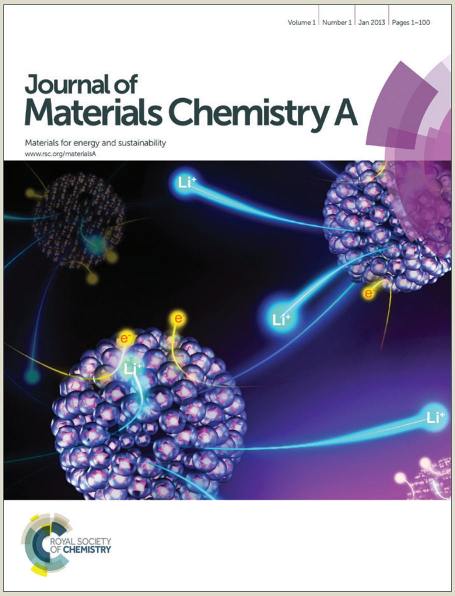
# Journal of Materials Chemistry A



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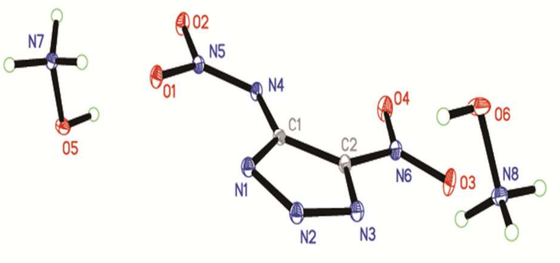


4-R-5-nitro-1,2,3-triazolate salts (R = -$CH_3$, -$NH_2$, -$NO_2$, -$N_3$, and -$NHNO_2$) were systematically synthesized with nitrogen-rich cations. Among the energetic salts, hydroxylaminium 4,5-dinitro-1,2,3-triazolate and dihydroxylaminium 4-nitramino-5-nitro-1,2,3-triazolate exhibit excellent energetic performances (38.0 GPa, 9302 m/s, 256.1 s; 38.8 GPa, 9464 m/s, 251.1 s).

# Nitrogen-rich energetic 4-R-5-nitro-1,2,3-triazolate salts (R = -$CH_3$, -$NH_2$, -$N_3$, -$NO_2$ and -$NHNO_2$) as high performance energetic materials

Long Liu,[a] Yanqiang Zhang,*[a] Zhimin Li,[a] and Suojiang Zhang*[a]

A series of 4-R-5-nitro-1,2,3-triazolate salts (R = -$CH_3$, -$NH_2$, -$NO_2$, -$N_3$, and -$NHNO_2$) were synthesized with cations of ammonium, hydroxylammonium, hydrazinium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium, respectively. The resulting energetic salts were characterized with $^1H$ and $^{13}C$ NMR, IR spectroscopy, elemental analysis, and some with single crystal X-Ray diffraction. Their key properties were measured or calculated such as melting and decomposition temperatures, density, detonation pressure and velocity, and impact and friction sensitivities. The results show that guanidinium salts possess the highest thermal stability in each group with decomposition temperatures as 265, 251, 221, 142, and 216 °C, respectively. Hydroxylammonium 4,5-dinitro-1,2,3-triazolate and dihydroxylammonium 4-nitramino-5-nitro-1,2,3-triazolate exhibit much higher detonation performances (38.0 GPa, 9302 m/s; 38.8 GPa, 9464 m/s) than cyclotrimethylenetrinitramine (34.9 GPa, 8748 m/s). Moreover, the high specific impulses (256.1 and 251.1 s) from the formula calculations based on the two salts further support their application prospects.

## Introduction

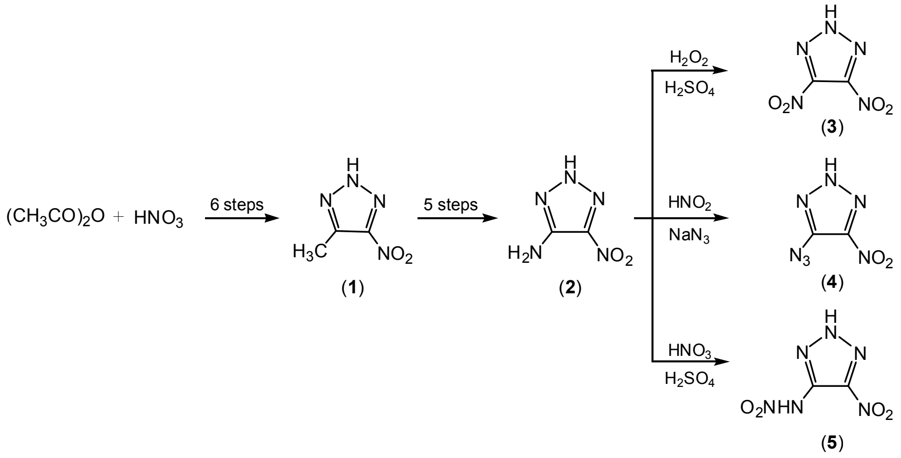
Nitrogen-rich compounds are the main area of high energy density materials (HEDMs) due to high positive heats of formation and environmental benignness.[1-6] Azoles such as pyrazole, imidazole, triazole, and tetrazole, are regarded as the core structures of nitrogen-rich materials,[7-11] which have been widely investigated. With good detonation performances, some energetic azole derivatives are acidic in varying degrees as a result of the electron withdrawing effect of energetic group substituents (-$NO_2$ and -$N_3$) on azole rings upon the N-H group,[9,12,13] which enhances their reactivities with metals and become a big obstacle of applications. Salification has been proved to be an effective way to solve the acidity problem of azoles. The resulting energetic salts usually possess advantages over covalent molecules with lower vapor pressures, higher thermal stabilities, and lower sensitivities.

A lot of azole-based energetic salts have been designed and synthesized,[1,14-17] such as pyrazolate,[17-19] imidazolate,[10,20,21] 1,2,4-triazolate,[5,7,22,23] 1,2,3-triazolate,[24-28] and tetrazolate[9,15,29]. Considering that 1,2,3-triazole possesses even higher thermal stability and heat of formation than 1,2,4-triazole, we prepared the derivatives of 1,2,3-triazole systematically, including 4-R-5-nitro-1,2,3-triazole (R = -$NO_2$, -$N_3$, and -$NHNO_2$).[12,24] These derivatives are acidic to be incompatible with many organic and inorganic components so that they are hardly used in spite of the excellent detonation performances and acceptable sensitivities. Salification of the energetic 1,2,3-triazole derivatives can be critically valuable for their applications.

In this paper, a series of energetic salts of 4-R-5-nitro-1,2,3-triazolate (R = -$CH_3$, -$NH_2$, -$NO_2$, -$N_3$, and -$NHNO_2$) were synthesized with nitrogen-rich cations such as ammonium, hydroxylammonium, hydrazinium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium. These salts were fully characterized with $^1H$ and $^{13}C$ NMR, IR spectroscopy, elemental analysis, simultaneous thermogravimetric analysis and differential thermal analysis (TG/DTA), hammer and friction tests, and in some cases with single crystal X-Ray diffraction. Their heats of formation and detonation properties were calculated with Gaussian 09 and Explo 5 (version 6.01) programs, respectively. Furthermore, some salts with good detonation performances were used as energetic components to substitute cyclotrimethylenetrinitramine (RDX) in LOVA propellant, and the specific impulses were calculated by using Explo 5 program.

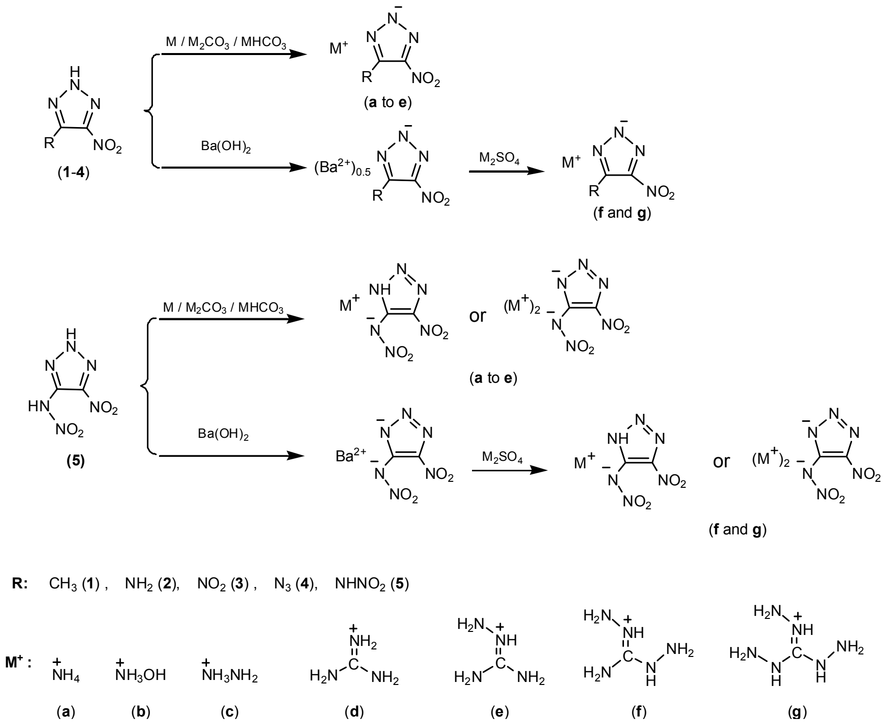
## Results and Discussion

4-R-5-nitro-1,2,3-1H-triazole (**1-5**, R = -$CH_3$, -$NH_2$, -$NO_2$, -$N_3$, and -$NHNO_2$) were synthesized by multi-step reactions from acetic anhydride and nitric acid (100%) according to the reference methods (Scheme 1).[12,24]



