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Nitrogen-rich Salts of 1-Aminotetrazol-5-one：Oxygen-ContainingInsensitive Energetic Materials with High Thermal Stability

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Abstract: 1-aminotetrazol-5-one (ATO) is a new insensitive nitrogen-rich energetic compound with quite attractive detonation properties (D=8.88 km/s, P=35.0 GPa), but its formation always requires harsh conditions to facilitate the process. In this contribution we presented an improved synthesis route of ATO in excellent yields and high purity. A large variety of nitrogen-rich salts of ATO were synthesized by means of Brønsted acid-base or metathesis reactions, and confirmed by single-crystal X-ray diffraction for the first time. These compounds were fully characterized by FT-IR and multinuclear NMR spectroscopy, elemental analysis (EA) and differential scanning calorimetry (DSC). All the salts except **7a** decompose at the temperatures over220^{o}C; in particular, the aminoguanidinium salt and 3,4-diamino-1,2,4-triazolium salt are fairly stable with the decomposition temperature of 259^{o}C and 261.5^{o}C, respectively. Based on heats of formation calculated with Gaussian 09 and combined with experimentally determined densities, detonation properties of the energetic salts were obtained. They exhibit good thermal stability, excellent impact sensitivities (>40 J), reasonable detonation pressures (23.6~31.0 GPa) and velocities (7.53~8.72 km/s) and might be as potentially insensitive energetic materials.

Introduction

Energetic materials include explosives, propellants, and pyrotechnics that are used for variousmilitary and civilian applications[1-3]. Explosives with improved high-temperature properties are usually termed as ‘‘heat-resistant’’ or ‘‘thermally stable’’, which can be applied in specific fields, such as drilling oil-wells, space exploration, safer explosive production and so forth[4,5].Recently, lots of money and studies have been invested for synthesizing environmentally friendly explosives in order to meet the aim of producing materials which are safer, more reliable, and stable at high temperatures[6, 7]. Analysis of the structures of these well-known thermally stable explosives clearly suggests that the introduction of heterocyclic rings is a general approach to improve the thermal stability[8-10].Thermal stability can also been hanced by the salt formation. Indeed, salt-based energetic materials often possess advantages over nonionic molecules, such as

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lower vapor pressure, better thermal stability[11-14].

As we all known, the introduction of oxygen-containing groups in energetic compounds can improve the oxygen balance and the density which can improve the detonation performance[15, 16]. Many nitrogen rich compounds exhibit excellent detonation performances combined with some energetic substituents such as nitro ($-NO_2$)[17-19], nitrate ester group ($-ONO_2$)[20, 21], nitramine ($-NHNO_2$)[22, 23], azido($-N_3$) utilized as propellants, pyrotechnics or explosives. However, most of them are sensitive responding to the impact, friction and electrostatic discharge. In order to balance the contradiction of insensitivity and high energy, it is necessary to synthesis insensitive nitrogen rich energetic compounds.

As we can see in Figure 1, the introduction of oxygen atom in tetrazole greatly improves the density. In theory, the amino groups are helpful at improving the thermal stability, and both amino groups and oxygen in the molecule can increase hydrogen bonds that help to stabilize the material substantially. 1-aminotetrazol-5-one (ATO) is an insensitive nitrogen-rich energetic compound with high thermal stability (decompose temperature over 240°C) and quite attractive detonation properties (D=8.88 km/s, P=35.0 GPa). Confalone and Robert first reported ATO in 1983[24], however, it was difficult to repeat them in accordance with the literature conditions.

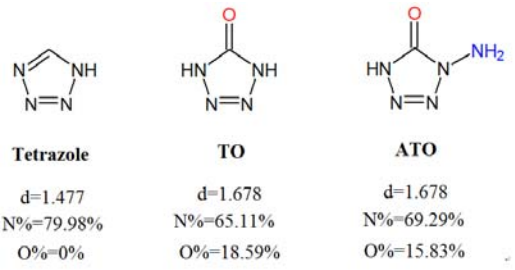


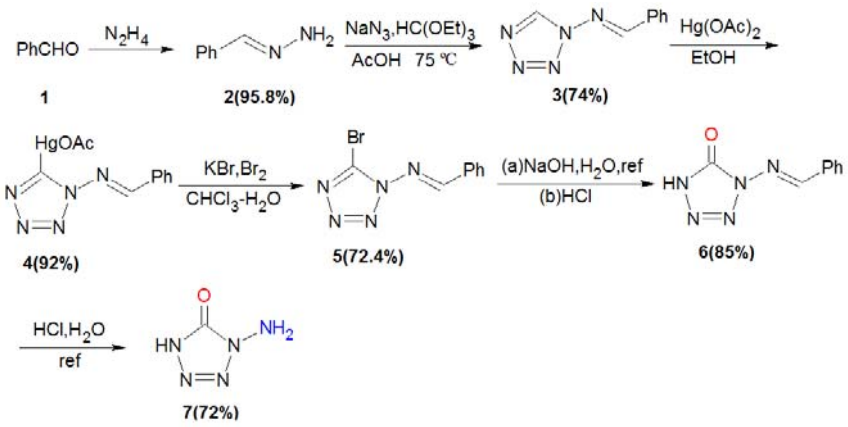
Figure 1.Structures and properties of tetrazole, tetrazol-5-one (TO) and 1- amino-tetrazol-5-one(ATO)

Here, our efforts are in improving a synthesis route of ATO in excellent yields and high purity compared to the traditional ones. A series of nitrogen-rich energetic salts of ATO have been synthesized as well. All of their molecular structures were characterized by X-ray single crystal diffraction.Their detailed structure characters were investigated by Fourier transform infrared spectrometer (FT-IR), nuclear magnetic resonance (NMR), mass spectroscopy (MS) and elemental analysis (EA) technologies. Their decomposition temperatures were obtained by differential scanning calorimetry (DSC). The theoretical explosive properties indicated that they are promising insensitive nitrogen rich energetic compounds.

Results and Discussion

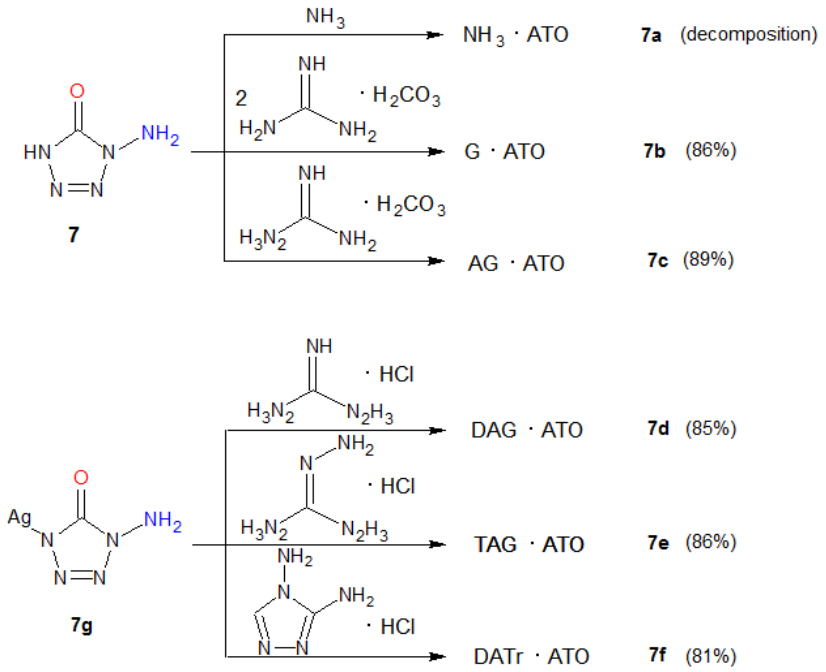
Synthesis. In the existing method, 1-(benza1amino)tetrazole was converted to its mercury derivative which further reacted with chlorine radical to form 5-chloro-1-(benza1amino)tetrazol. Then 5-chloro-1-(benza1amino)tetrazol was hydrolyzed to the protected tetrazolone. Finally the

Schiff basewas hydrolyzed to yield the desired 1-aminotetrazol-5-one. There are some disadvantages of the existing method:① Chlorine was bubbled into a mixture of mercury derivative and acetone, but this would emit irritating and poisonous cholroacetone. ②The authors used ethanol-water as solvent in the hydrolysis of 5-chloro-1-(benza1amino)tetrazol, however, chlorotetrazole could react with ethanol, and the product was contaminated by the by-product. This made it difficult to collect and purifythe product. ③ ATO was obtained purely by extracting the residue with warm 95% ethanol, but we found that ATO was insoluble in ethanol. So it was difficult to repeat them in accordance with the literature conditions. Here, we provided a modified method. The synthesis route is described in **Scheme 1**. We used benzaldehyde as the starting reagent via six steps, thereinto, step1 is a procedure according to the literature[25]. The synthesis of compound **3** was reported in the literature[26]. Then compound **3** wasmercurized with mercuric acetate in ethanol. Compound **4** was bromized by using KBr-Br_2[27, 28]. Compound **5** was hydrolyzed in sodium hydroxide solution at reflux temperature, then cooling the solution and tuned the pH to 1~2, the product was extracted by ethyl acetate. Finally, compound **6** was hydrolyzed in acidic medium at reflux temperature, and benzaldehyde was removed by steam distillation. The clear solution was evaporated under reduced pressure and the product was obtained purely by washing with cold ethanol.



