triazole<sup>[5]</sup> have exceptionally high heats of formation and are highly endothermic in nature. Recently, many types of energetic compounds containing different energetic moieties have been investigated and synthesized.<sup>[6]</sup>

The synthesis of tetrazoles as energetic materials and intermediates to energetic materials has been in focus for the last two decades. Most of the energy derives from positive heats of formation rather than from oxidation of a carbon backbone. 1,5-Diaminotetrazole (DAT),<sup>[7]</sup> as a simple tetrazole derivative, exhibits a relatively high thermal stability owing to the electron-donating side groups. In addition, DAT has a high heat of formation; therefore, it can

E-mail: gcheng@mail.njust.edu.cn http://www.njust.edu.cn/ by IR, Raman, and NMR spectroscopy and elemental analysis. In addition, the structures of **2**, **4**, and **5** were further confirmed by single-crystal X-ray diffraction analyses. Compound **5** decomposes at 183 °C, whereas **3** and **4** are less stable and decompose at 139 and 164 °C, respectively. The heats of formation, detonation parameters, and impact sensitivity of **1–5** were investigated by theoretical and experimental methods.

be used as a valuable substrate in the preparation of highenergy-density materials. However, DAT, like most other tetrazole derivatives, is oxygen deficient. To find practical use as a high explosive, the introduction of oxidizing groups to DAT is required.

Furoxan (1,2,5-oxadiazole 2-oxide) is a highly energetic heterocycle of the isoxazole family and a *N*-oxide derivative of furazan. As such, the introduction of a furoxan ring to organic compounds has been proved to increase crystal density and improve explosive performance compared to that for nitro groups.<sup>[8]</sup> Firstly, the aromatic nature of the furoxan moiety makes the molecule thermally stable. Secondly, the planarity of the ring helps to increase the crystal density owing to the dense packing of molecules. Thirdly, furoxan, which has a "latent" nitro group within one side of its ring, is an effective structural unit that itself is an explosive group. By introducing a furoxan ring into high-energy-density molecules, the density can be increased by ca.  $300 \text{ m s}^{-1}$ .<sup>[9]</sup>

Considering these factors, the combination of the two different energetic units (tetrazole and furoxan) into one molecule is expected to produce good energetic materials with excellent properties such as good thermal stability and low sensitivity. In this paper, we describe the synthesis of 4- (1-amino-5-aminotetrazolyl)methyleneimino-3-methylfuroxan (1) from 3-methyl-4-formylfuroxan<sup>[10]</sup> and 1,5-di-aminotetrazole.<sup>[11]</sup> The nitration of **1** with 100% nitric acid

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resulted in a nitroiminotetrazole derivative 4-(1-amino-5nitriminotetrazolyl)methyleneimino-3-methylfuroxan (2), which exhibits good detonation performance because it combines the strongly oxidizing nitroimino group, a furoxan ring, and the energetic nitrogen-rich backbone in one molecule. Furthermore, three energetic salts were obtained. These compounds were fully characterized by IR spectroscopy, Raman spectroscopy, elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, and single-crystal structure analyses. Their densities, heats of formation, thermal behavior, and detonation parameters were further investigated by experimental and theoretical methods.

#### **Results and Discussion**

#### Synthesis

As shown in Scheme 1, 4-(1-amino-5-aminotetrazolyl)methyleneimino-3-methylfuroxan (1) was prepared in a high yield of 75% by the condensation reaction of 4-formyl-3methylfuroxan with 1,5-diaminotetrazole in water at 75 °C. An initial attempt to synthesize 4-(1-amino-5-nitriminotetrazolyl)methyleneimino-3-methylfuroxan (2) by nitration of 1 with a mixture of excess 95% nitric acid and 98% sulfuric acid was unsuccessful. However, compound 2 was obtained in 41% yield by the nitration of 1 with 100% nitric acid (Scheme 1). Compound 2 is neither hygroscopic nor sensitive towards light and air. The formation of the nitrogen-rich salts was accomplished in a straightforward manner by acid–base reactions between 2 and energetic bases in aqueous solutions. The structures of the resulting compounds are supported by <sup>1</sup>H and <sup>13</sup>C NMR, IR, and Ra-



Scheme 1. Synthesis of 4-(1-amino-5-aminotetrazolyl)methyleneimino-3-methylfuroxan (1), 4-(1-amino-5-nitriminotetrazolyl)methyleneimino-3-methylfuroxan (2), and salts (3–5).

man spectroscopy and elemental analysis. The structures of 1, 2, 4, and 5 were further confirmed by single-crystal X-ray diffraction.