**Scheme 1** Synthesis of 4-R-5-nitro-1,2,3-2H-triazole (R= $-CH_3$, $-NH_2$, $-NO_2$, $-N_3$, and $-NHNO_2$)

Reactions of **1-5** with ammonia, hydroxylamine, hydrazine, guanidine carbonate and aminoguanidine bicarbonate resulted in the formation of salts (**a-e**), shown in Scheme 2. Other salts (**f**, **g)** were readily synthesized by metathesis reactions of barium salts of **1-5** with diaminoguanidium and triaminoguanidinium sulphate, respectively. The structures of salts were confirmed by $^1$H and $^{13}$C NMR, IR spectroscopy, and elemental analysis. **1** and **2** could not react with hydroxylamine to form stable salts (**1b**, **2b**) as their acidities are reduced by the electron-donating inductive effects of methyl and amino groups. **4** is unstable in alkaline conditions so that bases were added to the solutions of **4** with strict stoichiometry. Salts **4a**-**4g** cannot be kept in DMSO for long time so that their NMR tests were conducted immediately once they were dissolved. **3c** and **4b** were purified with recrystallization with many solvents, and all the tries failed. The divalent salts of **5a**-**5g** were tried with the same method. However, the resulting **5a**, **5d** and **5g** were confirmed as the monovalent salts, respectively.



**Scheme 2** Synthesis of energetic salts

Structures of all salts were supported by characterizations, such as $^1$H and $^{13}$C NMR, IR spectroscopy, and elemental analysis. Salts **3a**, **3e**, **3f**, **4d**, **5a**, and **5b** were further confirmed by single crystal X-ray diffraction. In the $^1$H NMR spectra, the NH proton signals of their precursors disappeared after salt formations, thus the observed signals from the cations were assigned accordingly. In the $^{13}$C NMR spectra, the very weak signals ranging from 138 to 146 ppm were assigned to the carbon atoms connected to -NO$_2$ group. In the IR spectra, the absorption bands of -NO$_2$ groups are in the range of 1400-1600 cm$^{-1}$. Intense absorption bands in the range of 3100-3500 cm$^{-1}$ could be assigned to the N-H bonds of the nitrogen-rich cations.

## Properties of energetic salts

Thermal stabilities of all salts were determined using a SHIMADZU DTG-60H system at a heating rate of 5 °C/min (Table 1). Salts of **1** and **2** melt with the points ranging from 113 (**1c**) to 237 °C (**2d**), and decompose from 171 (**2c**) to 265 °C (**1d**). Salts of **3** show moderate thermal stabilities with decomposition temperatures ranging from 178 (**3b**) to 206 °C (**3e**). Salts of **4** decompose without melting, and exhibit relatively poor thermal stabilities between 102 (**4g**) and 142 °C (**4d**). For salts of **4**, the decrease of thermal stabilities after salt formations may be due to the electron transfer participated by -$N_3$ group at a high temperature. Salts of **5** decompose directly from 155 (**5c**) to 216 °C (**5d**), except that salts **5b**, **5e**, and **5f** melt at 105, 176, and 147 °C, respectively. With the same energetic anions, guanidine-based salts show the highest thermal stabilities in each corresponding type of salts.

**Table 1** Properties of the energetic salts

| Salts | $T_m$[a] [°C] | $T_d$[b] [°C] | $\rho$[c] [g/cm$^3$] | $\Delta H$[d] [kJ/mol] | $\Delta H_f$[e] [kJ/mol]/[kJ/g] | $P$[f] [Gpa] | $D$[g] [m/s] | $IS$[h] [J] | $FS$[i] [N] |
|---|---|---|---|---|---|---|---|---|---|
| **1a** | 116 | 159 | 1.50 | 539 | 117/0.806 | 20.1 | 7839 | >40 | >360 |
| **1c** | 113 | 200 | 1.48 | 523 | 277/1.729 | 22.0 | 8188 | >40 | >360 |
| **1d** | 199 | 265 | 1.42 | 506 | 100/0.534 | 16.1 | 7239 | >40 | >360 |
| **1e** | 141 | 233 | 1.44 | 497 | 193/0.954 | 18.1 | 7612 | >40 | >360 |
| **1f** | 153 | 211 | 1.55 | 489 | 310/1.427 | 23.6 | 8489 | >40 | >360 |
| **1g** | 157 | 201 | 1.55 | 476 | 426/1.834 | 25.2 | 8724 | >40 | >360 |
| **2a** | 120 | 124 | 1.62 | 552 | 140/0.972 | 22.5 | 7945 | >40 | >360 |
| **2c** | 149 | 171 | 1.64 | 537 | 298/1.849 | 29.2 | 9067 | >40 | >360 |
| **2d** | 237 | 251 | 1.57 | 509 | 131/0.696 | 21.4 | 8066 | >40 | >360 |
| **2e** | 175 | 219 | 1.61 | 503 | 222/1.093 | 24.7 | 8557 | >40 | >360 |
| **2f** | 152 | 191 | 1.58 | 491 | 343/1.572 | 25.3 | 8676 | >40 | >360 |
| **2g** | 169 | 181 | 1.66 | 489 | 448/1.921 | 30.2 | 9354 | >40 | >360 |
| **3a** |  | 194 | 1.68 | 528 | 130/0.738 | 28.9 | 8418 | 12.5 | 160 |
| **3b** | 126 | 178 | 1.86 | 530 | 173/0.901 | 38.0 | 9302 | 11 | 108 |
| **3d** |  | 221 | 1.70 | 500 | 107/0.491 | 26.3 | 8292 | 17.5 | >360 |
| **3e** | 114 | 206 | 1.71 | 492 | 199/0.854 | 27.6 | 8532 | 25 | 360 |
| **3f** | 120 | 192 | 1.64 | 479 | 321/1.292 | 26.2 | 8436 | 15 | 80 |
| **3g** | 114 | 195 | 1.74 | 480 | 423/1.610 | 31.7 | 9129 | 12.5 | 72 |
| **4a** |  | 136 | 1.65 | 533 | 488/2.835 | 30.2 | 8856 | 3.5 | 64 |
| **4c** |  | 115 | 1.63 | 515 | 649/3.468 | 29.6 | 8884 | 4 | 96 |
| **4d** |  | 142 | 1.60 | 495 | 476/2.223 | 23.8 | 8229 | 4 | 56 |
| **4e** |  | 112 | 1.63 | 489 | 566/2.470 | 26.2 | 8611 | 4 | 144 |
| **4f** |  | 110 | 1.59 | 478 | 686/2.809 | 26.4 | 8646 | 2 | 80 |
| **4g** |  | 102 | 1.60 | 471 | 796/3.071 | 28.1 | 8896 | 7.5 | 120 |
| **5a** |  | 214 | 1.83 | 529 | 159/0.831 | 35.4 | 9139 | 2.5 | 80 |
| **5b** | 105 | 185 | 1.85 | 1483 | 119/0.496 | 38.8 | 9464 | 7 | 64 |
| **5c** |  | 155 | 1.73 | 1451 | 347/1.457 | 34.2 | 9505 | 2 | 80 |
| **5d** |  | 216 | 1.75 | 496 | 141/0.605 | 28.4 | 8639 | 10 | 288 |
| **5e** | 176 | 187 | 1.57 | 1249 | 329/1.021 | 24.1 | 8405 | 10 | >360 |
| **5f** | 147 | 200 | 1.58 | 1202 | 594/1.686 | 26.7 | 8814 | 15 | >360 |
| **5g** |  | 205 | 1.65 | 467 | 466/1.675 | 28.3 | 8799 | 2 | 72 |
| RDX |  | 234 | 1.82 |  | 61.4/0.28 | 33.8 | 8750 | 7.5 | 120 |

[a] Melting temperature. [b] Onset decomposition temperature. [c] Density at 25°C. [d] Lattice energy. [e] Heat of formation of salts. [f] Detonation pressure. [g] Detonation velocity. [h] Impact sensitivity. [i] Friction sensitivity.

