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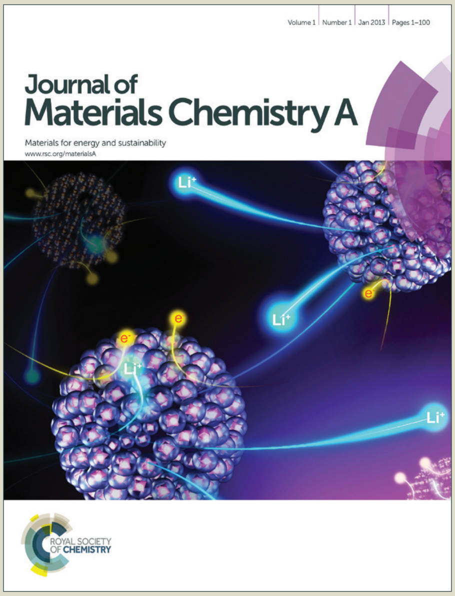

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PAPER

Nitrogen-rich salts based on polyamino substituted N,N'-azo-1,2,4-triazole: a new family of high performance energetic materials

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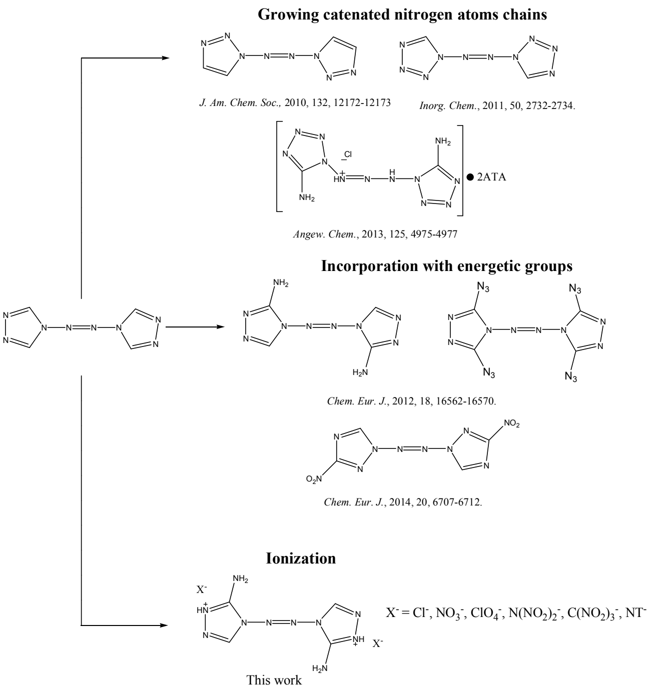
A new family of nitrogen-rich energetic salts based on 3,3'-diamino-4,4'-azo-1,2,4-triazole containing a N,N'-azo linkage were synthesized and fully characterized by IR, ^{1}H and ^{13}C NMR spectrum, elemental analysis, differential scanning calorimetry (DSC), and sensitivities towards impact, friction and electrostatics. The crystal structures of chloride **2**, nitrate **3**, perchlorate **4** and isomerization product **10** have been determined by single-crystal X-ray diffraction analysis. All the salts exhibit high thermal stabilities with decomposition temperatures over 200 °C except for nitroformate **6**. The densities of salts **2**-**7** measured fall in the range from 1.71 to 1.99 g cm^{-1}. Theoretical performance calculations (Gaussian 03 and EXPLO5) provided detonation pressures and velocities for the energetic salts in the ranges 26.3 to 45.7 GPa and 8042 to 9580 m s^{-1}, respectively. Also, these salts exhibit reasonable impact sensitivities (IS = 8-40 J) and friction sensitivities (FS = 90-360 N). These salts exhibit excellent thermal stabilities, high detonation properties and reasonable sensitivities, which, in some cases, are superior to those of TNT, TATB and HMX, and present a favorable balance between energy and stability of energetic materials. Meanwhile, these salts exhibit excellent specific impulses (265 to 301 s), which make them competitive energetic materials.