#### Single-Crystal X-ray Analysis

Single crystals of 1, 4, and 5 were obtained by slow evaporation of solutions of 1, 4, and 5 in MeOH/H<sub>2</sub>O, and single crystals of 2 were obtained by recrystallization from water. Their ORTEP and packing diagrams are shown in Figures 1–4, and the crystallographic data are summarized in Table 1. The bond lengths and angles are also listed in the Supporting Information (Tables S1–S16).



Figure 1. (a) Thermal ellipsoid plot (50%) and labeling scheme for 1. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball-and-stick packing diagram of 1 viewed down the b and c axes. Dashed lines indicate strong hydrogen bonds.

Compound 1 crystallizes with a calculated density of  $1.546 \text{ g cm}^{-3}$  in the space group  $P2_1/c$  with four formula units in the unit cell. The ring geometries of the tetrazole and furoxan rings are in good agreement with those previously reported.<sup>[12]</sup> The N6–C2 and C1–N1 bond lengths are 1.277 and 1.330 Å, respectively. The dihedral angle between the two planes is 5.936°. The molecular unit is depicted in Figure 1 (a). The hydrogen bonds build up a dense 3D network as shown in Figure 1 (b). The 3D network consists of condensed "rhombic prisms" built by the molecules





Figure 2. (a) Thermal ellipsoid plot (50%) and labeling scheme for 2. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball-and-stick packing diagram of 2 viewed down the *a* and *c* axes. Dashed lines indicate strong hydrogen bonds.



Figure 3. (a) Thermal ellipsoid plot (50%) and labeling scheme for 4. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball-and-stick packing diagram of 4 viewed down the *a* axis. Dashed lines indicate strong hydrogen bonds.



Figure 4. (a) Thermal ellipsoid plot (50%) and labeling scheme for 5. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball-and-stick packing diagram of 5 viewed down the *b* axis. Dashed lines indicate strong hydrogen bonds.

of 1. The oxygen atom (O2) of the *N*-oxide group is involved in the formation of a weak intermolecular hydrogen bond with the NH fragment [H···O is 0.8600 Å, N···O 2.892(3) Å, N–H···O angle 143°].

Compound **2** crystallizes in the space group  $P2_1/c$  with four formula units in the unit cell and a density of 1.712 gcm<sup>-3</sup>, which is significantly higher than that of **1**. This result nicely confirms the concept of increased density by the introduction of NO<sub>2</sub> groups.<sup>[13]</sup> The unit cell of **2** is depicted in Figure 2 (a). Correspondingly, the bonds C1– N1 (1.271 Å) and C2–N6 (1.321 Å) are shortened compared to the values of 1.363(2) and 1.356(2) Å for **1**. The tetrazole ring is slightly distorted, and the dihedral angle between the two planes is 7.62(1)°. From Figure 2 (b), it can be clearly seen that intermolecular hydrogen bonds are formed in the compound, and the extensive hydrogen-bonding interactions contribute to an increase in density. Analysis of the crystal packing of **2** shows that the 3D network is Z-shaped.

Compounds 4 and 5 crystallize in the space group  $P2_1/c$  with four formula units in the unit cell. The structure of 5 shows only a slightly higher density (1.681 g cm<sup>-3</sup>) than that



	1	2	4	5			
Formula	C <sub>5</sub> H <sub>6</sub> N <sub>8</sub> O <sub>2</sub>	C <sub>5</sub> H <sub>5</sub> N <sub>9</sub> O <sub>4</sub>	$C_7H_9N_{13}O_4$	$C_7H_9N_{13}O_4$			
FW [gmol <sup>-1</sup> ]	210.18	255.18	339.27	339.27			
Temperature [K]	291	291	173	173			
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic			
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$			
a [Å]	6.2287(11)	6.268(4)	7.7870(19)	12.589(3)			
b Å	8.0735(12)	16.508(9)	17.917(4)	5.3365(10)			
c Å	17.9653(17)	9.862(5)	10.411(2)	20.130(4)			
	90	90	90	90			
β[°]	91.840(3)	104.01(6)	111.121(2)	97.582(2)			
γ [°]	90	90	90	90			
Cell volume [Å <sup>3</sup> ]	903.0(2)	990.0(9)	1355.0(5)	1340.5(4)			
Z	4	4	4	4			
$\rho_{\rm calcd.} [\rm g \rm cm^{-3}]$	1.546	1.712	1.663	1.681			
Absorption correction	multiscan						
$\theta$ range for data collection[°]	3.27-25.99	2.56-22.97	2.27-26.00	2.44-23.72			
Refinement method	full-matrix least squares on $F^2$						
Goodness-of-fit on $F^2$	1.034	1.038	1.043	1.027			
$R_1, wR_2 [I > 2\sigma(I)]$	0.0571, 0.1325	0.0492, 0.1320	0.0481, 0.1226	0.0450, 0.1043			
$R_1, wR_2$ (all data)	0.0698, 0.1412	0.0523, 0.1368	0.0818, 0.1515	0.0662, 0.1154			
Largest diff. peak and hole [eÅ-3]	0.207 and -0.239	0.332 and -0.301	0.420 and -0.506	0.214 and -0.269			