Densities of the salts were measured with a gas pycnometer at 25 °C, and found to be in the range of 1.42 (**1d**) and 1.86 g/cm$^3$ (**3b**). The corresponding salts of **3** and **5** have the similar densities, and are higher than those of salts of **4**, which is in agreement with their molecular precursors.[12] Hydroxylammonium salts possess the highest density as 1.86 (**3b**) and 1.85 g/cm$^3$ (**5b**) in their corresponding series.

Heats of formation ($\Delta H_f$) are another important factor in designing energetic compounds, which are predicted by the Born-Haber energy cycles.[30-32] Here the heats of formation of energetic salts can be calculated by the following equations:

$$\Delta H_f^o(ionic\ salt,\ 298\ K) = \Delta H_f^{\circ}(cation,\ 289\ K) + \Delta H_f^{\circ}(anion,\ 289\ K) - \Delta H_L$$

(1)

$$\Delta H_L = U_{POT} + [p(n_M / 2 - 2) + q(n_X / 2 - 2)]RT$$

(2)

$$U_{POT} = \gamma(\rho_m / M_m)^{1/3} + \delta$$

(3)

where $\Delta H_L$ is the lattice energy of salt; $U_{pot}$ the lattice potential energy; $\rho_m$ the density; $M_m$ the formula mass of salts; the values for $p$, $q$, $\gamma$, and $\delta$ are taken from the literature.[30]

Heats of formation of all cations and anions were computed using the Gaussian 09 program package with the atomization method of G2 enthalpies.[33] The calculated heats of formation of salts vary between 0.491 (**3d**) and 3.468 kJ/g (**4c**). The azido-based salts exhibit higher heats of formation than the corresponding other types of salts. In each series of salts, guanidinium salts show lower values than the other corresponding salts.

Based on the $\Delta H_f$ and density values, detonation pressures ($P$) and velocities ($D$) were calculated using Explo 5 program. As shown in Table 1, detonation pressures range from 16.07 (**1d**) to 38.78 GPa (**5b**), and detonation velocities from 7239 (**1d**) to 9505m/s (**5c**). Some salts possess the excellent detonation performance, such as **3b** (38.0 GPa, 9302 m/s), **5a** (35.4 GPa, 9139 m/s), **5b** (38.8 GPa, 9464 m/s), and **5c** (34.2, 9505 m/s). Sensitivities of impact and friction were measured by BAM methods. Salts of **1** and **2** are placed as insensitive explosives with the impact (>40 J) and friction sensitivities (>360 N), respectively. Among the energetic salts, the hydroxylammonium salts show acceptable thermal stabilities, high densities, and excellent detonation performances.

Considering that salts **3b** (38.0 GPa, 9302 m/s, 11 J, 108 N) and **5b** (38.8 GPa, 9464 m/s, 7 J, 64 N) exhibit balanced performances and sensitivities, their further evaluations were conducted as solid propellants. Here, **3b** and **5b** were applied as energetic components to substitute RDX in LOVA propellants, respectively. Specific impulses of the composites were also calculated by using Explo 5 (version 6.01) program (Table 2). The specific impulses of **3b**-based ($C_2$) and **5b**-based ($C_3$) propellants were calculated to be 256.1 and 251.1 s, which are even higher than the corresponding RDX-based propellant (C1, 244.6 s).

**Table 2** Composition of propellants and their specific impulses

| Entry | NC[a] | CA[b] | GAP[c] | RDX | **3b** | **5b** | $I_{sp}$[d] |
|---|---|---|---|---|---|---|---|
| C1 | 10 | 9 | 6 | 75 | 0 | 0 | 244.6 |
| C2 | 10 | 9 | 6 | 0 | 75 | 0 | 256.1 |
| C3 | 10 | 9 | 6 | 0 | 0 | 75 | 251.1 |

[a] Nitrocellulose [%, w/w]. [b] Cellulose acetate [%, w/w]. [c] Glycidyl azide polymer [%, w/w]. [d] Specific impulse [s].

## X-Ray crystallography

Crystals **3a, 3e**, **3f**, **4d**, **5a** and **5b** suitable for single crystal X-ray diffraction were obtained by slow evaporation of their solutions (**3a**, **3e** and **3f** with ethanol; **4d**, **5a** and **5b** with methanol) in room temperature, respectively. The tests were accomplished at 153 K for **3a**, **4d**, **5a**, **5b**, and 163 K for **3e**, **3f**. The crystallographic data and refinement details are summarized in Table 3. Salts **3a**, **3f** and **5b** crystallized in triclinic space group *P-1*, whereas **3e**, **4d** and **5a** in monoclinic space groups *P21/c*, *Pc*, and *P21/c,* respectively. Among the crystals, **5a** possesses the highest calculated density of 1.881 g/cm$^3$. More information of crystals is shown in supporting information.

**Table 3** Crystallographic data and structure determination details for **3a**, **3e**, **3f**, **4d**, **5a**, and **5b**

| | **3a** | **3e** | **3f** | **4d** | **5a** | **5b** |
|---|---|---|---|---|---|---|
| Formula | $C_2H_4N_6O_4$ | $C_3H_7N_9O_4$ | $C_3H_8N_{10}O_4$ | $C_3H_6N_{10}O_2$ | $C_2H_4N_7O_4$ | $C_2H_8N_8O_6$ |
| $Mol_{wt}$ [g/mol] | 176.11 | 233.18 | 248.19 | 214.18 | 191.13 | 240.16 |
| Crystal system | triclinic | monoclinic | triclinic | monoclinic | monoclinic | triclinic |

| | | | | | | |
|---|---|---|---|---|---|---|
| Space group | *P-1* | *P21/c* | *P-1* | *Pc* | *P21/c* | *P-1* |
| a [Å] | 9.2802(15) | 7.304(2) | 6.553(2) | 3.5714(10) | 7.9369(18) | 3.9086(13) |
| b [Å] | 9.4120(11) | 6.3952(18) | 8.471(3) | 9.496(3) | 9.884(2) | 7.562(3) |
| c [Å] | 9.6659(14) | 18.719(5) | 9.078(3) | 12.886(4) | 8.6066(19) | 14.930(5) |
| α [°] | 61.762(9) | 90 | 93.386(5) | 90 | 90 | 95.806(5) |
| β [°] | 77.352(13) | 90.354(4) | 91.224(7) | 90.883(4) | 91.979(4) | 91.521(5) |
| γ [°] | 64.011(9) | 90 | 98.007(5) | 90 | 90 | 101.793(5) |
| V [$Å^3$] | 668.51(16) | 874.4(4) | 497.9(3) | 437.0(2) | 674.8(3) | 429.3(3) |
| Z | 4 | 4 | 2 | 2 | 4 | 2 |
| Temperature [K] | 153 | 163 | 163 | 153 | 153 | 153 |
| $\rho_{calcd}$ [$g/m^3$] | 1.750 | 1.771 | 1.656 | 1.628 | 1.881 | 1.858 |
| μ [$mm^{-1}$] | 0.163 | 0.158 | 0.147 | 0.137 | 0.174 | 0.177 |
| F [000] | 360.0 | 480 | 256 | 220 | 392 | 248 |
| Crystal size [mm] | 0.21×0.34 ×0.52 | 0.34×0.41 ×0.52 | 0.20×0.35 ×0.56 | 0.28×0.42 ×0.44 | 0.16×0.18 ×0.45 | 0.05×0.11 ×0.58 |
| θ range [°] | 2.39 to 31.5 | 2.8 to 31.5 | 2.4 to 31.5 | 2.7 to 31.5 | 2.6 to 29.1 | 2.8 to 29.1 |
| Limiting indices | $-13 \leq h \leq 12$<br>$-13 \leq k \leq 13$<br>$-14 \leq l \leq 13$ | $-10 \leq h \leq 10$<br>$-9 \leq k \leq 9$<br>$-26 \leq l \leq 27$ | $-9 \leq h \leq 9$<br>$-12 \leq k \leq 12$<br>$-13 \leq l \leq 13$ | $-5 \leq h \leq 5$<br>$-13 \leq k \leq 13$<br>$-17 \leq l \leq 18$ | $-10 \leq h \leq 7$<br>$-13 \leq k \leq 13$<br>$-11 \leq l \leq 11$ | $-5 \leq h \leq 5$<br>$-10 \leq k \leq 10$<br>$-20 \leq l \leq 19$ |
| Reflections with I>2σ(I) | 3547 | 2658 | 2686 | 2095 | 1606 | 1883 |
| $R_1$, $wR_2$ | 0.0337, 0.0894 | 0.0356, 0.0847 | 0.0364, 0.0925 | 0.0268, 0.0557 | 0.0307, 0.0702 | 0.0325, 0.0878 |
| CCDC | 1046183 | 1046184 | 1046185 | 1046186 | 1046187 | 1046189 |