Introduction

After decades of efforts in the preparation of energetic materials, higher performance and lower sensitivity remain to be the key concerns.[1] Desirable characteristics for new energetic compounds include positive heat of formation, high density, high detonation pressure and velocity, high thermal stability, and low sensitivity toward external forces such as impact and friction. In the development of energetic materials, nitrogen-rich compounds based on C/N heteroaromatic rings with high nitrogen content are at the forefront of high energy materials research, such as triazole,[2] tetrazole,[3] triazine,[4] tetrazine.[5] Different with traditional energetic compounds, their high energy is mainly derived from their high positive enthalpy of formation rather than from the combustion of the carbon backbone or cage strain, which is directly attributed to the large number of inherently energetic N-N and C-N bonds in the molecule.[6] Great interests are shown in the combination of high nitrogen compounds with energetic substituents such as nitro (-NO_2), nitrato (-ONO_2), and nitramine (-$NHNO_2$) functionalities, because these compounds have satisfactory oxygen content.[7] However, the requirements of insensitivity and high energy along with positive oxygen balance are quite often contradictory to each other, making the desired combination of a large energy content with a maximum possible chemical stability to ensure safe synthesis and handling becoming the main challenge. During the last decades, several strategies for the design of energetic materials that combine the increasing demand for high performing materials with high thermal and mechnical stabilities have been developed by numerous research groups.[8-9] A further way of improving the energetic properties is the ionization of the heteroaromatic rings, as ionic compounds displayed more attractive energetic properties than their atomically similar nonionic analogues,[10-12] such as lower vapor pressure, and higher densities. Meanwhile, the stabilities of the energetic ionic compounds can be greatly enhanced by making the cation fuel and the anion oxidizer.

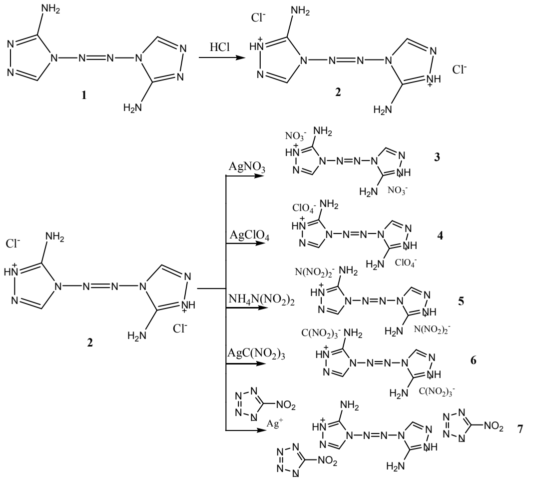
Recently, in pursuit of new high-nitrogen structures, a fascinating class of compounds containing long catenated nitrogen atom chains has been reported.[13-20] 4,4'-Azo-1,2,4-triazole[21] and 1,1'-azo-1,2,3-triazole[13] were obtained through oxidative azo coupling of the N-NH_2 moiety. Compared with the C,C'-azo linkage, the N,N'-azo linkage brings a longer chain of catenated nitrogen atoms in high-nitrogen compounds, which will increase the heats of formation and densify the compounds in return. Based on the azobis-azole backbones, various energetic substituents such as amino (-NH_2),[2] nitro (-NO_2)[22-23] and azido (-N_3)[2] have been introduced into the heteroaromatic rings to adjust the properties. However, energetic salts based on N,N'-azobisazole backbones have been investigated to a less extent.[16, 20] (Scheme 1) Although coupling of 1,5-diaminotetrazole involving diazotization and nucleophilic substitution resulted in the formation of a cocrystal with the longest nitrogen chain to date, the anion is non-energetic Cl atom. In this study, a series of energetic salts were synthesized based on 3,3'-diamino-4,4'-azo-1,2,4-triazole cation containing a N,N'-azobisazole backbone, which was combined with some oxygen-rich anions, and fully characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). Their detonation properties have also been calculated. Furthermore, the structures of 3,3'-diamino-4,4'-azo-1,2,4-triazole chloride (**2**), 3,3'-diamino-4,4'-azo-1,2,4-triazole nitrate (**3**) and 3,3'-diamino-4,4'-azo-1,2,4-triazole perchlorate (**4**) have been determined by single-crystal X-ray analysis.



Scheme 1 Energetic Compounds with Catenated Nitrogen Atoms Chains.