Scheme 1. A modified synthesis route of 1- aminotetrazol-5-one

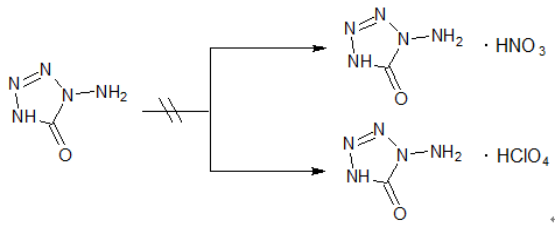
Compounds **7a~7c** were prepared via the treatment of ATO with carbonate and hydroxide. Compounds **7d~7f** were obtained by the reaction of silver salt of ATO and hydrochlorate(**Scheme 2**). All reactions were performed in aqueous solution. The overall yield is 81%~89%.



Scheme 2. Synthesis of 1- aminotetrazol-5-one salts

The ammonium salt of ATO **(7a)** can only be stable in aqueous solution since all the attempts to remove solvent will cause its decomposition. Fortunately, the single crystal of **7a** was obtained temporarily, because there will be a decomposition of the solid **7a** after 2 days at room temperature.

Unfortunately, it seems impossible to synthesis nitrate or perchlorate of ATO because of its weak acidic property (**Scheme 3**).



Scheme 3.

Spectroscopy. The structures of ATO and its salts were supported by IR, MS, NMR analysis as well as elemental analysis. In the IR spectra, strong absorption bands at 1720~1640 cm^{-1} are attributed to the carbonyl group, and 3500~3300 cm^{-1} are attributed to the amino group. In the mass spectrometry, negative data is 99.95($CH_2N_5O^-$ anion). In the ^{13}C NMR spectra, resonance bands for carbonyl group appear between 150 and 165 ppm.

The ^{15}N NMR spectra of compounds **7**, **7a~7f** are given in **Figure 2**. Compounds **7**, **7b~7f**

were measured in DMSO-d_6 and compound **7a** was dissolved in D_2O. The chemical shifts are given with respect to CH_3NO_2 as an internal standard. The assignments are based on the literature values of similar compounds[2, 6, 29-31].

On the basis of the values of the chemical shifts of guanidine and ammonium moieties, NH(-312.39~-283.85ppm), NH_2(-329.71~-305 ppm), and NH_4^+(-371.11 ppm) groups can be assigned to the resonances at highest field. ATO shows 5 signals at δ= -23.00 ppm(N3), -44.85 ppm(N4), -168.12 ppm(N5), -182.30 ppm(N2), -317.31 ppm(N1). The N1 nitrogen atom of the $CH_2N_5O^-$ anion is observed at a chemical shift between -319 and -317 ppm for compounds **7a~7f**. The nitrogen atoms N2 and N5 are shifted to lower field upon deprotonation in compounds **7a**, **7b** and **7d**. The atoms N2, N3, N4 and N5 signals of compounds **7e** and **7f** could be observed in the same range compared with the primary ATO structure. The signal of N6 in the spectrum of compound **7c** could not be observed due to a fast proton exchange. Similar to the compound **7f**, the signals of N9 and N10 are not visible.

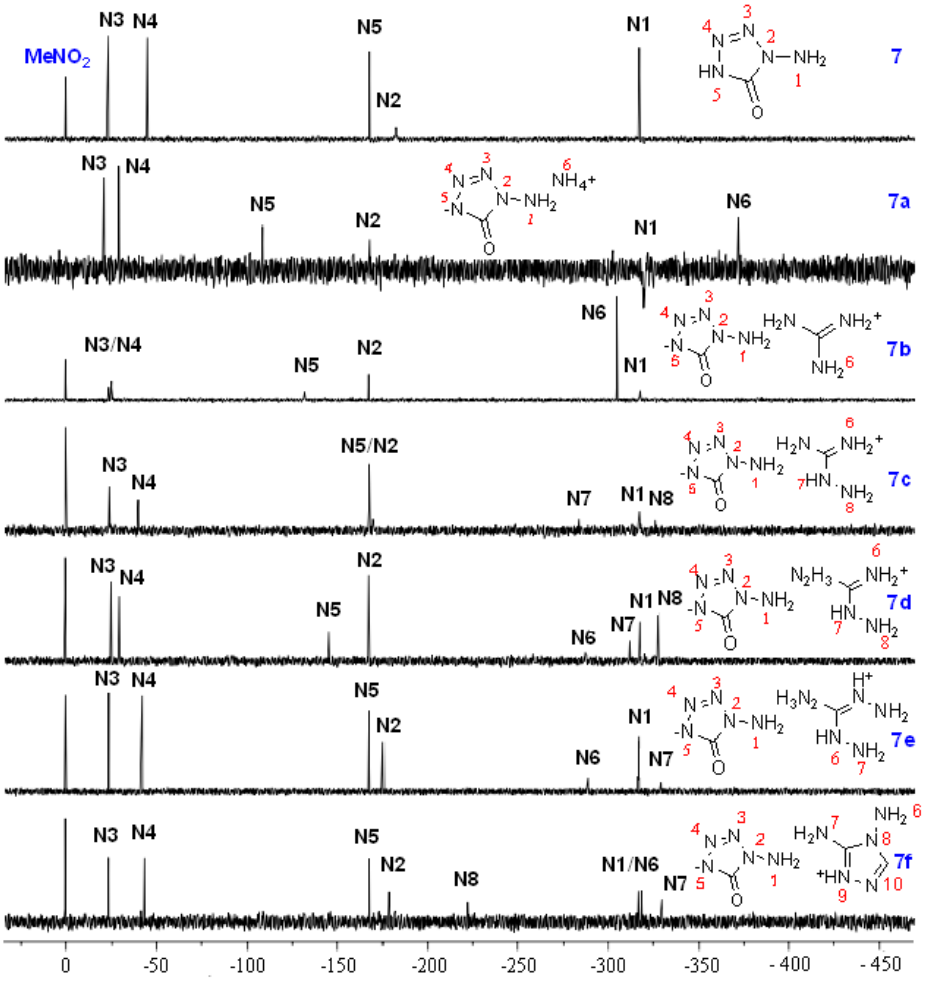


Figure 2.[15]N NMR spectra of 1- amino-tetrazol-5-one and its salt.

Single Crystal X-ray Structure Analysis. Compounds **7**, **7a~7f** have been fully

characterized by X-ray single crystal diffraction technology. In **Table S1**, we summarized the selected crystallographic results and refinement details. The structure of ATO has been mentioned in the literature[24], however, there were no details presented.

ATO **(7)** adopts the orthorhombic symmetry in space group *Pbca* with a calculated crystal density of 1.796 g/cm^3. Theketo tautomer is a notable feature of these crystals tructures, as seen from the relevant bond lengths for the tetrazole rings: the C5-O1 bond lengths in **7** are almost identical at about 1.22Å, which corresponds to C=O bond lengths commonly found for carbonyl groups. The N–N bond lengths in the tetrazolate ring of **7**vary from 1.272(2)–1.347(2) Å, which are between N–N single bonds (1.454Å) and N=N double bonds (1.245 Å). These findings support the presence of a delocalized π-system in the five-membered ring of compound **7**.In all of the investigated structures, the tetrazole rings are (almost) planar, including the C-oxide oxygen atom and the N5 nitrogen atom, andH5B is twisted out of the plane by 13.1^o.