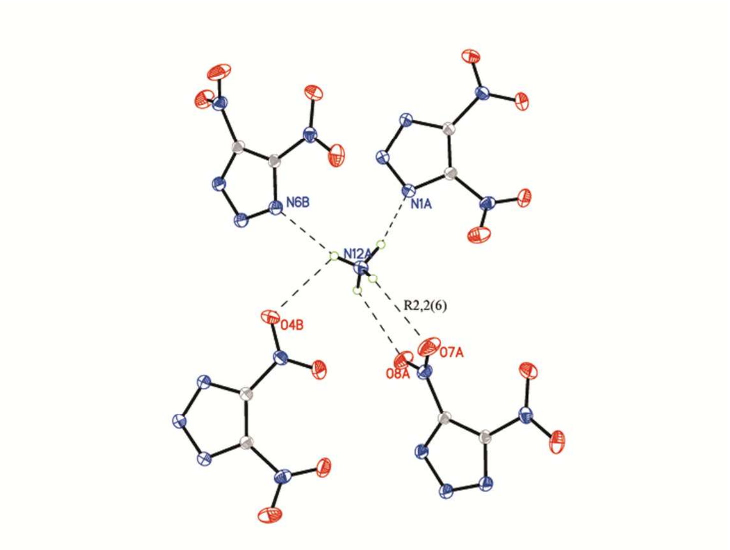
$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{[w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Extensive hydrogen bonds are an obvious characteristic for the structures of energetic salts, which can be confirmed by single crystal X-ray diffraction analyses. Interestingly, the hydrogen bonds are very effective for energetic salts to lower their impact and friction sensitivities. For the above crystals, the main hydrogen bond interactions between cations and anions were shown in Figures 1 to 4. The data of some selected hydrogen bonds are listed in supporting information (Table S1).

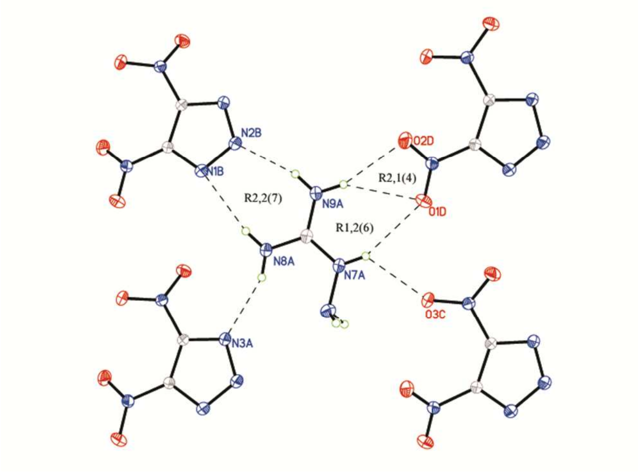
For **3a, 3e** and **3f**, one cation interacts with four anions through different kinds of hydrogen bonds (Fig. 1). All hydrogen atoms of ammonium for **3a** participate in forming hydrogen bonds (Fig. 1a), including a bifurcated hydrogen bond of N(12)-H(12A)…O(4) = 2.531(16)

Å, 112.4(13)° and N(12)-H(12A)…N(6) = 2.237(18) Å, 153.817(13)°. Hydrogen bonds of N(12)-H(12C)…O(8) = 2.50(2) Å, 130.8(14)° and N(12)-H(12A)…O(7) = 2.485(19) Å, 125.5(16)° form a ring of **R2, 2(6)**.[34] For **3e**, all hydrogen atoms of aminogunidium participate in forming hydrogen bonds, except the N(6)$H_2$ group. Two bifurcated hydrogen bonds are formed as H(9) with O(1) (2.494(17) Å, 146.8(13)° and O(2) (2.397(17) Å, 160.5(15)°) in one nitro group; H(7) with O(1) (2.444(16) Å, 150.6(14)°) and O(3) (2.285(16) Å, 124.5(12)°) in two nitro groups. These hydrogen bonds result three types of symmetric rings of **R2**, **2(7)**; **R1**, **2(6)**; and **R2**, **1(4)**.[34] The cations and anions of **3e** stack in parallel pairs that alternate in orientation with other pairs. For **3f**, the interactions between cations and anion form three bifurcated hydrogen bonds as N(6)-H(6B)…O(4) = 2.430(14) Å, 148.8(12)° and N(6)-H(6B)…N(3) = 2.469(14) Å, 145.4(12)° for H(6)B; N(7)-H(7)…O(2) = 2.338(14)Å, 132.7(12)° and N(7)-H(7)…O(3) = 2.541(14)Å, 137.8(12)° for H(7); N(10)-H(10A)…O(2) = 2.480(15) Å, 150.6(13)° and N(10)-H(10A)…O(3) = 2.516(15)Å, 133.1(13)° for H(10)A. Two types of rings of **R2, 1(7)** and **R2, 1(5)** are formed by combing with the backbone of anions, respectively.[34]

**(a)**



(b)



(c)

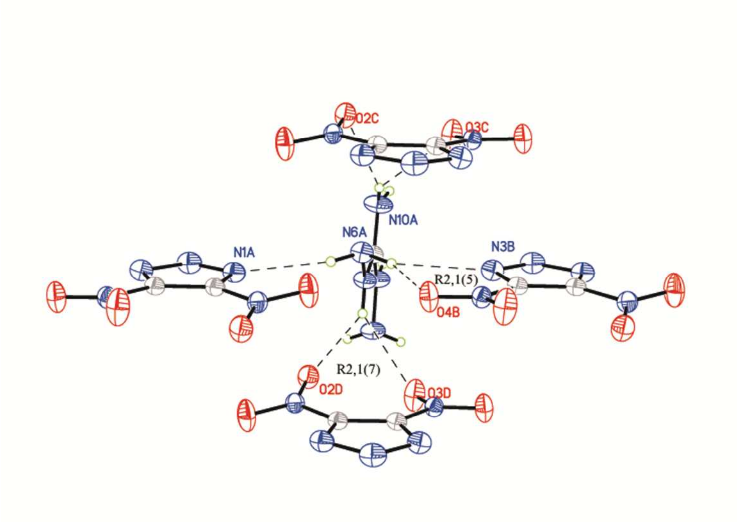
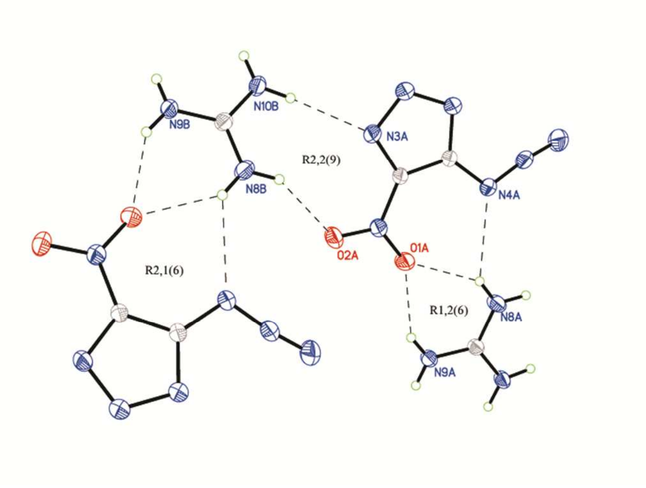


**Fig. 1** (a) View of the hydrogen bonds of one ammonium cation and four anions for **3a**; (b) View of the hydrogen bonds of one aminoguanidinium cation and four anions for **3e**; (c)

View of the hydrogen bonds of one diaminoguanidinium cation and four anions for **3f**. All ellipsoids are set at 30% probability.

The interactions between cations and anions for **4d** are similar to those of **3e** (Fig. 2). The ring motifs of **R2**, **1(6)**; **R1**, **2(6)**; and **R2**, **2(9)** are formed between backbones of one cation and one anion through hydrogen bonds.[34] These hydrogen bonds and π…π interactions of triazole rings induce the cations and anions to stack diagonally and form a three dimensional network.