Table 1. Crystallographic data for 1, 2, 4, and 5.

of 4 (1.663 gcm<sup>-3</sup>). The structure of the anion is similar to that of the corresponding acid 2. The C2–N6 bond lengths (1.353 and 1.362 Å, respectively) in 4 and 5 are both longer than that of 2, which may be attributed to the protonation of the tetrazole ring. In the structure of 4, a hydrogen atom occupies two positions at N11 (0.77) and N5 (0.23). Further details are provided in the Supporting Information.

#### NMR Spectroscopy

Compounds 1–5 in [D<sub>6</sub>]DMSO were analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Figures S1–S10). In the <sup>1</sup>H NMR spectra, the C–H proton resonances are observed as sharp signals at  $\delta$  = 9.08 (1), 9.31 (2), 9.30 (3), 9.26 (4), and 9.25 ppm (5). In addition, the methyl proton signals are found at  $\delta$  = 2.35–2.44 ppm. The highly acidic N–H proton resonance is found as a broad resonance at  $\delta$  = 11.65 ppm for 2. The N–H proton resonance of the triazole cation of 3 is found at  $\delta$  = 7.92 ppm, whereas that of the triazole cation of 4 is found at  $\delta$  = 9.43 ppm. The 3-amino-1,2,4-triazole cation of 5 shows signals at  $\delta$  = 8.31 (CH) and 8.04 ppm (NH<sup>+</sup>).

In all of the <sup>13</sup>C NMR spectra, the shifts corresponding to the cations and anions in this study are in good agreement with previously recorded shifts for the relevant cations and anions.<sup>[14]</sup> In the <sup>13</sup>C NMR spectra of the salts 3–5, the resonance of the carbon atom of the tetrazole ring is observed at lower field ( $\delta$  = ca. 153.5 ppm) than that of **2** ( $\delta$  = 152.3 ppm) as a consequence of the deshielding effect produced by the delocalization of the negative charge.

#### Thermal Behavior and Sensitivities

The thermal stabilities of the above compounds were determined by differential scanning calorimetric (DSC) measurements at 5 °C min<sup>-1</sup> (Figures S11–S15). The decomposition temperatures are given as peak maximum temperatures (Table 2). The highest decomposition temperature (205 °C) was observed for 1, and the lowest decomposition temperature (139 °C) was obtained for the salt 3. The DSC curve of 3 shows an endothermic event with a heat variation starting at 133 °C, followed by two exothermic events ( $T_d = 139$ and 154 °C). The endothermic event at 133 °C is characteristic of a melting process. Nitriminotetrazole 2 showed an

Table 2. Properties of 1–5 compared with those of TNT and RDX.

	1	2	3	4	5	TNT	RDX
$\rho^{[a]} [g cm^{-3}]$	1.546	1.712	1.663 <sup>[j]</sup>	1.663	1.681	1.65	1.816
$Q^{[b]}[Jg^{-1}]$	4894	6441	5784	5508	5090	4271	
$\widetilde{D}^{[c]}$ [m s <sup>-1</sup> ]	6980	8060	7690	7600	7510	6881	8977
$P^{[d]}$ [GPa]	19.65	27.94	25.01	24.41	23.98	19.50	35.17
$\Delta_{\rm f} H_{\rm m}^{\rm [e]}$ [kJ mol <sup>-1</sup> ]	544.40	742.99	995.05	901.26	759.41	-295.00	92.60
$T_{\rm m}^{\rm [f]}$ [°C]	200	140	133	150	179	80	_
$T_{\rm dec}^{\rm [g]}$ [°C]	205	146	139	164	183	295[17]	205[16]
ESD <sup>[h]</sup> [J]	0.180	0.050	0.500	0.750	0.600	_	$0.1 - 0.2^{[17]}$
IS <sup>[i]</sup> [J]	7.6	5.8	20	32	24	15[17]	7.5 <sup>[17]</sup>