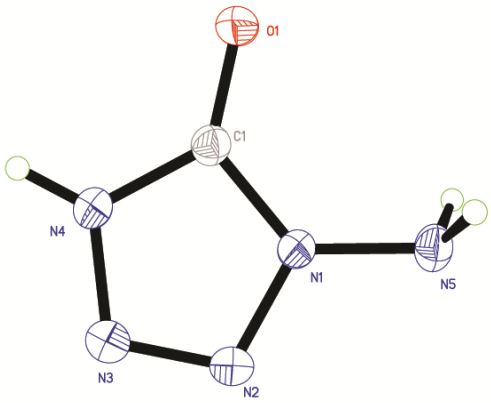


Figure 3. View of the molecular unit of 1-aminotetrazol-5-one (**7**) with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of **7**: bond lengths [Å]N(1)-N(2) 1.347(2), N(1)-C(1) 1.357(2), N(1)-N(5) 1.3818(19), N(2)-N(3) 1.272(2), N(3)-N(4) 1.347(2), N(4)-C(1) 1.345(2), N(4)-H(4) 0.8600, N(5)-H(5B) 0.8900, N(5)-H(5C) 0.8900, O(1)-C(1) 1.224(2);angles[deg]N(2)-N(1)-C(1) 111.23(14), N(2)-N(1)-N(5) 119.65(14), C(1)-N(1)-N(5) 129.00(15), N(3)-N(2)-N(1) 107.70(15), N(2)-N(3)-N(4) 107.84(15), C(1)-N(4)-N(3)111.56(16),C(1)-N(4)-H(4) 124.2, N(3)-N(4)-H(4)124.2,N(1)-N(5)-H(5B)109.2, N(1)-N(5)-H(5C) 109.2, H(5B)-N(5)-H(5C) 109.5, O(1)-C(1)-N(4) 130.49(17), O(1)-C(1)-N(1) 127.88(17), N(4)-C(1)-N(1) 101.63(15).

7a adopts the monoclinic space group *P2(1)/c* with two ions in the unit cell (V = 476.24 Å^3). As show in **Figure 4**, the asymmetric unit contains one crystallographically independent ATO anion, and one ammonium cation, in which the proton transfer from the tetrazole of ATO to ammonia was confirmed. The density is 1.647 g/cm^3. The deprotonation of compound **7** does not yield significant changes in the bond lengths of the anion. The N–N bond lengths in the tetrazolate ring of **7a** vary from 1.288(4)–1.345(4) Å, which are similar to those in **7**. The largest changes can be observed in the C-oxide bondlength, which shortens by about 0.03 and 0.04 Å compared with compound **7**.

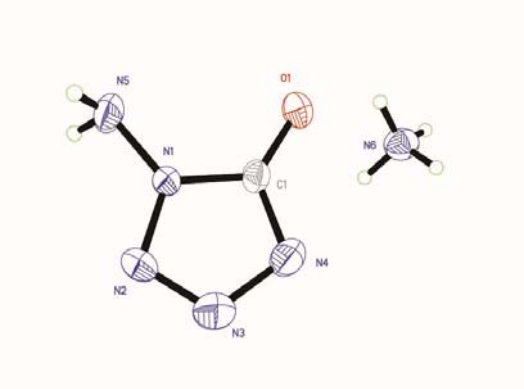


Figure 4. View of the molecular unit of ammonium 1-aminotetrazol-5-oneate (**7a**) with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of 7a: bond lengths [Å] N(6)-H(6A) 0.9000, N(1)-N(2) 1.345(4), N(1)-C(1) 1.349(4), N(2)-N(3) 1.288(4), N(1)-N(5) 1.396(4), N(3)-N(4) 1.359(4), N(4)-C(1) 1.335(4); angles [deg]H(6A)-N(6)-H(6D) 109.9, H(6A)-N(6)-H(6B) 108.1.

Crystals of guanidinium 1-aminotetrazol-5-oneate **(7b)**were obtained from water. Compound **7b** crystallizes in the monoclinic space group *C2/c* with eight cation/anion pairs in the unit cell. Its calculated density is 1.569 g/cm^3(**Figure5**). It should be noticed that there are a large number hydrogen bonds between N5-H5 and N8-H8 with the distances ranging from 2.884 Å to 3.423 Å.

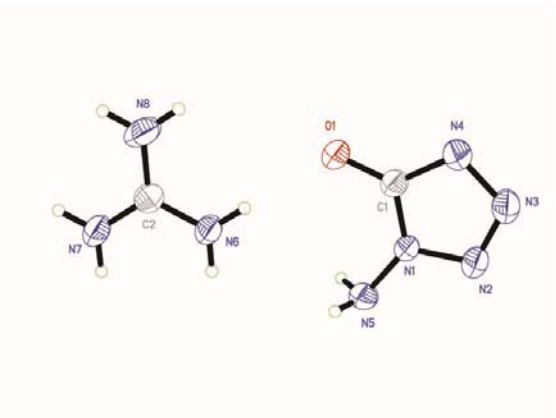


Figure 5.View of the molecular unit of guanidinium 1-aminotetrazol-5-oneate (**7b**) with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of 7b: bond lengths [Å] N(6)-C(2) 1.317(2), N(7)-C(2)1.316(3), N(8)-C(2) 1.318(3), angles [deg] N(7)-C(2)-N(6) 119.97(19),N(7)-C(2)-N(8) 120.15(19), N(6)-C(2)-N(8) 119.9(2).

Aminoguanidinium 1-aminotetrazol-5-oneate **(7c)** depicted in **Figure 6** crystallizes in the monoclinic space group *P2(1)/n* with two ions in the unit cell. The density is 1.597 g/cm^3 and the cell volume is 728.49 Å^3. Again, the largest changes can be observed in C(2)-O(1) bond length(1.262Å), which is 0.04 Å longer than the standard C=O double bond caused by the tetrazolone- hydroxytetrazole tautomerism.

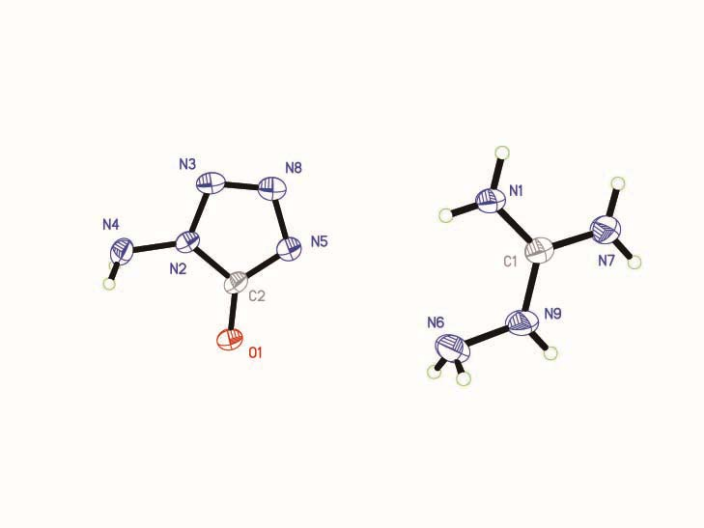


Figure6. View of the molecular unit of aminoguanidinium 1-aminotetrazol-5-oneate **(7c)** with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of 7c: bond lengths [Å] C(1)-N(1) 1.3169(13), C(1)-N(9) 1.3266(14), C(1)-N(7), 1.3317(14), N(6)-N(9) 1.4046(15); angles [deg] N(1)-C(1)-N(9) 120.54(10), N(1)-C(1)-N(7) 121.67(10), N(9)-C(1)-N(7) 117.79(10), C(1)-N(9)-N(6) 119.22(10).

Single crystals of diaminoguanidinium 1-aminotetrazol-5-oneate **(7d)**were obtained from water-ethanol. Compound **7d** crystallizes in the monoclinic space group *P2(1)/n* with a cell volume of 823.79 $Å^3$ and a density of 1.534 g/cm^3. The molecular is shown in **Figure 7**. Compound **7d** contains a network of hydrogen bonds with D···A distances ranging from 2.875 Å to3.485 Å.The torsion angle of N(7)-N(8)-C(2)-N(6) is 0.1˚(4), indicating the diaminoguanidiniumcation is nearly planar, because of the sp^2 hybridization of atom C(2).

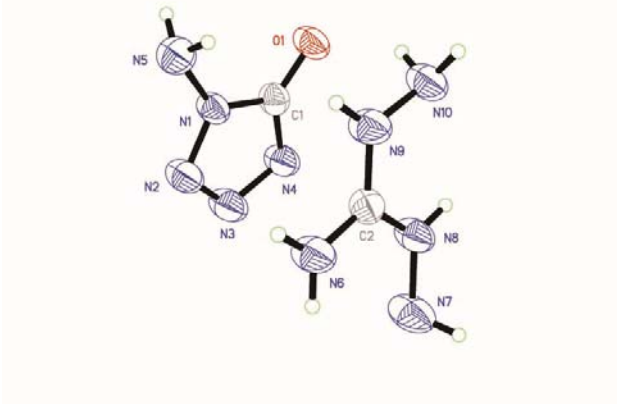


Figure7. View of the molecular unit of diaminoguanidinium 1-aminotetrazol-5-oneate (**7d**) with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of 7d: bond lengths [Å] N(6)-C(2)1.324(3), N(8)-C(2) 1.319(3), N(9)-C(2) 1.330(3), N(7)-N(8) 1.408(3), N(9)-N(10) 1.412(2);angles [deg] C(2)-N(8)-N(7) 119.8(2), C(2)-N(9)-N(10) 118.87(19), N(8)-C(2)-N(6) 120.8(2), N(8)-C(2)-N(9) 119.0(2), N(6)-C(2)-N(9) 120.2(2).