**(a)**



**(b)**

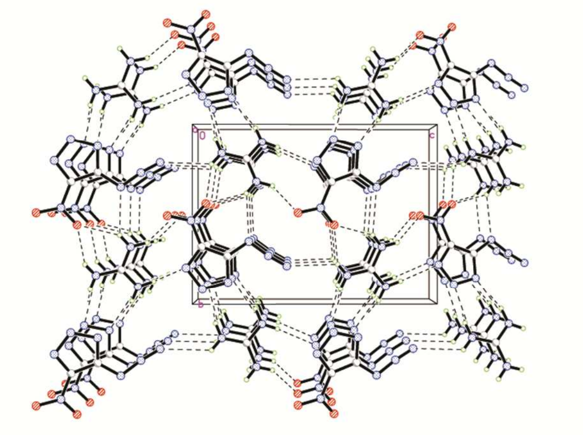
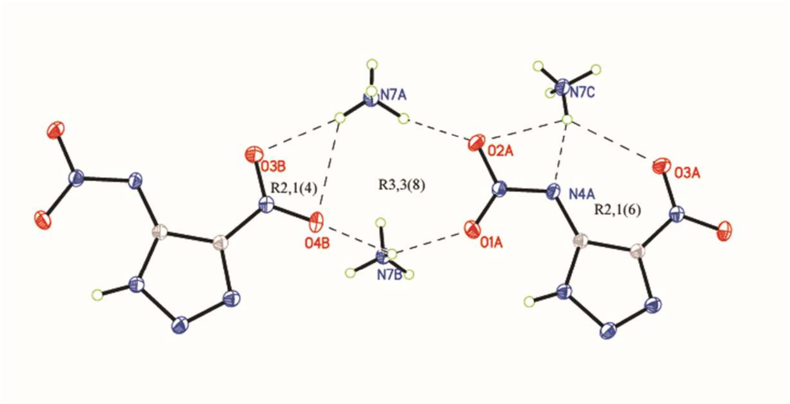


**Fig. 2** (a) View of the hydrogen bonds between cations and anions for **4d**, ellipsoids set at 30% probability. (b) Ball and stick packing diagram of **4d** viewed down the *a* axis. Dashed lines indicate strong hydrogen bonding.

Different from the other salt precursors (**1-4**), 4-nitromino-5-nitro-1,2,3-triazole (**5**) possesses two acidic protons per molecule so that it can form monovalent or divalent salts. The transfer of one proton per molecule of **5** to guanidine is confirmed by Fig. 3a, while the transfer of two protons per molecule of **5** to hydroxylamine by Fig. 3b. For **5a**, the hydrogen atoms in ammonium participate in several bifurcated hydrogen bonds and form the rings of **R3, 3(8)**; **R2, 1(4)** and **R2, 1(6)**.[34] For **5b**, all hydrogen atoms in hydroxylammonium participate in the bifurcated hydrogen bonds, especially including two types of four-center bifurcated hydrogen bonds (**D3, 1(4)**). One is the interactions between H(6) and O(2) (1.70(2)Å, 172.5(19)°), N(4) (2.57(2) Å, 116.7(16)°), N(5) (2.49(2) Å, 146.5(17)°); another is between H(7) and O(1) (1.97(2) Å, 170.6(16)°), O(2) (2.370(18)Å, 115.3(14)), N(5) (2.479(19), 142.5(15). Moreover, there exist other strong hydrogen bonds, such as O(5)-H(50)…N(1) = 1.80(2) Å, 161(2)° and N(7)-H(7C)…N(1) = 1.871(18) Å, 170.2(14)°. These extensive hydrogen bonds form a complex three-dimensional network and contribute to the high density (1.858g/cm$^3$) of **5b**.

(a)



(b)

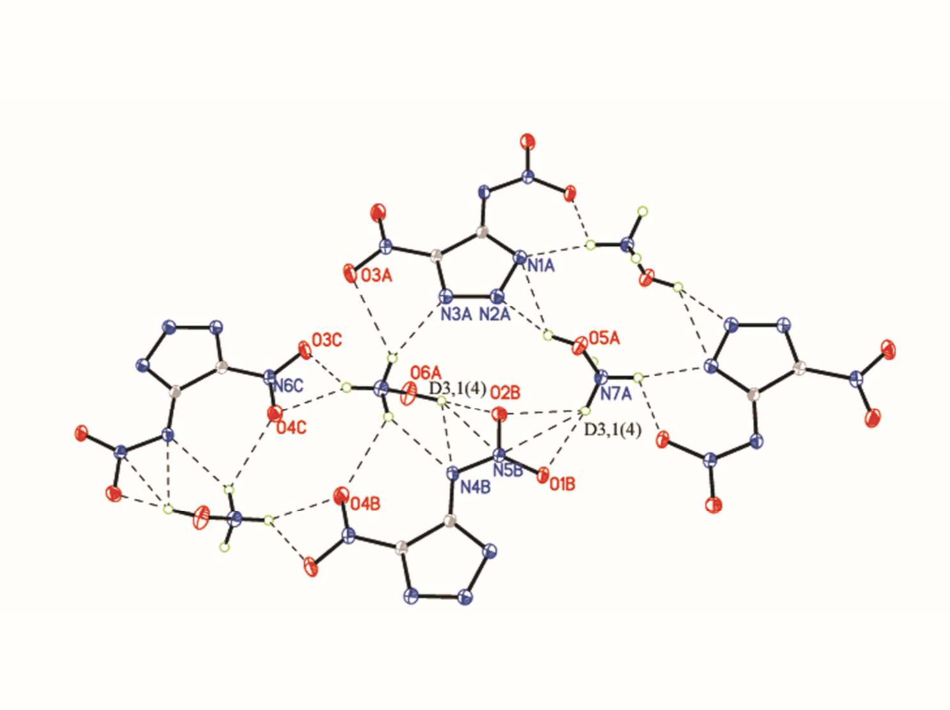


**Fig. 3** (a) View of the hydrogen bonds between cations and anions for **5a**. (b) View of the hydrogen bonds between cations and anions for **5b**. All ellipsoids are set at 30% probability.

## Conclusions

Energetic salts of 5-R-4-$NO_2$-1,2,3-triazolate (R= -$CH_3$, -$NH_2$, -$NO_2$, -$N_3$, and -$NHNO_2$) were synthesized with cations of ammonium, hydroxylammonium, hydrazinium, guanidinium, aminoguanidinium, diaminoguanidinium, and triaminoguanidinium, respectively. The characterizations (including $^1$H and $^{13}$C NMR, IR spectroscopy, and elemental analysis) supported structures of the salts. Based on single crystal X-Ray diffraction, it indicates that there are complex three-dimensional networks of hydrogen bons in these energetic salts. The detonation performances and sensitivities of salts were calculated by Explo 5 program and measured by BAM tests, respectively. Considering the performances/sensitivities balance, hydroxylammonium 4,5-dinitro-1,2,3-triazolate (**3b**) shows most interesting properties (38.0 GPa, 9302 m/s, 11J, and 108 N) among the obtained salts. Furthermore, the high specific impulse (256.1 s) from the formula calculations based on **3b** supports its application prospects.

## Experimental section

***Caution*:** Although we have experienced no difficulties in the syntheses and characterization of these compounds, these materials should be handled with severe protective measures. All of the energetic materials should be handled in very small amounts.

**Reactants:** All reagents are of analytical grade and used as received. Ammonia (25%, Beijing Chemical Works), hydroxylamine (50%, Alfa Aesar), hydrazine hydrate (80%, Xilong Chemical Co., Ltd), guanidine carbonate (>99%, Alfa Aesar), aminoguanidine bicarbonate (>99%, Alfa Aesar), ethanol (>99.7%, Beijing Chemical Works), Methanol (>99.5%, Xilong Chemical Co., Ltd), ethyl acetate (>99.8%, Beijing Chemical Works), and diethyl ether (>99.0%, Beijing Chemical Works).

**General methods:** $^{1}H$ and $^{13}C$ spectra were recorded on a Bruker 600 MHz spectrometer with $d_6$-DMSO as the locking solvent relative to $Me_4Si$. IR spectra were recorded on a Thermo Nicolet 380 spectrometer using KBr pellets at room temperature. Elemental analyses were carried out on a Vario EL elemental analyzer. The melting and decomposition temperatures were obtained on a simultaneous differential scanning calorimetry and thermogravimetric analyzer at a heating rate of 5 °C/min. Densities were measured at room temperature using a Micromeritics Accupyc 1340 instrument. Sensitivities were measured by using a BAM Fallhammer BFH-10 and a BAM friction apparatus FSKM-10. Single crystal X-ray diffraction data were obtained using a Bruker CCD area detector-equipped diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.7103Å). The structures were solved and refined using the SHELXTL software package[35] and absorption data were corrected using SADABS[36]. The structures were refined by full-matrix least squares on $F^2$. Crystallographic data as well as details of the data collection and refinement results for the salts were summarized.

**General procedure for synthesis of the salts (a-e)**: Bases including ammonia (25%, 0.5 mL, 4.6 mmol), hydroxylamine (50%, 0.5 mL, 6.5 mmol ), hydrazine hydrate (80%, 0.5 mL, 12.8 mmol), guanidine carbonate (0.090 g, 0.5 mmol), aminoguanidine bicarbonate (0.136 g, 1.0 mmol) were added to a methanol solution (20 ml) of **1** (0.128 g, 1.0 mmol), **2** (0.129 g, 1.0

mmol), **3** (0.159 g, 1.0 mmol), and **5** (0.087 g, 0.5 mmol), respectively. For compound **4**, the above bases were added to an ethyl acetate solution (20 ml) of **4** (0.155 g, 1.0 mmol), respectively. After the mixture was stirred for 0.5 h at room temperature (50 °C for guanidine carbonate and aminoguanidine bicarbonate), the solvent was evacuated under reduced pressure to give crude product. For compound **4**, crude products were precipitated directly from the reaction solutions.