[a] Density from X-ray diffraction. [b] Heat of explosion. [c] Calculated detonation velocity. [d] Calculated detonation pressure. [e] Calculated molar enthalpy of formation. [f] Melting point (onset). [g] Temperature of decomposition (peak of maximum). [h] Electrostatic discharge sensitivity. [i] Impact sensitivity. [j] Calculated with the same density as that of **4**.



exothermic decomposition in the temperature range 135– 155 °C with a peak maximum at 146 °C. In comparison with the decomposition temperature of **2**, those of both the triazole salts **4** and **5** were higher. Therefore, these studies show that salts **4** and **5** presented here have higher thermal stabilities than that of **2**, which is probably attributable to the extensive hydrogen bonding, as observed in the crystal structures, and the higher electron density within the tetrazole ring. Salt **4** undergoes a three-step decomposition, and the exothermic peaks are presented at 164, 169, and 174 °C, respectively.

Impact-sensitivity measurements were performed by using the standard BAM method.<sup>[15]</sup> Additionally, all compounds were tested for sensitivity toward electrical discharge by using an ESD JGY-50 III electric spark tester. The data are shown in Table 2. The sensitivity of parent compound 1 (7.6 J) is similar to that of RDX (7.5 J). The nitration product 2 is more sensitive (5.8 J) than RDX; however, the impact sensitivities for salts 3–5 of 20–32 J are much higher than that of RDX. As can be seen from Table 2, similar trends are observed in the electrostatic discharge sensitivity results. Although 2 is sensitive (50 mJ) to electrostatic discharge, 3 (500 mJ), 4 (750 mJ), and 5 (600 mJ) are significantly less sensitive.

#### Heats of Formation and Detonation Parameters

To investigate the energetic properties of these new compounds, the gas-phase enthalpies of formation of the above compounds were calculated by using the Gaussian 03 suite of programs.<sup>[18]</sup> The lattice energy of the ionic salts were predicted by using the formula suggested by Jenkins et al.<sup>[19]</sup> The results are listed in Table 2. The resulting heats of formation of these compounds vary between 544.4 (1) and 995.1 kJ mol<sup>-1</sup> (3). The predicted heats of explosion of 1–5 vary between the low value for the nitrogen-rich compound 1 (4894 J g<sup>-1</sup>) to the high value for nitramine compound 2 (6441 J g<sup>-1</sup>).

The *P* and *D* values in Table 2 indicate that no compound can reach the detonation performance of RDX (8977 m s<sup>-1</sup>, 35.17 GPa); however, **2** (8060 m s<sup>-1</sup>, 27.94 GPa) exhibits superior detonation performance than that of TNT (6881 m s<sup>-1</sup>, 19.50 GPa). The corresponding parameters of salts **3**, **4**, and **5** are better than that of TNT, whereas the result of **1** (6980 m s<sup>-1</sup>, 19.65 GPa) is similar to that of TNT.

# Conclusions

The parent compound 1 was prepared in 75% yield through the condensation reaction of 4-formyl-3-methyl-furoxan with 1,5-diaminotetrazole. It was fully characterized, and its structure was confirmed by single-crystal X-ray diffraction. The new nitramine derivative 4-(1-amino-5-nitriminotetrazolyl)methyleneimino-3-methylfuroxan (2) was prepared by nitration of 1 with 100% nitric acid. In comparison with 1, it shows a lower decomposition point (146 vs. 205 °C). The nitrogen-rich salts of 2 with bases such

as 1-amino-1,2,3-triazole (3), 4-amino-1,2,4-triazole (4), and 3-amino-1,2,4-triazole (5) were investigated and characterized by IR, Raman, and NMR spectroscopy and elemental analysis. Furthermore, the structural characteristics for 2, 4, and 5 were further confirmed by single-crystal Xray diffraction analyses. Compound 5 has high thermal stability with a decomposition temperature of 183 °C, whereas 3 and 4 are less stable and decompose at 139 and 164 °C, respectively. The heats of formation of 1–5 were predicted at the CSB-4M level of theory. All of the compounds have highly endothermic heats of formation; 5 has the highest heat of formation (995.1 kJ mol<sup>-1</sup>) of 1–5.