Results and Discussion

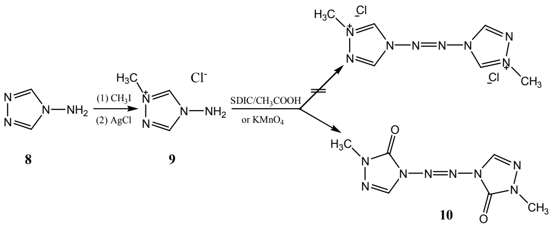
3,3'-Diamino-4,4'-azo-1,2,4-triazole (**1**) was selected as the substrate, as it had four positions which might be protonated, and good stability, prepared previously according to literature.[2] As shown in Scheme 2, 3,3'-diamino-4,4'-azo-1,2,4-triazole chloride (**2**) was obtained directly through protonation by concentrated HCl in methanol as yellow powder. Yellow crystals of **2** suitable for single crystal X-ray analysis were obtained by slow evaporation of water at room temperature. Synthesis of other new energetic salts based on 3,3'-diamino-4,4'-azo-1,2,4-triazole cation were performed according to Scheme 2. Compounds **3, 4, 6** and **7** were prepared from anions exchange of silver nitrate, silver perchlorate, silver nitroformate and silver nitrotetrazolate with compound **2** in water; compound **5** was prepared from anion exchange of ammonium dinitramide with compound **2** in ethanol.



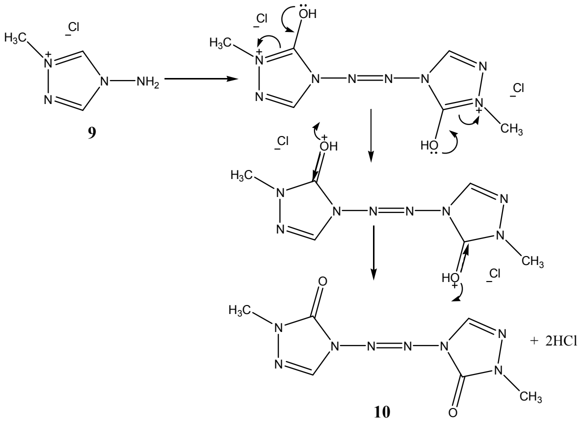
Scheme 2. Synthesis of Energetic Salts Based on 3,3'-Diamino-4,4'-azobis-1,2,4-triazole.

All of the prepared energetic salts proved to be stable in air and could be stored for extended periods. Their structures were confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis, and the data obtained are listed in the Experimental Section.

Encouraged by the success of 3,3'-diamino-4,4'-azo-1,2,4-triazole salts, we also attempted to achieve the protonation of 4,4'-azo-1,2,4-triazole through the traditional methylation and azo coupling reaction based on 4-amino-1,2,4-triazole, but failed, instead, 3,3'-dione-4,4'-azo-1,2,4-triazole (**10**) was obtained (Scheme 3 and Scheme 4), which was confirmed by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis, and its structure was also determined by single-crystal X-ray analysis. Meanwhile, the direct methylation of 4,4'-azo-1,2,4-triazole was also tried, which remained unreacted.



Scheme 3 The Azo Coupling of 4-Amino-1-methyl-1,2,4-triazole Chloride.



Scheme 4 Possible Reaction Pathway for Formation of Isomerization Product **10**.

The phase-transition temperatures (midpoint of melting point) and thermal stabilities of compounds **1**-**7** and **10** were determined by DSC at a heating rate of 5 K min^{-1}. As shown in Table 1, only salts **2** and **7** melted at 154.5 and 159.2 °C, respectively; all the other energetic salts decomposed directly. The neutral molecule **1** exhibited high thermal stability with a decomposition temperature of 283.1 °C. All the salts decomposed over 200 °C except for the nitroformate **6**, ranging from 209.7 (**7**) to 275.4 °C (**4**), which showed excellent thermal stabilities. Nitroformate **6** decomposed at 80.2 °C, consistent with the reported stabilities of nitroformate.[24] The isomerization product **10** showed a thermal degradation T_d = 258.1 °C. Salt **4** was found to be most thermally stable with a degradation temperature (T_d) of 275.4 °C, closely to those of TNT and HMX.