**General procedure for synthesis of the salts (f-g)**: $Ba(OH)_2$•$8H_2O$ (0.158 g, 0.5 mmol) was added to an 20 ml aqueous solution of **1-4** (1.0 mmol) and **5** (0.5 mmol). The mixture was stirred at 40 °C until all the solid was dissolved, and then diaminoguanidinium sulfate (0.138 g, 0.5 mmol) or triaminoguanidinium sulfate (0.153 g, 0.5 mmol) were added, respectively. After stirring at 40 °C for an additional 1 h, precipitation ($BaSO_4$) was filtered and the filtrate was evaporated under reduced pressure. The residue was dispersed in methanol (20 mL) and filtered. The filtrate was evaporated again to yield crude product.

**Ammonium 4-methyl-5-nitro-1,2,3-triazolate (1a):** Washed with ethyl ether (10 mL×3), and dried to give white solid (0.129 g, 89.6% yield). $^{1}H$ NMR ($d_6$-DMSO): $\delta = 7.20$ (s, $NH_4^+$, 4H), 2.37 ppm (s, $CH_3$, 3H). $^{13}C$ NMR ($d_6$-DMSO): $\delta = 151.29$ (s), 139.45 (s), 12.62 (s) ppm. IR (KBr): $\nu = 3294, 2999, 2798, 1553, 1491, 1401, 1375, 1306, 1211, 1174, 978, 939$ cm$^{-1}$. Anal. Calcd (%) for $C_3N_5H_7O_2$ (145.06): C 24.83, H 4.86, N 48.26. Found: C 24.54, H 4.69, N 48.31.

**Hydrazinium 4-methyl-5-nitro-1,2,3-triazolate (1c):** Washed with ethyl ether (10 mL×3), and dried to give white solid (0.123 g, 76.7% yield). $^{1}H$ NMR ($d_6$-DMSO): $\delta = 7.05$ (s, $N_2H_5^+$, 5H), 2.37 ppm (s, $CH_3$, 3H). $^{13}C$ NMR ($d_6$-DMSO): $\delta = 151.14, 137.84, 11.92$ ppm. IR (KBr): $\nu = 3361, 3301, 2842, 2732, 2606, 2138, 1552, 1474, 1395, 1304, 1215, 1174, 1099, 1079, 977, 929, 839$ cm$^{-1}$. Anal. Calcd (%) for $C_3N_6H_8O_2$ (160.07): C 22.50, H 5.04, N 52.48. Found: C 22.52, H 4.79, N 52.39.

**Guanidinium 4-methyl-5-nitro-1,2,3-triazolate (1d):** Washed with ethyl ether (10 mL×3), and dried to give white solid (0.175 g, 93.6% yield). $^{1}H$ NMR ($d_6$-DMSO): $\delta = 7.03$ (s, $NH_2$, 6H), 2.37 ppm (s, $CH_3$, 3H). $^{13}C$ NMR ($d_6$-DMSO): $\delta = 158.38, 151.32, 139.44, 12.66$ ppm. IR (KBr): $\nu = 3384, 3056, 1653, 1551, 1474, 1392, 1305, 1199, 1170, 978, 939$ cm$^{-1}$. Anal.

Calcd (%) for $C_4N_7H_9O_2$ (187.08): C 25.67, H 4.85, N 52.39. Found: C 25.72, H 4.72, N 52.99.

**Aminoguanidinium 4-methyl-5-nitro-1,2,3-triazolate (1e):** Washed with ethyl ether (10 mL×3), and dried to give white solid (0.193 g, 95.6% yield). $^1$H NMR ($d_6$-DMSO): $\delta$ = 8.70 (s, NH, 1H), 7.33 (s, $CNH_2$, 2H), 6.87 (s, $CNH_2$, 2H), 4.71 (s, $NNH_2$, 2H), 2.37 ppm (s, $CH_3$, 3H). $^{13}$C NMR ($d_6$-DMSO): $\delta$ = 159.27, 151.33, 139.50, 12.72 ppm. IR (KBr): $\nu$ = 3451, 3374, 3168, 2996, 1683, 1551, 1481, 1391, 1307, 1200, 1171, 1070, 979, 835 cm$^{-1}$. Anal. Calcd (%) for $C_4N_8H_{10}O_2$ (202.09): C 23.76, H 4.99, N 55.42. Found: C 23.80, H 4.91, N 56.11.

**Diaminoguanidinium 4-methyl-5-nitro-1,2,3-triazolate (1f):** washed with ethyl ether (10 mL×3) and dried to give white solid (0.211 g, 97.2% yield). $^1$H NMR ($d_6$-DMSO): $\delta$ = 8.61 (s, CNH, 2H), 7.18 (s, $CNH_2$, 2H), 4.60 (s, $NNH_2$, 4H), 2.36 ppm (s, $CH_3$, 3H). $^{13}$C NMR ($d_6$-DMSO): $\delta$ = 160.20, 151.34, 139.49, 12.77 ppm. IR (KBr): $\nu$ = 3377, 3177, 2900, 1694, 1640, 1555, 1471, 1391, 1301, 1209, 1170, 980, 928, 832 cm$^{-1}$. Anal. Calcd (%) for $C_4N_9H_{11}O_2$ (217.10): C 22.12, H 5.10, N 58.04. Found: C 22.40, H 4.94, N 57.22.

**Triaminoguanidinium 4-methyl-5-nitro-1,2,3-triazolate (1g):** washed with ethyl ether (10 mL×3) and dried to give white solid (0.232 g, 99.81% yield). $^1$H NMR ($d_6$-DMSO): $\delta$ = 8.61 (s, CNH, 3H), 4.51 (s, $NNH_2$, 6H), 2.36 ppm (s, $CH_3$, 3H). $^{13}$C NMR ($d_6$-DMSO): $\delta$ = 159.51, 151.34, 139.50, 12.76 ppm. IR (KBr): $\nu$ = 3318, 3210, 1687, 1545, 1480, 1393, 1295, 1169, 1129, 952, 837 cm$^{-1}$. Anal. Calcd (%) for $C_4N_{10}H_{12}O_2$ (232.11): C 20.69, H 5.21, N 60.32. Found: C 21.05, H 5.00, N 60.15.

**Ammonium 4-amino-5-nitro-1,2,3-triazolate (2a):** Crystallized in methanol to give yellow needles (0.129 g, 88.3% yield). $^1$H NMR ($d_6$-DMSO): $\delta$ = 7.19 (s, $NH_4^+$, 4H), 6.24 ppm (s, $NH_2$, 2H). $^{13}$C NMR ($d_6$-DMSO): $\delta$ = 138.37, 148.57 ppm. IR (KBr): $\nu$ = 3486, 3372, 3309, 3161, 2964, 2809, 1651, 1622, 1456, 1416, 1360, 1298, 1248, 1196, 1099, 1046, 974 cm$^{-1}$. Anal. Calcd (%) for $C_2N_6H_6O_2$ (146.11): C 16.44, H 4.14, N 57.52. Found: C 17.02, H 3.62, N 56.71.

**Hydrazinium 4-amino-5-nitro-1,2,3-triazolate (2c):** Crystallized in methanol to give yellow needles (0.102 g, 63.6% yield). $^1$H NMR ($d_6$-DMSO): $\delta$ = 5.88 ppm (s, $NH_2$, $N_2H_5^+$, 7H). $^{13}$C NMR ($d_6$-DMSO): δ = 150.62, 139.40 ppm. IR (KBr): ν = 3476, 3366, 3346, 2967, 2829, 2720, 2609, 1611, 1458, 1419, 1363, 1305, 1248, 1194, 1094, 1039, 943, 760 cm$^{-1}$. Anal. Calcd (%) for $C_2H_7N_7O_2$ (161.07): C 14.91, H 4.38, N 60.85. Found: C 15.09, H 4.06, N 60.77

**Guanidinium 4-amino-5-nitro-1,2,3-triazolate (2d):** Crystallized in methanol to give yellow needles (0.112 g, 59.4% yield). $^1$H NMR ($d_6$-DMSO): δ = 7.07 (s, $NH_2$, 6H), 5.80 ppm (s, $NH_2$, 2H). $^{13}$C NMR ($d_6$-DMSO): δ =158.41, 150.94, 139.54 ppm. IR (KBr): ν = 3469, 3422, 3370, 3310, 3170, 1688, 1643, 1607, 1436, 1363, 1304, 1238, 1192, 1098, 1052, 971 cm$^{-1}$. Anal. Calcd (%) for $C_3H_8N_8O_2$ (188.08): C 19.15, H 4.29, N 59.56. Found C 19.28, H 4.12, N 59.32.