# **Experimental Section**

**Caution!** Although none of the compounds described herein exploded or detonated in the course of this research, these materials should be handled with extreme care by using the best safety practices. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields, and ear plugs are strongly recommended.

General Methods: All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured with a Bruker Avance III 500 MHz Digital NMR Spectrometer operating at 500 and 126 MHz, respectively. FTIR spectra were recorded with a BOMEM MB Series 154S FTIR spectrometer. Raman spectra were measured with a RamTracer®-200 instrument. Mass spectra were recorded with an ultrafleXtreme MALDI-TOF/MS instrument with an electron impact (EI) ion source. Elemental analyses were performed with a Vario EL III instrument. TG and DSC studies were performed at a heating rate of 5 °Cmin<sup>-1</sup> in closed Al containers with a nitrogen flow of 30 mLmin<sup>-1</sup> with an STD-Q600 instrument. The electrostatic sensitivity test was performed with an ESD JGY-50 III electric spark tester. The impact-sensitivity tests were performed with an HGZ-1 drop hammer. Test specimens were kept between two hardened anvils, and a 2.0 or 5.0 kg drop weight was allowed to fall freely from different heights. Twenty-five tests were conducted for each compound.

X-ray Crystallography: The X-ray diffraction measurements for 1 and 2 were performed with a Rigaku RAXIS-RAPID imagingplate diffractometer at 291 K by using graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71075$  Å). The data were collected by the  $\omega$ -scan technique. The data for 4 and 5 were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryo-Flex low-temperature device was used to keep the crystals at a constant 173 K during the data collection. The data collection and the initial unit cell refinement was performed by using APEX2 (v2010.3-0).<sup>[20]</sup> Data Reduction was performed by using SAINT (v7.68A)<sup>[21]</sup> and XPREP (v2008/2).<sup>[22]</sup> Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1).<sup>[23]</sup> The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4)<sup>[24]</sup> system of programs. The full-matrix least-squares refinement on  $F^2$  included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined. Please see the CIF files. Relevant data are given in Tables S1-S16.



**Theoretical Study:** Computations were performed by using the Gaussian03 suite of programs. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee–Yan–Parr (B3LYP) functional<sup>[25]</sup> with the 6-311+G\*\* basis set.<sup>[26]</sup> All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies.

The predictions of heats of formation (HOF) used the hybrid DFT-B3LYP methods with the  $6-311+G^{**}$  basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title compounds are shown in Scheme 2. The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).



Scheme 2. Isodesmic and tautomeric reactions to compute the HOF.

$$\Delta H_{298} = \Sigma \Delta_{\rm f} H_{\rm P} - \Sigma \Delta_{\rm f} H_{\rm R} \tag{1}$$

 $\Delta_{\rm f} H_{\rm R}$  and  $\Delta_{\rm f} H_{\rm P}$  are the HOF of the reactants and products at 298 K, respectively, and  $\Delta H_{298}$  can be calculated from the following expression, see Equation (2).

$$\Delta H_{298} = \Delta E_{298} + \Delta (PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$$
(2)

 $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K;  $\Delta H_T$  is the thermal correction from 0 to 298 K. The  $\Delta(PV)$  value in Equation [(2)] is the *PV* work term. It equals  $\Delta nRT$  for the reactions of an ideal gas. For the isodesmic reactions,  $\Delta n = 0$ , so  $\Delta(PV) = 0$ . On the left side of Equation [(1)], apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from experiments<sup>[27–29]</sup> or from the high-level computing such as CBS-4M.

The detonation velocity (D) and detonation pressure (P) were evaluated by the empirical Kamlet–Jacobs (K–J) equations as shown in Equations (3), (4), (5).

$$P = 1.558 \ \rho^2 \Phi \tag{3}$$

$$D = 1.01\Phi^{1/2}(1+1.30\rho_0) \tag{4}$$

$$\Phi = 0.4889 N(MQ)^{1/2} \tag{5}$$

*D* is the predicted detonation velocity (km s<sup>-1</sup>), *P* is the detonation pressure (GPa), and  $\rho$  is the compound density (cm<sup>3</sup> mol<sup>-1</sup>).  $\Phi$ , *N*, *M* and *Q* are characteristic parameters of an explosive; *Q* is the chemical energy of detonation (kJ g<sup>-1</sup>). The crystal densities and the calculated heats of formation were used to compute the *D* and *P* values.