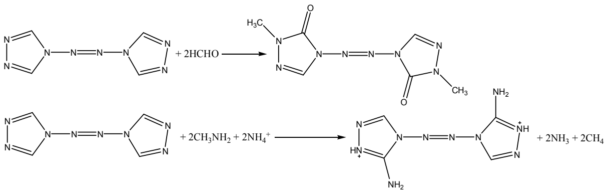
Table 1. The physicochemical properties of **1-7** and **10** compared with **TNT**, **TATB** and **HMX**

Salt	T_m[a]	T_d[b]	d_m[c]	OB[d]	N[e]	ΔH_c°[f]	ΔH_a°[g]	ΔH_f°[i]/ΔH_m°[j]	P[k]	D[l]	I_{sp}[m]	IS[n]	FS[o]	ESD[p]
1	—	283.1	1.61	-57.7	72.1	—	—	838.8/4.32	23.3	8115	235	>40	>360	-
2	154.2	244.7	1.71	-47.9	52.4	2306.1	-230.3[34]	1382.8/5.18	26.3	8042	265	>40	>360	-
3	—	238.5	1.77	-10	52.5	2306.1	-307.9[34]	1230.3/3.84	39.1	9432	300	>40	300	-
4	—	275.4	1.99	0	35.5	2306.1	-277.8[34]	1306.3/3.31	45.7	9501	294	24	90	-
5	—	231.2	1.80	0	54.9	2306.1	-156.2[34]	1560.1/3.82	42.0	9580	301	9.5	160	-
6	—	80.2	1.87	6.4	45.2	2306.1	-247.7[11]	1393.5/2.81	42.9	9569	291	—	—	-
7	159.2	209.7	1.79	-22.6	66.0	2306.1	112.8[35]	2105.2/4.96	37.0	9395	282	8	240	-
10	—	258.1	1.62	-57.1	50.0	—	—	343.8/1.53	19.2	7470	197	>40	>360	-
TNT[42]	80.4	295	1.65	-25	18.5	—	—	95.3/0.42	22.9	7483	225	15	—	—
TATB[43]	350	350	1.93	-18.6	32.6	—	—	-139.7/-0.60	31.8	8520	198	30-34	—	—
HMX[44]	276	287	1.91	0	37.8	—	—	104.8/0.35	39.7	9187	264	7.4	—	—

[a] Melting point (°C). [b] Decomposition temperature (°C). [c] Measured density (g cm^{-3}), using an ULTRAPYC 1200e v4.01, Automatic Density Analyzer. [d] CO oxygen balance (OB) is an index of the deficiency or excess of oxygen in a compound required to convert all C into CO and all H into H_2O. For a compound with the molecular formula of $C_aH_bN_cO_d$ (without crystal water), OB (%) =1600[(d-a-b/2)/M_w], M_w molecular weight of the salt. [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 salt (kJ mol^{-1}). [j] Enthalpy of the formation of salt per gram (kJ g^{-1}). [k] Detonation pressure (GPa). [l] Detonation velocity (m s^{-1}). [m] Specific impulse (isobaric combustion for the mixture at a chamber pressure=60.0 bar (s). [n] Impact sensitivity (J). [o] Friction sensitivity (N). [p] Rough sensitivity to the electrostatic discharge (+/-) : + = sensitive; - = insensitive.

As one of the most important physical properties affecting the performance of energetic materials, the densities of salts **2**-**7** were measured using an ULTRAPYC 1200e v4.01, automatic density analyzer at 25 °C. The results were summarized in Table 1, ranging from 1.71 to 1.99 g cm^{-3}, which place them in a class of relative dense compounds. Compared with the neutral molecule **1** (1.61 g cm^{-3}), the densities of the ionic salts improved a lot. The H atoms in the amino groups and the triazole rings, together with the O atoms in the anions formed strong intra and intermolecular hydrogen bonds, which might contribute to the high densities of these salts. The measured densities of **2**, **3** and **4** were nearly the same as those obtained from X-ray crystal structures, respectively, as shown in Table 1 and Table 2.