Triaminoguanidinium 1-aminotetrazol-5-oneate **(7e)** crystallizes in the orthorhombic space

group *Pbca*. The density is only 1.569 g/cm^3. The bond lengths of compound **7e** are very similar to Compound **7d**. Crystals of triaminoguanidinium 1-aminotetrazol-5-oneate were also obtained from water- ethanol. The molecular is shown in **Figure 8**.

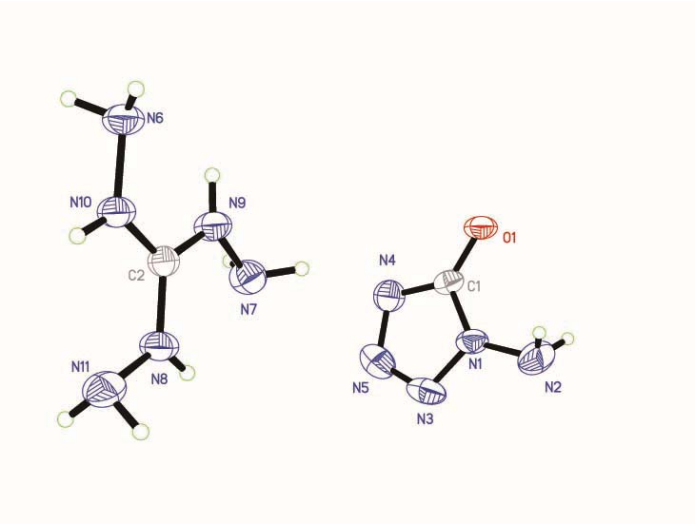


Figure8. View of the molecular unit of triaminoguanidinium 1-aminotetrazol-5-oneate (**7e**) with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of 7e: bond lengths [Å] C(2)-N(9) 1.3233(16), C(2)-N(10)1.3246(15), C(2)-N(8) 1.3270(16), N(6)-N(10)1.4124(15),N(7)-N(9) 1.4119(16), N(8)-N(11) 1.4045(16); angles [deg] N(9)-C(2)-N(10) 120.29(11), N(9)-C(2)-N(8) 119.48(11), N(10)-C(2)-N(8) 120.22(11), C(2)-N(8)-N(11) 118.83(11), C(2)-N(9)-N(7) 117.65(11), C(2)-N(10)-N(6) 117.56(11).

Crystals of 3,4-diamino-1,2,4-triazolium 1-aminotetrazol-5-oneate **(7f)** were obtained from water. The asymmetric unit consists of a tetrazole ring and a triazole ring. The structure is shown in **Figure 9**. Compound **7f** crystallizes in the triclinic space group *P-1* with a cell volume of 407.32Å^3 and a density of 1.632 g/cm^3. In contrast to guanidinium and (di-, tri) aminoguanidinium salts, compound **7f**has relative higher density.

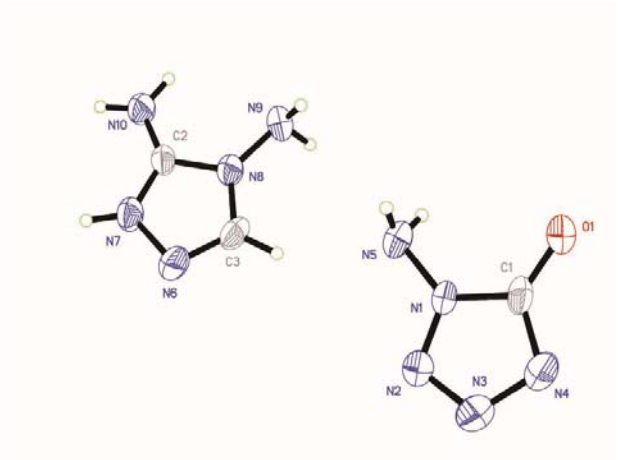


Figure 9. View of the molecular unit of 3,4-diamino-1,2,4-triazolium 1-aminotetrazol-5-oneate (**7f**) with thermal ellipsoids at the 50% probability level. Selected bond distances and angles in the anion of 7f: bond lengths [Å] N(6)-C(3) 1.279(5), N(6)-N(7) 1.393(4), N(7)-C(2) 1.311(5), N(8)-C(2) 1.363(5), N(8)-C(3) 1.370(5), N(8)-N(9) 1.398(4), N(10)-C(2) 1.296(5);angles [deg] N(10)-C(2)-N(7) 130.3(3), N(10)-C(2)-N(8) 124.9(3), N(7)-C(2)-N(8)

104.8(3), N(6)-C(3)-N(8) 112.1(4), C(3)-N(6)-N(7) 103.4(3),C(2)-N(7)-N(6) 112.8(3), C(2)-N(7)-H(7) 123.6, N(6)-N(7)-H(7) 123.6, C(2)-N(8)-C(3) 107.0(3), C(2)-N(8)-N(9) 121.9(3), C(3)-N(8)-N(9) 131.1(3).

The hydrogen bonds lengths and angles of compounds**7, 7a~7f** are summarized in supporting information (**Table S2~Table S8**). In the crystal structures, there are many types of hydrogen bonds. The first oneoccurs between the intramolecularnitrogenatom and aminogroup of ATO (N5-H5B···N2, compound **7).** The second one occurs betweentheintramolecular aminogroup and the oxygen atom ofcarbonyl moiety (N5-H5A···O1, compound **7b**). The third one occurs between theintermolecularaminogroup ofthe cation and the oxygen atom ofcarbonyl moiety (N1-H1A···O1, compound **7c**). The fourth one occurs between theimino group of the cation and the nitrogen atom of ATO ring (N9-H9···N4, compound **7d**). It can be seen from the packing diagram (**Figure S27~Figure S33**) that all of these hydrogen bonds are extendingthe structure into a bedded structure andmake an important contribution to enhance the thermal stabilityof the salts.

Thermal behavior. The decompositions and thermal stabilities of compounds **7, 7b~7f** were determined by DSC-TG measurements scanning at 10 ºC·min^{-1}. The results are showed in **Figure 10~15** and **Figure S34**. Compound **7** starts to melt from solid statement at 168.5 ºC with the peak temperature of 221.0 ºC, which is end at 224.7 ºC. As for **7b** and **7d**, the phase transition processes are at 184.5 ºC and 125.5 ºC. ATO shows a high melt point of 221 ºC compared with **7d**. At the meantime, its decomposition temperature is 220.7 ºC higher than **7e** (214.5ºC), which is due to the acidity of the hydrogen atom located at the 4-position and carbonyl group in the 5-position. Compounds **7c~7f** show lower melt point (**7c**: 197.5 ºC, **7d**: 153.0 ºC, **7e**: 154.5 ºC, **7f**: 170.0 ºC.) than **7**. The decomposition temperatures of all the ATO salts are above 220 ºC(except **7e**), which is a necessary requirement for potential RDX requirements (decompose at about 230 ºC). The decomposition temperatures increase depending on the cation except the compound **7e** (because triaminoguanidinium is an unstable molecule). In this case, compounds **7b~7f** decompose at 224.8 ºC, 220.6 ºC, 220.7 ºC, 214.5 ºC and 220.5 ºC. Compound **7f** has good thermal stability, due to its aromatic ring system in the cation. For a series of guanidinium salts, the increasing of amino groups tends to decrease the thermal stability.