**Starting Materials:** 4-Formyl-3-methylfuroxan,<sup>[10]</sup> 1,5-diamino-tetrazole,<sup>[11]</sup> 1-amino-1,2,3-triazole,<sup>[30]</sup> 4-amino-1,2,4-triazole,<sup>[31]</sup> and 3-amino-1,2,4-triazole<sup>[32]</sup> were synthesized according to literature procedures.

4-(1-Amino-5-aminotetrazolyl)methyleneimino-3-methylfuroxan (1): A suspension of DAT (1.0 g, 10 mmol) in water (10 mL) was added to a solution of 3-methyl-4-furaxancarbaldehyde (1.28 g, 10 mmol) in water (10 mL). Two drops of concentrated HCl were then added, and the mixture was heated at 75 °C for 1 h and then cooled. The precipitate was collected by filtration and washed with ice water, yield 1.58 g (75%), white powder. <sup>1</sup>H NMR (500 MHz,  $[D_6]$ -DMSO):  $\delta = 9.08$  (s, 1 H), 7.45 (s, 2 H), 2.44 (s, 3 H) ppm. <sup>13</sup>C NMR (126 MHz,  $[D_6]DMSO$ ):  $\delta = 152.5, 152.3, 142.5, 111.2,$ 8.7 ppm. IR:  $\tilde{v} = 3395$  (vw), 3086 (w), 3020 (vw), 2921 (vw), 1660 (m), 1599 (vs), 1464 (s), 1443 (s), 1354 (m), 1308 (v), 1265 (v), 1173 (v), 1094 (m), 1046 (s), 989 (m), 971 (m), 880 (v), 832 (s), 777 (m), 725 (m), 680 (m) cm<sup>-1</sup>. Raman:  $\tilde{v} = 1616$ , 1590, 1440, 1356, 1308, 1268, 1178, 1104, 1040, 990, 970, 876, 828, 772, 718, 614 cm<sup>-1</sup>. MS (EI): m/z (%) = 210 (18) [M]<sup>+</sup>, 142 (100), 125 (67) [M - CH<sub>3</sub>N<sub>5</sub>]<sup>+</sup>.  $C_5H_6N_8O_2$  (210.06): calcd. C 28.58, H 2.88, N 53.32; found C 28.56, H 2.86, N 53.33. Electrostatic discharge sensitivity (ESD): 180 mJ. Impact friction: 7.6 J.

4-(1-Amino-5-nitriminotetrazolyl)methyleneimino-3-methylfuroxan (2): At 0 °C, solid 1 (1.0 g, 4.76 mmol) was added in small portions to 100% HNO<sub>3</sub> (10 mL). The reaction mixture was stirred at 0 °C for 8 h. The solution was poured into ice water (50 mL) and then extracted with diethyl ether ( $25 \text{ mL} \times 4$ ). The combined organic phase was dried with anhydrous MgSO<sub>4</sub> and filtered. Compound 2 was obtained by slow evaporation, yield 0.5 g (41%). <sup>1</sup>H NMR (500 MHz,  $[D_6]DMSO$ ):  $\delta = 11.65$  (br), 9.31 (s, 1 H), 2.37 (s, 3 H) ppm. <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 152.3, 150.7, 145.0, 111.1, 8.5 ppm. IR:  $\tilde{v} = 3020$  (vw), 1627 (m), 1599 (m), 1569 (m), 1505 (s), 1474 (m), 1418 (vw), 1298 (w), 1274 (w), 1236 (vs), 1204 (s), 1121 (s), 1047 (m), 990 (m), 956 (s), 874 (m), 822 (m), 736 (m), 679 (m), 611 (m) cm<sup>-1</sup>. Raman:  $\tilde{v} = 1624$ , 1614, 1570, 1510, 1418, 1332, 1236, 1204, 1182, 1124, 1022, 990, 872, 756, 610,  $466 \text{ cm}^{-1}$ . C<sub>5</sub>H<sub>9</sub>N<sub>9</sub>O<sub>4</sub> (255.05): calcd. C 23.54, H 1.98, N 49.40; found C 23.58, H 1.99, N 49.36. ESD: 50 mJ. Impact friction: 5.8 J.