The heat of formation (HOF) is another important parameter in evaluating the performance of energetic salts, which can be calculated with good accuracy (including the heats of formation of the cation and anions, and the lattice energy of salts).[25-29] The heat of formation of the cation was calculated using the Gaussian 03 (Revision F.02) suite of programs:[30] the geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with 6-31+G* basis set,[31] and single-point energies were calculated at MP2/6-31+G* level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The HOF of the cation based on isodesmic reaction[32-33] (Scheme 5) was calculated to be 2306.1 kJ mol^{-1}, and the values for the anions are available in the literatures.[11, 34-35] As is summarized in Table 2, the positive heats of formation of salts **2**-**7** were calculated by using Born-Haber energy cycle.[36] All the salts have very high HOFs, which fall in the range from 1230.3 kJ mol^{-1} (**3**) to 2105.2 kJ mol^{-1}(**7**), far more than that of HMX (104.8 kJ mol^{-1}).



Scheme 5 Isodesmic Reactions for Calculating the Heats of Formation.

Oxygen balance (OB), which is an expression used to indicate the degree to which an explosive can be oxidized, is an important index for identifying the potential of energetic materials as explosives or oxidants. Salt **6** possesses positive oxygen balance at 6.4%, and salts **4** and **5** both have eight oxygen atoms, possessing zero oxygen balance, which are same as HMX (0%). Also, other salts have good oxygen balance, such as **3** (-10%), better than that of TATB (-18.6%); and **7** (-22.6%), which is a little better than that of TNT (-25%). Meanwhile, All these salts have high nitrogen content, most of them exceeding 50%, especially salt **6**, reaching as high as 66%, which is benefical to improve the oxygen balance.

Detonation velocity D (m s^{-1}) and detonation pressure P (GPa) as the characterization of a high explosive's performance, as well as specific impulse (I_{sp}) were calculated by EXPLO5 v6.01 computer program[37-41] based on the measured densities and calculated heats of formation. Meanwhile, the detonation data of TNT,[42] TATB,[43] and HMX[44] were also calculated using EXPLO5 v6.01 according to the reported densities and heats of formation as a comparison. As shown in Table 1, the detonation pressures of salts **2**-**7** range from 26.3 GPa (**2**) to 45.7 GPa (**4**): the oxygen-free salt **2** exhibits the lowest value 26.3 GPa, which is higher than that of TNT; the values of other oxygen-rich salts are all higher than that of TATB (31.8 GPa), especially salts **4**-**6**, exceeding that of HMX (39.7 GPa) with values all above 40 GPa. The detonation velocities of these salts range from 8042 m s^{-1} (**2**) to 9580 m s^{-1} (**5**): the oxygen-free salt **2** plays the lowest value, higher than that of TNT (7483 m s^{-1}); the values of oxygen-rich salts are all above 9300 m s^{-1}, higher than that of HMX, especially salts **4-6**, with values exceeding 9500 m s^{-1}, a requirement value of high energy density materials (HEDMs). Notably, all these salts exhibited very high specific impulses, lying in the range from 265 s (**2**) to 301 s (**5**), which are higher than that of HMX (264 s). Compared with oxygen-free salt **2**, oxygen-rich salts **3**-**7** possess more excellent detonation properties, stating that the improving of the oxygen balance will greatly promote the detonation properties of these series of energetic salts; meanwhile, the detonation properties of these salts improved a lot than the neutral molecule **1** (23.3 GPa, 8115 m s^{-1}). Especially salts **4-6**, all possess detonation pressures above 40 GPa and detonation velocities over 9500 m s^{-1}, as well as specific impulses over 290 s, which make them the candidates for high detonation properties energetic materials.

Sensitivity deserves closer attention by researchers because it is closely linked with the safety of handling and applying explosives. In this study, sensitivities towards impact, friction and electrostatic discharge were tested using standard procedures,[45-47] which are listed in Table 1. None of these compounds exhibited sensitivity towards electrostatic discharge of approximately 20 kV. The chloride **2**, nitrate **3** and isomerization product **10** are insensitive towards impact at more than 40 J, and the perchlorate **4** is much less sensitive at 24 J. The dinitramide **5** and 5-nitrotetrazolate **7** are sensitive at 9.5 J and 8 J, respectively, which are still less sensitive than that of HMX (7.4 J). Most of these salts are less sensitive towards friction (≥ 240 N), except for the perchlorate **4** (90 N) and dinitramide **5** (160 N). As for the extremely deliquescent nature of nitroformate **6**, the impact and friction sensitivity test could not be carried out with accuracy given that water is extremely efficient at reducing the sensitivity of energetic materials.