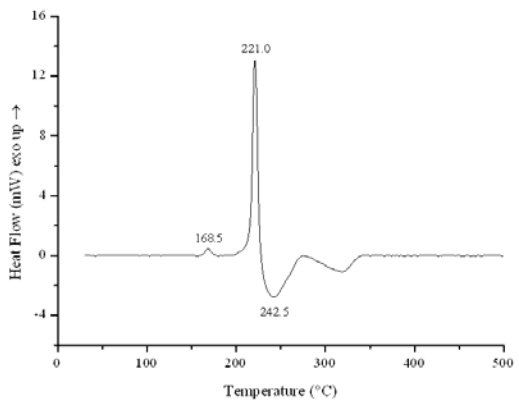


Figure 10.DSC of ATO **(7)**

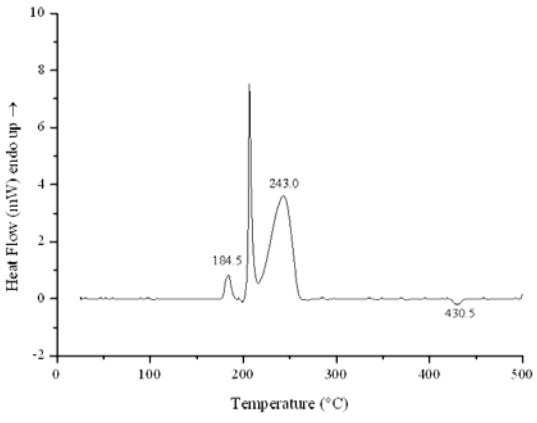


Figure 11.DSC of ATO·G **(7b)**

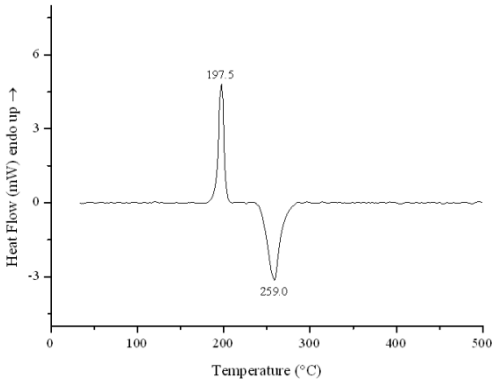


Figure 12. DSC of ATO·AG **(7c)**

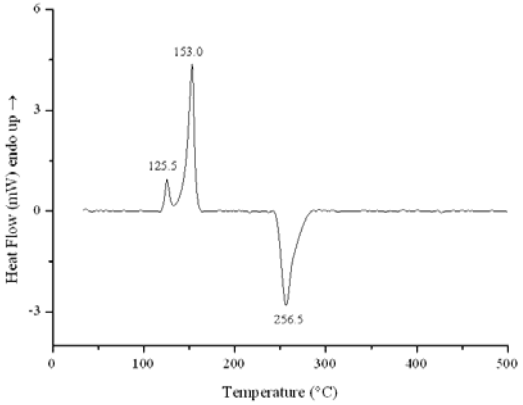


Figure 13. DSC of ATO·DAG **(7d)**

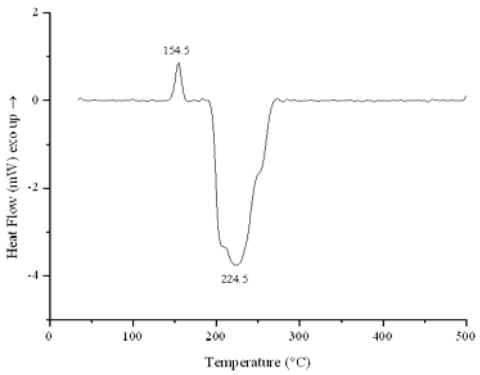


Figure 14.DSC of ATO·TAG **(7e)**

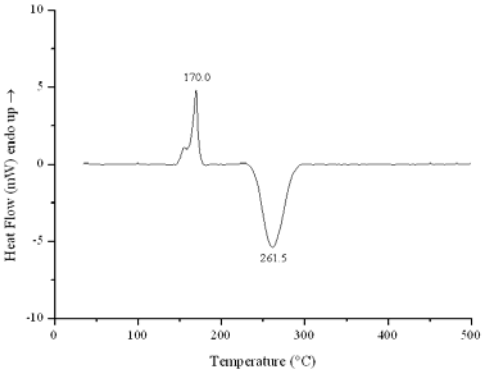


Figure 15.DSC of ATO·DATr **(7f)**

Theoretical Calculation. In order to predicate the explosive performance of the series compounds, the heats of formation (HOF) and the detonation properties were evaluated in detail. For the six derivative salts, the enthalpies have been calculated through three parts including the HOFs of cations and anions, as well as the Madelung energies in the system (ΔH_L as formula 1 showed)[33].All the structures including molecules and ions were optimized firstly. Then the corresponding thermo dynamic properties were obtained as well. All the calculations have been accomplished using gradient-corrected density functional theory (BP86/6-311++G(3d, 2p))[34]with Gaussian 09 programs[35]. The HOFs of organic cations and anions are computed by using the method of isodesmic reactions[36].

$$\Delta H_f^o(ionicsalts, 298K) = \sum \Delta H_f^o(cationsalts, 298K) + \sum \Delta H_f^o(anionsalts, 298K) - \Delta H_L \quad (1)$$

The ΔH_L is the lattice energy of the ionic salts: $\Delta H_L = U_{pot} + [p(\mathrm{nM}/2-2) + \mathrm{q}(nX/2-2)]RT$. nM and nX depend on the nature of the ions Mp^+ and Xq^-, respectively, which are equal to 6 in our systems. The lattice potential energy equals to U_{POT}/kJ mol=$\gamma(\rho_m/M_m)^{1/3} + \delta$, where ρ_m is the real density (g/cm^3) and M_m is the chemical formula mass of the ionic material (g), and the constants γ

($kJ \cdot mol^{-1} \cdot cm$) and δ ($kJ \cdot mol^{-1}$) are assigned literature values[37].

The empirical Kamlet-Jacobs (K-J) equations[32] widely employed to evaluate the energy performance of energetic compounds were used to estimate the detonation velocity and detonation pressure of title compounds.

The results are showed in **Table 1**. The HOF of ATO is $342.98 kJ \cdot mol^{-1}$, and the salt **7e** shows the highest value at 743.27 $kJ \cdot mol^{-1}$. All of the ATO and its salts exhibit positive heats of formation. The values of HOF is rising with the increase of nitrogen content from **7b** to **7e** (ATO·G to ATO·TAG). **Table 1** shows that for **7** to **7f** , the calculated detonation pressures (P) range from 23.4~35.0GPa, which is comparable to that of TNT (19.5 GPa) and RDX (35.2 GPa). The calculated detonation velocities (D) fall in the range 7.53 $km \cdot s^{-1}$ (comparable to TNT, 6.88 $km \cdot s^{-1}$) to 8.88 $km \cdot s^{-1}$ (comparable to RDX, 8.98 $km \cdot s^{-1}$).

Table 1. The physico chemical properties of 7-7f compared with those of TNT and RDX

compounds	T_m[a]	T_d[b]	d_c[c]	OB[d]	N[e]	ΔH_c^o[f]	ΔH_a^o[g]	ΔH_L^o[h]	ΔH_f^o[i]	P[j]	D[k]	IS[l]
7	221.0	227.1	1.796	-23.76	69.3	-	-	-	342.98	35.0	8.88	>40
7a	-	-	1.647	-40.68	75.7	753.38	82.45	580.82	255.01	28.7	8.26	-
7b	184.5	224.8	1.569	-50.00	70.0	743.07	82.45	539.02	286.50	25.0	7.83	>40
7c	197.5	220.6	1.597	-50.29	72.0	865.79	82.45	527.73	420..51	26.7	8.16	>40
7d	153.0	220.7	1.534	-50.52	73.7	1035.9	82.45	509.99	608.36	28.4	8.41	>40
7e	154.5	214.5	1.569	-50.73	75.0	1162.99	82.45	502.17	743.27	31.0	8.72	>40
7f	170.0	220.5	1.632	-48.00	70.0	914.57	82.45	502.66	494.36	23.6	7.53	>40
TNT[38]	80.4	295	1.65	-25	18.5	-	-	-	95.3	19.5	6.88	15
RDX[39]	240.1	230	1.82	0	37.8	-	-	-	83.8	35.2	8.98	7.4

[a]melting point (^{o}C). [b]Decomposition temperature (^{o}C). [c]Measured crystal density (g·cm^{-3}). [d]CO oxygen balance. [e]Nitrogen content (%). [f]Molar enthalpy of the formation of cation (kJ·mol^{-1}). [g]Molar enthalpy of the formation of anion (kJ·mol^{-1}). [h]Lattice energy(kJ·mol^{-1}).[i]Molar enthalpy of the formation of ATO and salt. [j]Detonation pressure (GPa). [k]Detonation velocity (km·s^{-1}).[l]Impact sensitivity (J).