General Procedure for Synthesis of Salts 3–5: A solution of 1amino-1,2,3-triazole (0.084 g, 1 mmol), 4-amino-1,2,4-triazole (0.084 g, 1 mmol) and 3-amino-1,2,4-triazole (0.084 g, 1 mmol) in  $H_2O$  (5 mL) was added dropwise to a suspension of 2 (0.255 g, 1 mmol) in  $H_2O$  (5 mL) under stirring. The mixture was stirred at room temperature for 2 h. The precipitate was then removed by filtration and washed with a small amount of ice water. The filtrate was dried to afford the crude product. Salts 3, 4, and 5 were then recrystallized from methanol.

**3:** 0.32 g of white solid was obtained (yield 94%). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 9.30 (s, 1 H), 7.92 (s, 1 H), 7.68 (s, 1



H), 2.36 (s, 3 H) ppm. <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO):  $\delta$  = 152.3, 151.5, 144.7, 131.6, 123.6, 111.2, 8.5 ppm. IR:  $\tilde{v}$  = 3267 (vw), 3150 (w), 1626 (s), 1606 (m), 1525 (w), 1469 (m), 1433 (m) 1385 (w), 1301 (s), 1279 (vs), 1257 (vs), 1227 (vs), 1173 (m), 1131 (m), 1080 (m), 1007 (m), 968 (w), 868 (m), 820 (w), 787 (s), 758 (s), 689 (m), 612 (s) cm<sup>-1</sup>. Raman:  $\tilde{v}$  = 1606, 1522, 1438, 1384, 1304, 1184, 1128, 1084, 1004 cm<sup>-1</sup>. C<sub>7</sub>H<sub>9</sub>N<sub>13</sub>O<sub>4</sub> (339.09): calcd. C 24.78, H 2.67, N 53.68; found C 24.72, H 2.69, N 53.66. ESD: 500 mJ. Impact friction: 20 J.

**4:** 0.30 g of white solid was obtained (yield 88%). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta = 9.43$  (s, 2 H), 9.26 (s, 1 H), 2.35 (s, 3 H) ppm. <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO):  $\delta = 153.5$ , 152.5, 143.8, 143.5, 111.2, 8.5 ppm. IR:  $\tilde{v} = 3278$  (w), 3140 (w), 1624 (m), 1606 (m), 1434 (m), 1333 (m), 1269 (vs), 1233 (s), 1130 (v), 1087 (w), 1025 (m), 954 (m), 864 (m), 821 (s), 759 (m), 734 (m), 670 (m), 624 (s), 610 (s) cm<sup>-1</sup>. Raman:  $\tilde{v} = 1608$ , 1520, 1490, 1388, 1302, 1234, 1182, 1128, 1082, 1006 cm<sup>-1</sup>. C<sub>7</sub>H<sub>9</sub>N<sub>13</sub>O<sub>4</sub> (339.09): calcd. C 24.78, H 2.67, N 53.68; found C 24.90, H 2.68, N 53.65. ESD: 750 mJ. Impact friction: 32 J.

**5:** 0.26 g of white solid was obtained (yield 77%) <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO):  $\delta = 9.25$  (s, 1 H), 8.32 (s, 1 H), 8.02 (br, 1 H), 2.35 (s, 3 H) ppm. <sup>13</sup>C NMR (126 MHz, [D<sub>6</sub>]DMSO):  $\delta = 154.1$ , 152.5, 150.2, 143.6, 138.8, 111.2, 8.5 ppm. IR:  $\tilde{v} = 3251$  (vw), 3072 (vw), 1682 (s), 1624 (s), 1607 (m), 1520 (m), 1470 (m), 1412 (m), 1303 (m), 1279 (vs), 1237 (s), 1139 (w), 1092 (s), 1049 (m), 1014 (m), 948 (s), 878 (w), 827 (m), 730 (w), 671 (m), 619 (s) cm<sup>-1</sup>. Raman:  $\tilde{v}$  1606, 1518, 1490, 1418, 1370, 1336, 1302, 1236, 1184, 1138, 1092, 1046, 1012, 882 cm<sup>-1</sup>. C<sub>7</sub>H<sub>9</sub>N<sub>13</sub>O<sub>4</sub> (339.09): calcd. C 24.78, H 2.67, N 53.68; found C 24.77, H 2.72, N 53.21. ESD: 600 mJ. Impact friction: 24 J.

**Supporting Information** (see footnote on the first page of this article): Structural characterization and overview of selected crystallographic data of 1, 2, 4, and 5.

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