X-ray crystallography: Crystals of **2** and **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of water from an aqueous solution at room temperature and normal pressure. Compound **2** crystallized in the triclinic space group P-1 with two H_2O per molecule, having a density of 1.681 g cm^{-3} at 93(2) K, and compound **3** crystallized in the monoclinic space group P2(1)/n with a calculated density of 1.761 g cm^{-3} at 293(2) K. Crystal of **4** suitable for X-ray diffraction analysis was obtained by slow evaporation of methanol at room temperature and normal pressure. Compound **4** crystallized in the triclinic space group P-1 with a calculated density of 2.004 g cm^{-3} at 173(2) K. Their structures are shown in Fig. 1, Fig. 2 and Fig. 3, and the crystallographic data and selected bond lengths and angles of compounds **2, 3** and **4** are summarized in Table 2 and Table 3, respectively. Common in these structures is the cation, which adopts a planar confirmation. Notable feature of the cation is the azo bonds, which lie at 1.24~1.25 Å in salts **2**, **3** and **4**, nearly equilong with azo bond in the neutral molecule 4,4'-azo-1,2,4-triazole [1.249 Å]. The C(2)-N(2) [1.28-1.29 Å] bond is the shortest one in all C-N$_{ring}$ bonds, also slightly shorter than C-N$_{amine}$ bond C(1)-N(5) [1.30-1.31 Å]. Meanwhile, compared with the structure of 4,4'-azobis-1,2,4-triazole, the C(1)-N(1) [1.33 Å to 1.31 Å] bond is a little longer, and the C(1)-N(3) [1.36 Å to 1.37 Å] bond is a little shorter, which may attribute to the electron-donating property and the protonation of the triazole.

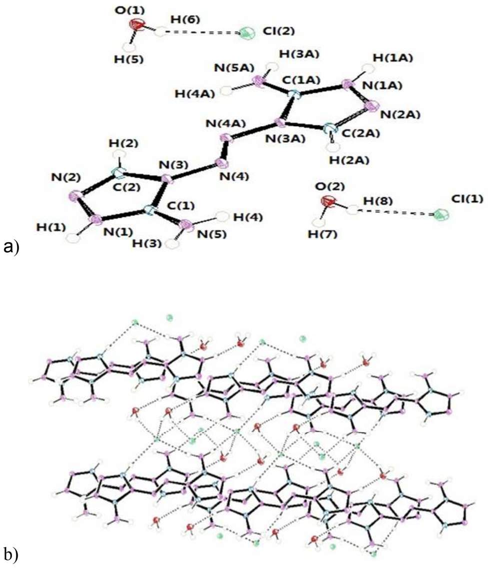


Fig. 1 (a) ORTEP Representation of the Molecular Structure of **2**. Displacement Ellipsoids are Shown at 50% Probability Level. (b) Unit Cell Packing of **2**. The Dashed Lines Indicate Hydrogen Bonding.

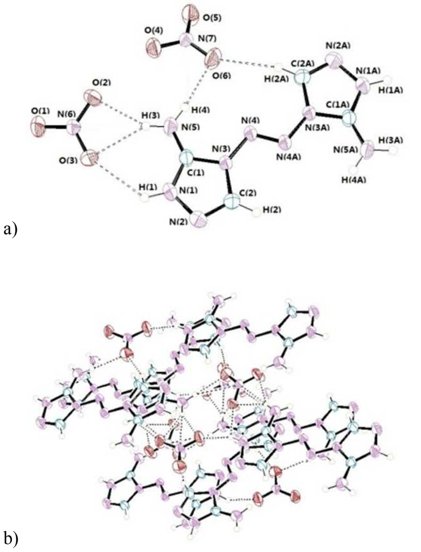
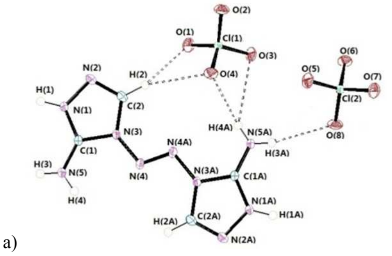
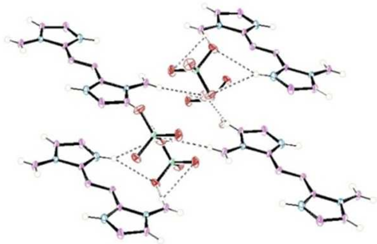