Conclusions

In this contribution, an improved synthesis route of 1-aminotetrazol-5-one was presented. And the nitrogen-rich energetic salts of 1-aminotetrazol-5-one(**7a**~**7f**) were synthesized and characterized to explore the new energetic materials. All of the energetic salts exhibit relative lower densities (1.534~1.647 g·cm^{-3}) than ATO (1.796·cm^{-3}) but show better thermal stabilities (>220 ^{o}C). All the salts except **7a**are insensitive towards impact (>40J), which made these salts safe to deal with and they could be applied in some specific areas. Most of them possess promising detonation properties based on moderate density and high heats of formation. Compounds **7**, **7d**, and **7e** show good detonation pressures (for **7**: 35.0 GPa, **7d**: 28.4 GPa, **7e**: 31.0 GPa), and excellent detonation velocities (for**7**: 8.88km·s^{-1}, **7d**:8.41 km·s^{-1}, **7e**: 8.72km·s^{-1}). Calculated detonation values of these compounds are comparable to those of explosives such as

RDX (P=35.2 GPa, D=8.98 km·s^{-1}) and TNT (P=19.5 GPa, D=6.88 km·s^{-1}). Based on the reasonable detonation properties and superior stabilities, 1-aminotetrazol-5-one and its salts might be of interest for thermally stable energetic materials and promote research into safer, more reliable, and stable energetic materials.

Experimental Section

Caution! 1- Aminotetrazol-5-one and their derivatives are energetic compounds, therefore proper protective measures (safety glasses, face shield, leather coat, earplugs and thick gloves) should be used.Silver 1-aminotetrazol-5-oneate is sensitive towards friction, impact, and electrostatic discharge. It should be synthesized only in 1~2 mmole amounts.

Instrumentation and Measurement. ^{1}H NMR, ^{13}C NMR and ^{15}N NMR were recorded on a 400MHz (Varian mecury-plus 400 or Bruker AVANCE III) and 500MHz (Agilent DDR2) nuclear magnetic resonance spectrometers operating at 101 and 50.67 MHz, by using CD_3SOCD_3 , $CDCl_3$, D_2O and CD_3COCD_3 as solvent. Chemical shifts in ^{1}H NMR and^{13}C NMR is relative to Me_4Si, and ^{15}N NMR to $MeNO_2$. The mass spectra was recorded with ESI ion source on a Agilent 500-MS and SHIMADZU LCMS 2010 mass spectrometer. IR spectra were recorded using KBr pellets for solids on a Nicolet Nexus 470 FT-IR spectrometer. Elemental analyses were carried out using a Vario El III elemental analyzer. DSC-TG was performed with a PekinElmer (PE) STA6000 synchronous thermal analyzer in a dry nitrogen atmosphere with flowing rate of 20 mL·min^{-1} and the sample (0.9~2.5mg) was powdered and put in the ceramic crucible with a linear heating rate of 10 ^{o}C·min^{-1}.The impact sensitivity was determined by using a BAM fallhammer apparatus with 5 kg drop weight on 15 mg samples.

X-ray crystallographic studies. The structures of **7**, **7a**~**7f** were determined by X-ray analysis with Bruker SMART-1000 and Bruker APEX II Smart CCD diffractometer at 296~298K. The crystals were irradiated using graphite mono-chromated Mo K_α radiation (λ = 0.71073Å). Data collection and refinement were performed with Bruker SMART. The structures were solved with SHELXS-97 program [40], refined with SHELXL-97 program[41]. The finalized CIF files were

checked with checkCIF[42]. Intra- and inter-molecular contacts were analyzed with Mercury software. CCDC-1018898 **(7)**, CCDC-1018899 **(7a)**, CCDC-1018904 **(7b)**, CCDC-1018893 **(7c)**, CCDC-1018919 **(7d)**, CCDC-1018921 **(7e)** and CCDC-1018905 **(7f)** contain the supplementary crystallographic data for this paper.

Benzaldehydehydrazone **(2)**

Hydrazine hydrate（80%, 22 ml, 0.35 mol）was dissolved in methanol (40 ml), while stirring in ice water bath, benzaldehyde（21.2 g, 0.2 mol） was added dropwise. The mixture was stirred for 30 min and then heated to reflux. After stirring for additional 4 h, the methanol was distilled under vacuum to produce a slight yellowish oil, then the mixture was poured into water (300 ml) and extracted with dichloromethane (80 ml×3), the combined organic phases were dried over magnesium sulfate and filtered, the solvent was evaporated at ambient temperature in a vacuum, a yellow oil was obtained (23 g, 95.8%).

^{13}CNMR ($CDCl_3$, 101MHz, ppm):143.2, 135.1, 130.3, 128.7, 126.3. **MS (ESI^+)**: 121.1(M+H).

1-(Benza1amino)-tetrazole**(3)**

Benzaldehydehydrazone (45g, 0.375mol), ethyl orthoformiate (113 ml, 0.675 mol), sodium azide (29.3 g, 0.45 mol) and acetic acid were mixed and stirred at 75 ℃ for 4 h. Then the mixture was poured into cold water (1100 ml), the product was collected by filtration and washed with water (200 ml×3), then dried in an oven. An off white solid was obtained (48 g, 74%).

^{1}HNMR (DMSO-d_6, 400MHz, ppm): 9.92 (1H, s), 9.44 (1H, s), 8.00 (2H, J=8.09, s), 7.62 (3H, J_1=J_2=7.19, J_3=15.41, td).

^{13}CNMR (DMSO-d_6, 101MHz, ppm): 160.5, 140.7, 133.3, 131.3, 129.3. **MS (ESI^+)**: 174.08 (M+H), 196.06 (M+Na).

IR (KBr, cm^{-1}): 3433.17, 3130.64, 3060.00, 2992.03, 1974.24, 1902.08, 1734.05, 1693.97, 1638.67, 1600.26, 1572.64, 1450.18, 1338.70, 1316.45, 1270.53, 1218.11, 1178.84, 1154.02, 1075.18, 991.62, 960.19, 872.84, 767.46, 693.22, 647.45, 592.66, 506.22. **EA**: Calcd C 55.48%, H 4.07%, N 40.44%; found C 55.62%, H 3.98%, N 40.33%.

5-(Acetoxymercuri)-l-(benzalamino)tetrazole **(4)**

A solution of mercuric acetate (64.8 g, 0.204 mol) in ethanol (500 ml) at 75 ℃ which was acidified by the addition of acetic acid (5 mL) was added a solution of 1-(benza1amino)tetrazole (35.2 g, 0.203 mol) in hot ethanol (500 ml), after stired for 30 min the mixture was filtrated and 5-(acetoxymercuri)-l- (benzalamino)tetrazol was obtained as a white solid (80.7 g, 92%).

^{1}HNMR (DMSO-d_6, 400MHz, ppm): 9.47 (1H, s), 8.06 (2H, J=7.12, d), 7.61 (3H, J_1=J_2=7.12, J_3=6.97, J_4=14.49, qd), 1.96 (3H, s). **^{13}CNMR (DMSO-d_6, 101MHz, ppm)**: 179.8, 160.4, 144.8, 138.3, 137.2, 134.6, 134.5, 27.7. **IR (KBr, cm^{-1})**: 3433.81, 2175.37, 1741.67, 1699.11, 1582.54, 1449.50, 1403.31, 1363.93, 1313.41, 1220.73, 1174.35, 1085.61, 1027.74, 975.99, 931.30, 809.65, 759.51, 693.04, 618.98, 602.07, 531.76, 506.41.

5-Bromo-1-(benza1amino)tetrazole **(5)**

5-(Acetoxymercuri)-l-(benzalamino)tetrazole (39.2 g, 90.7 mmol) was suspended in a solution of potassium bromide (91 g, 0.765 mol) and water (200 ml) at room temperature, after vigorous stirring for 15 min bromine was added dropwise and stirring for another 15 min. The precipitate was collected by filtration to give 5-bromo-1-(benza1amino)tetrazole (16.5 g, 72.4%) as slight yellow powder. Rf=0.55 (PE:EA=3:1, V/V), mp: 125.6-125.9 ℃.

^{1}HNMR ($CDCl_3$, 400MHz, ppm): 9.28 (1H,s), 7.96 (2H, J=7.18, d), 7.58 (3H, J_1=J_2=7.31, J_3=31.37, td). **^{13}CNMR ($CDCl_3$, 101MHz, ppm)**: 159.5, 133.8, 132.5, 131.1, 129.8, 129.4.**MS(ESI^{+})**: 273.97/275.97 (M+Na). **IR (KBr, cm^{-1})**: 3433.39, 1607.83, 1593.60, 1571.49, 1492.86, 1454.28, 1416.07, 1396.41, 1368.86, 1343.62, 1315.96, 1265.26, 1223.89, 1181.45, 1153.60, 1097.66, 1042.02, 974.10, 873.99, 767.70, 692.31, 667.32, 602.96, 536.91, 507.30, 410.72. **EA**: Calcd C 38.12%, H 2.40%, N 27.78%; found C 39.14%, H 2.43%, N 27.78%.