**Aminoguanidinium 4-amino-5-nitro-1,2,3-triazolate (2e):** Crystallized in methanol to give yellow solid (0.174 g, 85.67% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.60 (s, NH, 4H), 7.21 (s, $CNH_2$, H), 7.02 (s, $CNH_2$, 2H), 5.74 (s, $NH_2$, 2H), 4.70 ppm (s, $NNH_2$,2H). $^{13}$C NMR ($d_6$-DMSO): δ = 159.24, 151.02, 139.62 ppm. IR (KBr): ν = 3449, 3333, 3248, 1657, 1475, 1433, 1366, 1296, 1187, 1088, 998 cm$^{-1}$. Anal. Calcd (%) for $C_3N_9H_9O_2$ (203.09): C 17.74, H 4.47, N 62.05. Found C 18.13, H 4.50, N 61.70.

**Diaminoguanidinium 4-amino-5-nitro-1,2,3-triazolate (2f):** Crystallized in methanol to give yellow needles (0.217 g, 99.5% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.69 (s, NH, 2H), 7.23 (s, $CNH_2$, 2H), 5.77 (s, $NH_2$, 2H), 4.61 ppm (s, $NNH_2$, 4H). $^{13}$C NMR ($d_6$-DMSO): δ = 160.23, 150.98, 139.60 ppm. IR (KBr): ν = 3414, 3374, 3293, 3168, 1699, 1666, 1604, 1552, 1440, 1365, 1305, 1237, 1194, 1109, 969, 889 cm$^{-1}$. Anal. Calcd (%) for $C_3N_{10}H_{10}O_2$ (218.10): C 16.52, H 4.62, N 64.20. Found C 16.41, H 4.32, N 63.27.

**Triaminoguanidinium 4-amino-5-nitro-1,2,3-triazolate (2g):** Crystallized in methanol to give yellow solids (0.232 g, 99.80% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.61 (s, NH, 3H), 5.71 (s, $NH_2$, 2H), 4.51 ppm (s, $NH_2$, 6H). $^{13}$C NMR ($d_6$-DMSO): δ = 159.51, 151.05, 139.64. IR (KBr): ν = 3334, 1689, 1558, 1466, 1399, 1366, 1286, 1185, 1134, 1010, 955 cm$^{-1}$. Anal. Calcd (%) for $C_3N_{11}H_{11}O_2$ (233.11): C 15.45, H 4.75, N 66.07. Found C 15.16, H 4.53, N 65.53.

**Ammonium 4,5-dinitro-1,2,3-triazolate (3a):** Compound **3a** was prepared according to the reference method.[24] $^1$H NMR ($d_6$-DMSO): δ = 7.10 ppm (s, $NH_4^+$, 4H). $^{13}$C NMR ($d_6$-DMSO): δ = 145.12 ppm. IR (KBr): ν = 3277, 2984, 2814, 1520, 1471, 1424, 1386, 1363, 1302, 1134, 856, 815, 752 cm$^{-1}$. Anal. Calcd (%) for $C_2N_6H_4O_4$ (176.03): C 13.64, H 2.29, N 47.73. Found C 12.93, H 1.96, N 47.46.

**Hydroxylammonium 4,5-dinitro-1,2,3-triazolate (3b):** Crystallized in ethanol to give yellow needles (0.056 g, 29.1% yield). $^1$H NMR ($d_6$-DMSO): δ = 9.38 ppm (s, $NH_3OH^+$, 4H). $^{13}$C NMR ($d_6$-DMSO): δ = 140.92 ppm; IR (KBr): ν = 3188, 3070, 2682, 1565, 1521, 1504, 1423, 1323, 1295, 1236, 1194, 1018, 979, 895, 821 cm$^{-1}$. Anal. Calcd (%) for $C_2N_6H_4O_5$ (192.09): C 16.44, H 2.76, 47.94. Found C 16.89, H 2.98, N 46.94

**Guanidinium 4,5-dinitro-1,2,3-triazolate (3d):** Crystallized in ethanol to give yellow solid (0.088 g, 40.2% yield). $^1$H NMR ($d_6$-DMSO): δ = 6.98 ppm (s, $CNH_2$, 6H). $^{13}$C NMR ($d_6$-DMSO): δ = 157.81, 140.21 ppm. IR (KBr): ν = 3476, 3416, 3307, 3200, 1670, 1650, 1570, 1532, 1487, 1440, 1351, 1310, 1289, 1170, 1020, 978, 819, 766 cm$^{-1}$. Anal. Calcd (%) for $C_3N_8H_6O_4$ (218.13): C 16.52, H 2.77, N 51.37. Found C 15.62, H 2.96, N 52.32.

**Aminoguanidinium 4,5-dinitro-1,2,3-triazolate (3e):** Crystallized in ethanol to give yellow plates (0.122 g, 52.4% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.58 (s, CNH, 4H), 7.27 (s, $CNH_2$, 2H), 6.75 (s, $CNH_2$, 2H), 4.70 ppm (s, $NNH_2$, 2H). $^{13}$C NMR ($d_6$-DMSO): δ = 158.71, 140.84 ppm. IR (KBr): ν = 3425, 3368, 3232, 3127, 1699, 1662, 1569, 1523, 1504, 1434, 1386, 1362, 1303, 1193, 1132, 976, 920, 857, 812, 752 cm$^{-1}$. Anal. Calcd (%) for $C_3N_9H_7O_4$ (233.15): C 15.45, H 3.03, N 54.07. Found C 15.52, H 2.96, N 53.32.

**Diaminoguanidinium 4,5-dinitro-1,2,3-triazolate (3f):** Crystallized in methanol to give yellow plates (0.240 g, 96.8% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.55 (s, CNH, 2H), 7.15 (s, $CNH_2$, 2H), 4.60 ppm (s, $NNH_2$, 4H). $^{13}$C NMR ($d_6$-DMSO): δ = 159.67, 145.08. IR (KBr): ν = 3443, 3358, 3337, 1688, 1550, 1516, 1495, 1374, 1360, 1302, 1177, 1130, 1080, 977, 862, 820, 754, 659 cm$^{-1}$. Anal. Calcd (%) for $C_3N_{10}H_8O_4$ (248.16): C 14.52, H 3.25, N 56.44. Found C 15.43, H 3.12, N 56.48.

**Triaminoguanidinium 4,5-dinitro-1,2,3-triazolate (3g):** Crystallized in methanol to give yellow solid (0.196 g, 74.5% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.60 (s, NH, 3H), 4.50 ppm (s,

$NH_2$, 6H). $^{13}C$ NMR ($d_6$-DMSO): δ = 158.99, 144.42. IR (KBr): ν = 3374, 3319, 3210, 1685, 1521, 1383, 1297, 1129, 948, 854, 816 $cm^{-1}$. Anal. Calcd (%) for $C_3N_{11}H_9O_4$ (263.17): C 13.69, H 3.45, N 58.54. Found C 13.24, H 3.18, N 57.67.

**Ammonium 4-azido-5-nitro-1,2,3-triazolate (4a):** yellow solid (0.147 g, 85.5% yield). $^1H$ NMR ($d_6$-DMSO): δ = 6.88 ppm (s, $NH_4^+$, 4H). $^{13}C$ NMR ($d_6$-DMSO): δ = 142.47, 139.62 ppm. IR (KBr): ν = 3449, 3227, 2971, 2820, 2345, 2247, 2138, 1676, 1536, 1443, 1399, 1357, 1307, 1189, 1120, 1074, 984, 845 $cm^{-1}$. Anal. Calcd (%) for $C_2H_4N_8O_2$ (172.05): C 13.96, H 2.34, N 65.11. Found C 13.90, H 2.59, N 64.48.

**Hydrazinium 4-azido-5-nitro-1,2,3-triazolate (4c):** yellow solid (0.137 g, 73.0% yield). $^1H$ NMR ($d_6$-DMSO): δ = 7.02 ppm (s, $N_2H_5^+$, 5H). $^{13}C$ NMR ($d_6$-DMSO): δ = 139.62, 141.83 ppm. IR (KBr): ν = 3329, 2974, 2754, 2142, 1543, 1471, 1419, 1359, 1322, 1213, 1156, 1103, 1098, 962. Anal. Calcd (%) for $C_2H_5N_9O_2$ (187.06), C 12.84, H 2.69, N 67.37. Found C 12.70, H 2.89, N, 66.23.