Fig. 2 (a) ORTEP Representation of the Molecular Structure of **3**. Displacement Ellipsoids are Shown at 50% Probability Level. (b) Unit Cell Packing of **3**. The Dashed Lines Indicate Hydrogen Bonding.





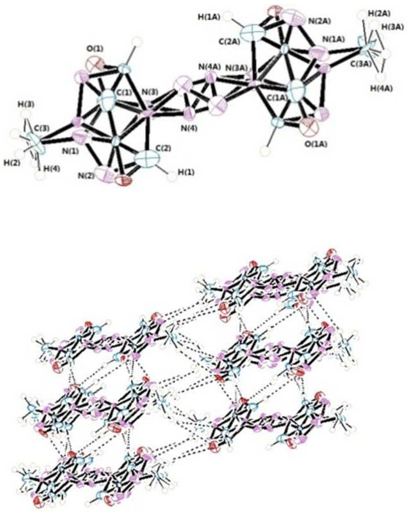
b)

Fig. 3 (a) ORTEP Representation of the Molecular Structure of **4**. Displacement Ellipsoids are Shown at 50% Probability Level. (b) Unit Cell Packing of **4**. The Dashed Lines Indicate Hydrogen Bonding.

Table 2 Crystal Data and Structure Refinement Details of **2**, **3**, **4** and **10**

Crystal	**2**·2H$_2$O	**3**	**4**	**10**
Formula	$C_4H_{12}N_{10}O_2Cl_2$	$C_4H_8N_{12}O_6$	$C_4H_8N_{10}O_8Cl_2$	$C_6H_8N_8O_2$
M_w	303.14	320.22	395.10	224.20
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P2(1)/c	P-1	P-1
T [K]	93(2)	293(2)	173(2)	153(2)
λ [Å]	0.71073	0.71073	0.71075	0.71073
a [Å]	5.186(2)	7.2555(15)	4.9462(9)	5.854(4)
b [Å]	7.387(3)	8.8270(18)	7.1522(17)	8.130(5)
c [Å]	8.416(4)	9.796(2)	9.503(2)	10.650(7)
α [°]	109.629(4)	90	97.491(7)	109.96(3)
β [°]	96.520(6)	105.70(3)	94.118(8)	96.98(4)
γ [°]	94.311(7)	90	99.293(8)	100.02(3)
Volume [Å^3]	299.4(2)	604.0(2)	327.45(12)	460.0(5)
Z	1	2	1	2
ρ [g cm^{-3}]	1.681	1.761	2.004	1.619
μ [mm^{-1}]	0.558	0.159	0.569	0.129
F(000)	156	328	200	232
Crystal size/mm	0.47×0.27×0.25	0.20×0.18×0.14	0.24×0.22×0.20	0.21×0.09×0.0
θ Range [°]	2.60 to 32.54	3.12 to 27.85	2.17 to 29.11	3.60 to 27.49
Index ranges	$-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $-12 \leq l \leq 11$	$-9 \leq h \leq 9$, $-9 \leq k \leq 11$, $-12 \leq l \leq 12$	$-6 \leq h \leq 4$, $-9 \leq k \leq 9$, $-12 \leq l \leq 12$	$-7 \leq h \leq 6$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$
GOF	1.002	1.036	1.054	1.001
R1 (I > 2σ(I))	0.0402	0.0592	0.0330	0.0551
wR2 (I > 2σ(I))	0.0710	0.1391	0.0868	0.0919
refinement	SHELXL-97	SHELXL-97	SHELXL-2013	SHELXL-97
CCDC	963404	976507	979523	978800