1-(Benza1amino)tetrazol-5-one **(6)**

To a mixture of 5-bromo-1-(benza1amino)tetrazole (5.04 g, 20 mmol) and water (60 ml) was added sodium hydroxide (2 g, 50 mmol), the suspension was heated at the reflux temperature until the solid was dissolved. The solution was cooled, acidified with concentrated hydrochloric acid (pH=1) and extracted with ethyl acetate (25 ml×3), the combined organic phases were dried over

sodium sulfate and filtered, the solvent was evaporated in a vacuum to give a white solid (3.21 g, 85%). R_f=0.64（DCM: MeOH:AcOH=40:2:1, V/V）

^{1}HNMR (CD_3 $COCD_3$, 400MHz, ppm): 10.02 (1H, s), 8.67 (2H, J=6.13, d), 8.26 (3H, m). **^{13}CNMR (CD_3 $COCD_3$, 101MHz, ppm)**: 157.9, 138.4, 137.2, 134.3, 133.7, 132.8. **MS(ESI^+)**: 190.07 (M+H). **MS(ESI^-)**: 188.05 (M-H). **IR (KBr, cm^{-1})**: 3434.05, 3195.92, 3004.50, 2862.66, 2762.20, 1857.89, 1754.76, 1596.79, 1571.66, 1475.32, 1447.74, 1406.10, 1349.31, 1237.20, 1227.72, 1191.94, 1176.70, 1146.90, 1121.86, 1065.26, 1024.80, 986.82, 971.43, 867.27, 851.20, 828.52, 803.25, 764.02, 721.72, 689.09, 652.51, 636.35, 583.64, 546.26, 509.69, 459.83. **EA**: Calcd C 50.79%, H 3.73%, N 37.02%, found C 50.39%, H 3.52%, N 36.44%.

1-Aminotetrazol-5-one **(7)**

To a suspension of 1-(benza1amino)tetrazol-5-one (11 g, 58.2 mmol) and water (100 ml) was added concentrated hydrochloric acid (50 ml), then heated to reflux temperature, the benzaldehyde was blowed out by an air-line. The process was terminated after 2.5 h, and the clear solution was evaporated under reduced pressure to leave a yellow solid residue. The product was obtained pure by washing with cold ethanol to give a white solid (4.23 g, 72%). mp: 214.8~214.9 ℃

^{1}HNMR (DMSO-d_6, 400MHz, ppm): 14.17(1H, s), 5.94(2H, J=64.45, s). **^{13}CNMR (DMSO-d_6, 101MHz, ppm)**: 150.3

^{15}NNMR (DMSO-d_6, 50.67MHz, ppm): -23.00, -44.85, -168.12, -182.30, -317.31. **MS (ESI^-)**: 100.03 (M-H). **IR (KBr, cm^{-1})**: 3738.13, 3317.50, 3203.02, 3099.86, 3028.35, 1732.36, 1704.85, 1639.50, 1427.15, 1404.68, 1341.16, 1236.98, 1207.27, 1070.88, 987.85, 910.46, 795.89, 733.17, 714.55, 659.31, 566.89, 449.37. **EA**: Calcd 11.88%, H 2.99%, N 69.29% , found C 12.21%, H 2.99%, N 69.37%. **Sensitivity**: impact > 40 J.

Ammonium 1-aminotetrazol-5-oneate **(7a)**

Ammonium hydroxide (25%, 151 μl, 2 mmol) was added to a suspension of 1-aminotetrazol-5-one (202 mg, 2 mmol) and water (5 ml), after stirring for 10 min, the clear solution was slowly evaporated and single crystals was obtained.

^{13}CNMR (D_2O, 101MHz, ppm): 161.71. **^{15}NNMR (D_2O, 50.67MHz, ppm)**: -19.74, -27.97,

-107.45, -167.31, -318.85, -371.11. **MS(ESI$^-$)**: 99.95 ($CH_2N_5O^-$). **MS(ESI$^+$)**: 18.10(NH_4^+).

IR (KBr, cm^{-1}): 3317.42, 3202.97, 3095.55, 3028.08, 2853.11, 2772.53, 1731.88, 1638.53, 1459.52, 1427.62, 1405.15, 1341.24, 1237.22, 1207.54, 1071.16, 988.00, 910.98, 795.54, 733.23, 714.61, 659.08, 566.80, 450.81.

Guanidinium 1-aminotetrazol-5-oneate **(7b)**

Guanidinium carbonate (180 mg, 1 mmol) was added to a suspension of 1-aminotetrazol-5-one (202 mg, 2 mmol) and water (5 ml), after stirring for 10 min, the clear solution was evaporated under reduced pressure to give guanidinium 1-aminotetrazol-5-oneate as a white powder(275 mg, 86%).

^{13}CNMR (DMSO-d_6, 101MHz, ppm): 161.94, 158.45. **^{15}NNMR (DMSO-d_6, 50.67MHz, ppm)**: -24.18, -25.95, -131.98, -167.90, -305.00, -318.08. **MS (ESI$^-$)**: 99.95 ($CH_2N_5O^-$). **MS (ESI$^+$)**: 60.05($CH_6N_3^+$). **IR (KBr, cm^{-1})**: 3475.75, 3386.29, 3154.55, 2919.22, 2851.08, 1714.99, 1650.04, 1610.60, 1468.42, 1401.18, 1300.55, 1239.38, 1207.03, 1147.74, 1116.24, 989.86, 958.49, 809.49, 758.70, 718.46, 682.68, 567.04. **EA**: Calcd C 15.00%, H5.04%, N 69.97% , found C 15.14%, H 4.82%, N 69.83%.**Sensitivity**: impact > 40 J.

Aminoguanidinium 1-aminotetrazol-5-oneate **(7c)**

Aminoguanidine hydrogen carbonate (268 mg, 2 mmol) was added to a suspension of 1-aminotetrazol- 5-one (202 mg, 2 mmol) and water (5ml), after stirring for 10 min the clear solution was evaporated under reduced pressure to give aminoguanidinium 1-amino-tetrazol-5-oneate as a yellow powder (267 mg, 89%).

^{13}CNMR(DMSO-d_6, 101MHz, ppm):161.88, 159.26. **^{15}NNMR(DMSO-d_6, 50.67MHz, ppm)**: -23.72, -39.81, -168.12, -170.27, -283.85, -317.62, -326.43. **MS (ESI$^-$)**: 99.95 ($CH_2N_5O^-$). **MS (ESI$^+$)**: 75.05($CH_7N_4^+$). **IR (KBr, cm^{-1})**: 3389.13, 3334.82, 3118.97, 2919.07, 2849.79, 1693.11, 1616.41, 1585.90, 1433.23, 1402.93, 1365.96, 1282.76, 1224.21, 1209.38, 1169.97, 1118.35, 992.68, 948.55, 811.80, 763.59, 715.26, 681.85, 627.91, 517.77, 429.56. **EA**: Calcd C 13.71%, H 5.18%, N 71.97% , found C 14.26%, H 5.11%, N 70.84% . **Sensitivity**: impact > 40 J

Diaminoguanidinium 1-aminotetrazol-5-oneate **(7d)**

Silver 1-aminotetrazol-5-oneate (416 mg, 2 mmol) was added to a solution of diaminoguanidine hydrochloride (251 mg, 2 mmol), after stirring for 24 h, the filtrate was collected by filtration, and the clear solution was evaporated under reduced pressure to give diaminoguanidinium 1-aminotetrazol-5-oneate as a yellow powder (306 mg, 85%).

^{13}CNMR (DMSO-d_6, 101MHz, ppm): 160.07. **^{15}NNMR (DMSO-d_6, 50.67MHz, ppm)**: -24.83, -29.47, -145.70, -168.25, -287.45, -312.39, -318.07, -328.16. **MS (ESI$^-$)**: 99.95 ($CH_2N_5O^-$). **MS (ESI$^+$)**: 90.05($CH_8N_5^+$). **IR (KBr, cm^{-1})**: 3716.32, 3368.22, 3324.21, 3200.89, 3069.97, 2881.92, 1682.64, 1640.01, 1555.62, 1517.43, 1403.53, 1341.45, 1291.00, 1236.52, 1192.73, 1180.70, 1103.06, 1054.01, 998.39, 978.17, 950.01, 809.65, 783.53, 713.74, 650.40, 563.92. **EA**: Calcd C 12.63%, H 5.30%, N 73.65%; found C 12.75%, H 5.21%, N 72.91%. **Sensitivity**: impact > 40 J

Triaminoguanidinium 1-aminotetrazol-5-oneate **(7e)**

Silver 1-aminotetrazol-5-oneate (416 mg, 2 mmol) was added to a solution of triaminoguanidine hydrochloride (282 mg, 2 mmol), after stirring for 24 h, the filtrate was collected by filtration, the clear solution was evaporated under reduced pressure to give triaminoguanidinium 1-aminotetrazol-5-oneate as a yellow powder (353 mg, 86%).