**Guanidinium 4-azido-5-nitro-1,2,3-triazolate (4d):** Crystallized in methanol to give yellow plates (0.125 g, 58.4% yield). $^1H$ NMR ($d_6$-DMSO): δ = 6.95 ppm (s, $CNH_2$, 6H). $^{13}C$ NMR ($d_6$-DMSO): δ =158.37, 142.17, 139.70 ppm. IR (KBr): ν = 3460, 3373, 3193, 2817, 2142, 1670, 1540, 1465, 1418, 1368, 1313, 1236, 1197, 1067, 974. Anal. Calcd (%) for $C_3H_6N_{10}O_2$ (214.07): C 16.83, H 2.82, N 65.41. Found C 16.83, H 3.11, N 65.44.

**Aminoguanidinium 4-azido-5-nitro-1,2,3-triazolate (4e):** Crystallized in methanol to give yellow solid (0.176 g, 76.7% yield). $^1H$ NMR ($d_6$-DMSO): δ = 8.41 (s, CNH, 4H), 6.74 (s, NH, H), 4.18 ppm (d, $NH_2$, 2H). $^{13}C$ NMR ($d_6$-DMSO): δ = 158.49, 141.80, 139.55 ppm. IR (KBr): ν = 3425, 3359, 3169, 3006, 2898, 2149, 1685, 1541, 1479, 1417, 1363, 1315, 1232, 1199, 983, 846, 762, 575 $cm^{-1}$. Anal. Calcd (%) for $C_3N_{11}H_7O_2$ (229.08): C 15.72, H 3.08, N 67.23. found C 15.74, H 2.81, N 65.97.

**Diaminoguanidinium 4-azido-5-nitro-1,2,3-triazolate (4f):** Crystallized in methanol to give yellow solid (0.238 g, 97.5% yield). $^1H$ NMR ($d_6$-DMSO): δ = 8.40 (s, CNH, 2H), 7.16 (s, $CNH_2$, 2H), 4.60 ppm (s, $NNH_2$, 4H). $^{13}C$ NMR ($d_6$-DMSO): δ = 160.22, 142.16, 139.64 ppm. IR (KBr): ν = 3414, 3336, 3281, 3168, 2123, 1686, 1540, 1476, 1402, 1362, 1313, 1232, 1188, 1035, 981 cm$^{-1}$. Anal. Calcd (%) for $C_3N_{12}H_8O_2$ (244.09): C 14.76, H 3.30, N 68.84. Found C 14.73, H 3.11, N 67.34.

**Triaminoguanidinium 4-azido-5-nitro-1,2,3-triazolate (4g):** Crystallized in methanol to give yellow solid (0.257 g, 99.1% yield). $^1$H NMR (*d*$_6$-DMSO): δ = 8.54 (s, NH, 3H), 4.46 ppm (s, $NH_2$, 6H). $^{13}$C NMR (*d*$_6$-DMSO): δ = 159.38, 141.83, 138.14 ppm. IR (KBr): ν = 3319, 3211, 2138, 1685, 1539, 1467, 1414, 1364, 1314, 1226, 1186, 1128, 951 cm$^{-1}$. Anal. Calcd (%) for $C_3N_{13}H_9O_2$ (259.10): C 13.90, H 3.50, N 70.25. Found C 13.60, H 3.14, N 69.14.

**Ammonium 4-nitramino-5-nitro-1,2,3-1H-triazolate (5a):** Crystallized in methanol to give yellow needles (0.118 g, 61.8% yield). $^1$H NMR (*d*$_6$-DMSO): δ =14.85(s, NH, 1H), 7.29 ppm (s, $NH_4^+$, 4H). $^{13}$C NMR (*d*$_6$-DMSO): δ =141.38, 140.06 ppm. IR (KBr): ν = 3224, 3034, 1565, 1440, 1387, 1350, 1286, 1193, 982, 817,771 cm$^{-1}$. Anal. Calcd (%) for $C_2N_7H_5O_4$ (191.04): C 12.57, H 2.64, N 51.31. Found: C, 12.63, H 2.87, N 51.52.

**Di(hydroxylammonium) 4-nitramino-5-nitro-1,2,3-triazolate (5b):** Crystallized in methanol to give yellow needles (0.210 g, 87.6% yield). $^1$H NMR (*d*$_6$-DMSO): δ = 8.64 ppm (s, $NH_3OH^+$, 8H). $^{13}$C NMR (*d*$_6$-DMSO): δ =141.44, 140.09 ppm. IR (KBr): ν = 3069, 2679, 1566, 1519, 1434, 1384, 1324, 1294, 1194, 1017, 984, 820, 766 cm$^{-1}$. Anal. Calcd (%) for $C_2N_8H_8O_6$ (240.06): C 10.00, H 3.36, N 46.66. Found: C 9.67, H 3.60, N 45.27.

**Di(hydrazinium) 4-nitramino-5-nitro-1,2,3-triazolate (5c):** Crystallized in methanol to yellow solid (0.224 g, 94.1% yield). $^1$H NMR (*d*$_6$-DMSO): δ = 5.05 ppm (s, $N_2H_5^+$, 10H). $^{13}$C NMR (*d*$_6$-DMSO): δ = 144.19, 142.11 ppm. IR (KBr): ν = 3439, 3353, 2719, 2131, 1577, 1519, 1419, 1338, 1291, 1207, 1186, 1102, 1021, 971, 817 cm$^{-1}$. Anal. Calcd (%) for $C_2N_{10}H_{10}O_4$(238.09): C 10.09, H 4.23, N 58.81. Found C 9.96, H 4.27, N 58.36.

**Guanidinium 4-nitramino-5-nitro-1,2,3-1H-triazolate (5d):** Crystallized in methanol to give yellow solid (0.197 g, 84.7% yield). $^1$H NMR (*d*$_6$-DMSO): δ = 15.19 (s, NH, 1H), 6.91 ppm (s, $CNH_2$, 6H). $^{13}$C NMR (*d*$_6$-DMSO): δ = 158.31, 141.40, 140.03 ppm. IR (KBr): ν = 3480, 3420, 3305, 1672, 1649, 1572, 1553, 1486, 1438, 1350, 1315, 1288, 1197, 1169, 977, 819, 765, 596 cm$^{-1}$. Anal. Calcd (%) for $C_3H_7N_9O_4$ (233.06): C 15.45, H 3.03, N 54.07. Found C 15.62, H 2.94, N 53.94.

**Di(aminoguanidinium) 4-nitramino-5-nitro-1,2,3-triazolate (5e):** Crystallized in methanol to give yellow plates (0.207 g, 64.3% yield). $^1$H NMR ($d_6$-DMSO): δ =8.77 (s, CNH, 4H), 7.28 (s, $CNH_2$, 8H), 4.69 ppm (s, $NNH_2$, 4H). $^{13}$C NMR (d6-DMSO): δ =159.41, 147.51, 144.88 ppm. IR (KBr): ν = 3474, 3411, 3337, 1701, 1667, 1525, 1471, 1402, 1320, 1196, 1180, 1017, 946, 819 cm$^{-1}$. Anal. Calcd (%) for $C_4H_{14}N_{14}O_4$ (322.13): C 14.91, H 4.38 N 60.85. Found C 14.85, H 4.30, N 61.24.

**Di(diaminoguanidinium) 4-nitramino-5-nitro-1,2,3-triazolate (5f):** Crystallized in methanol to give yellow solid (0.349 g, 99.1% yield). $^1$H NMR ($d_6$-DMSO): δ = 8.92 (s, CNH, 2H), 7.31 (s, $NH_2$, 2H); 4.59 ppm (s, $NNH_2$, 4H). $^{13}$C NMR ($d_6$-DMSO): δ = 159.81, 145.40, 142.99 ppm. IR (KBr): ν = 3452, 3331, 3289, 1684, 1636, 1576, 1529, 1468, 1385, 1301, 1172, 1063, 1014, 979, 960, 923 cm$^{-1}$. Anal. Calcd (%) for $C_4N_{16}H_{16}O_4$ (352.27): C 13.64, H 4.58, N 63.62. Found C 14.26, H 4.26, N 62.69.

**Triaminoguanidinium 4-nitramino-5-nitro-1,2,3-1H-triazolate (5g):** Crystallized in methanol to give yellow solid (0.257 g, 92.3% yield). $^1$H NMR ($d_6$-DMSO): δ = 15.03 (s, NH, 1H), 8.59 (s, CNH, 2H), 4.50 ppm (s, $NNH_2$, 6H). $^{13}$C NMR ($d_6$-DMSO): δ = 159.49, 141.43, 140.06 ppm. IR (KBr): ν = 3320, 3219, 1685, 1569, 1491, 1433, 1406, 1349, 1318, 1289, 1209, 1173, 1131, 981, 814 cm$^{-1}$. Anal. Calcd (%) for $C_3H_{10}N_{12}O_4$ (278.09): C 12.45, H 3.62, N 60.42. Found C 11.89, H 3.95, N 60.21.

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