^{13}CNMR (DMSO-d_6, 101MHz, ppm): 159.12, 154.73. **^{15}NNMR (DMSO-d_6, 50.67MHz, ppm)**: -23.34, -42.09, -168.09, -175.58, -288.95, -317.36, -329.71. **MS (ESI$^-$)**: 99.95 ($CH_2N_5O^-$). **MS (ESI$^+$)**: 105.00($CH_9N_6^+$). **IR (KBr, cm^{-1})**: 3318.57, 3210.91, 1685.22, 1614.62, 1576.91, 1398.85, 1334.79, 1310.70, 1286.61, 1229.40, 1200.14, 1129.58, 1114.04, 1006.80, 952.00, 895.44, 806.44, 764.47, 734.29, 714.65, 682.07, 638.57, 608.06, 550.07, 452.38. **EA**: Calcd C 11.71%, H 5.40%, N 75.09% , found C 12.07%, H 5.31%, N 73.92%. **Sensitivity**: impact > 40 J.

3,4-Diamino-1,2,4-triazolium 1-aminotetrazol-5-oneate **(7f)**

Silver 1-aminotetrazol-5-oneate (416 mg, 2 mmol) was added to a solution of 3,4-diamino-1,2,4-triazole hydrochloride (271 mg, 2 mmol), after stirring for 24 h, the filtrate was collected by filtration, the clear solution was evaporated under reduced pressure to give 3,4-diamino-1,2,4-triazolium 1-aminotetrazol-5-oneate as a white powder (324 mg, 81%).

^{13}CNMR (DMSO-d_6, 101MHz, ppm): 153.46, 150.40, 140.93.**^{15}NNMR (DMSO-d_6, 50.67MHz, ppm)**: -23.31, -43.51, -168.22, -178.56, -222.49, -317.19, -318.97, -330.21. **MS (ESI^-)**: 99.95 ($CH_2N_5O^-$). **MS (ESI^+)**: 100.00($C_2H_6N_5^+$). **IR (KBr, cm^{-1})**: 3317.63, 3206.01, 3083.17, 2952.85, 2730.24, 1705.64, 1652.02, 1574.08, 1423.06, 1402.67, 1319.41, 1296.13, 1251.47, 1237.17, 1224.49, 1200.84, 1111.23, 1017.69, 982.99, 950.59, 935.41, 899.73, 810.73, 794.23, 762.67, 716.69, 687.65, 669.70, 640.62, 558.22, 494.68, 404.95. **EA**: Calcd C 18.00%, H 4.03%, N 68.98% , found C 18.35%, H 4.21%, N 69.33%. **Sensitivity**: impact > 40 J

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Notes and references

[1] Y. C. Li, Q. Cai, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu, S. P. Pang, *J. Am. Chem. Soc.* **2010**, *132*, 12172-12173.

[2] Y. H. Joo, J. M. Shreeve, *J. Am. Chem. Soc.* **2010**, *132*, 15081-15090.

[3] C. L. He, J. H. Zhang, D. A. Parrish, J. M. Shreeve., *J. Mater. Chem. A.* **2013**, *1*, 2863-2868.

[4] W. Liu, Q. H. Lin, Y. Z. Yang, X. J. Zhang, Y. C. Li, Z. H. Lin, S. P. Pang, *Chem. Asian J.* **2014**, *9*, 479 - 486.

[5] L. Liang, H. Huang, K. Wang, C. Bian, J. Song, L. Ling, F. Zhao, Z. Zhou, *J. Mater. Chem.* **2012**, *22*, 21954-21964.

[6] T. M. Klapötke, F. A. Martin, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*, 1487-1501.

[7] V. Thottempudi, H. X. Gao, J. M. Shreeve, *J. Am. Chem. Soc.* **2011**, *133*, 6464-6471.

[8] N. Fischer, T. M. Klapötke, M. Reymann, J. Stierstorfer, *Eur. J. Inorg. Chem.* **2013**, 2167-2180.

[9] Y. H. Joo, J. M. Shreeve, *Angew. Chem., Int. Ed.* **2010**, *49*, 7320-7323.

[10] R. Wang, H. Xu, Y. Guo, R. Sa, J. M. Shreeve, *J. Am. Chem. Soc.* **2010**, *132*, 11904-11905.

[11] D. Fischer, T. M. Klapötke, J. Stierstorfer, *Angew. Chem. Int. Ed.* **2014**, *53*, 8172 -8175.

[12] N. Fischer, D. Izsák, T. M. Klapötke, S. Rappenglück, J. Stierstorfer, *Chem. Eur. J.* **2012**, *18*,

4051 - 4062.
[13] H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2007**, *19*, 1731-1739.
[14] G. H. Tao, Y. Guo, D. A. Parrish, J. M. Shreeve, *J. Mater. Chem.* **2010**, *20*, 2999-3005.
[15] E. Lieber, T. Enkoji, R. C. Burrows., *Inorg. Synth.* **1960**, *6*, 62-63.
[16] C. M. Sabaté, H. Delalu, E. Jeanneau, *Chem. Asian J.* **2012**, *7*, 2080-2089.
[17] A. A. Dippold, T. M. Klapötke, *J. Am. Chem. Soc* . **2013**, *135*, 9931-9938.
[18] A. Langlet, N. V. Latypov, U. Wellmar, P. Goede, *Propell. Explos. Pyrot.* **2004**, *29*, 344-348.
[19] M. Göbel, T. M. Klapötke, P. Mayer, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1043-1050.
[20] D. E. Chavez, M. A. Hiskey, D. L. Naud, D. Parrish, *Angew. Chem. Int. Ed.* **2008**, *47*, 8307-8309.
[21] S. Cudziło, M. Nita, A. Chołuj, M. Szala, W. Danikiewicz, G. Spólnik, S. Krompiec, S. Michalik, M. Krompiec, A. Świtlicka, *Propell. Explos. Pyrot.* **2012**, *37*, 261-266.
[22] K. Karaghiosoff, T. M. Klapötke, P. Mayer, H. Piotrowski, K. Polborn, R. L. Willer, J. J. Weigand, *J. Org. Chem.* **2006**, *71*, 1295-1305.
[23] R. L. Willer, R. A. Henry, *J. Org. Chem.* **1988**, *53*, 5371-5374.
[24] P. N. Confalone, R. B. Woodward, *J. Am. Chem. Soc.* **1983**, *105*, 902-906.
[25] D. C. Moebius, J. S. Kingsbury, *J. Am. Chem. Soc.* **2009**, *131*, 878-879.
[26] P. N. Gaponik, V. P. Karavai, *Khimiya Geterotsiklicheskikh Soedinenii* **1983**, *6*, 841-482.
[27] H. E. Carter, H. D. West, *Org. Synth.* **1940**, *20*, 81-84.
[28] H. E. Carter, H. D. West, *Org. Synth.* **1955**, *3*, 774-775.
[29] Q. Zhang, J. Zhang, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2013**, *19*, 11000 - 11006.
[30] F. Boneberg, A. Kirchner, T. M. Klapötke, D. G. Piercey, M. J. Poller, J. Stierstorfer, *Chem. Asian J.* **2013**, *8*, 148-159.
[31] F. Boneberg, A. Kirchner, T. M. Klapötke, D. G. Piercey, M. J. Poller, J. Stierstorfer, *Chem. Asian J.* **2013**, *9*, 148-159.
[32] M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys.* **1968**, *48*, 23-25.
[33] H. X. Gao, C. F. Ye, C. M. Piekarski, J. M. Shreeve, *J. Phys. Chem.* **2007**, *111*, 10718-10731.
[34] R. G. Parr, W. Yang., *Density Functional Theory of Atoms and Molecules. Oxford University Press, New York.* **1989**.
[35] M. J. Frisch, .*Gaussian 09, Gaussian, Inc. Wallingford* **2009**.
[36] K. B. Wiberg, J. W. Ochterski, *J. Comput. Chem.* **1997**, *18*, 108-114.
[37] H. D. B. Jenkins, *Inorg. Chem.* **2002**, *41*, 2364-2367.
[38] Y. Q. Zhang, Y. Guo, Y. H. Joo, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2010**, *16*, 10778-10784.
[39]D. D. Diaz, S. Punna, P. Holzer, A. K. Mcpherson, K. B. Sharpless, V. V. Fokin, M. G. Finn, *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4392-4403.
[40] G. M. Sheldrick, *SHELXS-97，Program for the Solution of Crystal Structure* **University of Göttingen, Germany.1997**.
[41] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement from Diffraction Data* **University of Göttingen, Germany. 1997**.
[42] http://checkcif.iucr.org/