In addition, an X-ray quality of isomerization product **10** was obtained by slow evaporation of water at room temperature and normal pressure. The crystallographic data and selected bond lengths and angles of compound **10** are summarized in Table 2 and Table 4, respectively. As is shown in Fig. 4, compound **10** crystallized in the triclinic space group P-1 with a calculated density of 1.619 g cm^{-3} at 153(2) K. The molecule presents two possible positions as for the crystal disorder. The structure adopts a planar conformation with two almost planar triazole rings and a planar N4 chain. The keto tautomer is a notable feature of the isomerization product: the C-O bond lengths in compound **10** lie at 1.22 Å, almost identical and correspond to C=O bond lengths commonly found for carbonyl groups. Moreover, there are slight differences between **10** and 4,4'-azo-1,2,4-triazole with respect to the bond lengths,[21] as seen in Table 4. The lengths of azo bonds linked the triazole rings increased from 1.249 Å in 4,4'-azo-1,2,4-triazole to 1.265 Å in compound **10**, which is probably due to the electron-withdrawing property of the C=O group. The C-N bonded to the triazole rings N(1)-C(3) [1.406 Å] is longer than all the C-N bonds in the triazole rings [1.299-1.391 Å], which may attribute to the electron-donating property of the –CH_3 group.



a)

b)

Fig. 4 (a) View of the Molecular Unit of **10**. Thermal Ellipsoids Represent 50% Probability. The Molecule Takes Two Possible Positions (N1:N1'=(0.599:0.401). (b) Unit Cell Packing of **10**. The Dashed Lines Indicate Hydrogen Bonding.

Table 3 Selected bond lengths/Å and angles/° of compounds **2**, **3** and **4.**

	2	3	4
Bond lengths			
N(1)-C(1)	1.3323(17)	1.3271(20)	1.3311(2)
N(1)-N(2)	1.3938(13)	1.3890(19)	1.3832(2)
N(2)-C(2)	1.2918(17)	1.2829(20)	1.2881(2)
N(3)-C(1)	1.3684(14)	1.3689(18)	1.3723(3)
N(3)-C(2)	1.3933(16)	1.3974(19)	1.3898(2)
N(3)-N(4)	1.3725(16)	1.3711(16)	1.3736(3)
N(4)-N(4A)	1.2495(12)	1.2386(15)	1.2453(2)
N(5)-C(1)	1.3128(15)	1.3018(20)	1.3003(2)
Bond angles			
C(1)-N(1)-N(2)	111.675(102)	112.306(128)	112.514(9)
N(1)-N(2)-C(2)	105.545(100)	105.506(140)	105.242(11)
C(1)-N(3)-C(2)	107.842(98)	107.834(122)	107.785(10)
C(1)-N(3)-N(4)	120.266(95)	119.867(119)	120.138(10)
C(2)-N(3)-N(4)	131.870(103)	132.247(119)	131.941(9)
N(3)-N(4)-N(4A)	110.235(93)	110.958(115)	110.338(10)
N(1)-C(1)-N(3)	104.943(98)	104.414(129)	104.18(1)
N(1)-C(1)-N(5)	129.351(112)	130.472(147)	129.653(9)
N(3)-C(1)-N(5)	125.706(110)	125.113(141)	126.165(11)
N(2)-C(2)-N(3)	109.992(102)	109.926(135)	110.253(9)

Table 4 Selected bond lengths/Å and angles/° of compound **10.**

Bond lengths			
N(1)-C(1)	1.3533(65)	N(3)-C(2)	1.3824(120)
N(1)-N(2)	1.3752(127)	N(3)-N(4)	1.3738(91)
N(1)-C(3)	1.4062(139)	N(4)-N(4A)	1.2651(67)
N(2)-C(2)	1.2985(80)	C(1)-O(1)	1.2218(75)
N(3)-C(1)	1.3914(128)		
Bond angles			
C(1)-N(1)-N(2)	112.526(609)	C(2)-N(3)-N(4)	129.454(814)
C(1)-N(1)-C(3)	130.145(627)	N(3)-N(4)-N(4A)	110.358(537)
N(2)-N(1)-C(3)	117.183(807)	N(1)-C(1)-N(3)	102.640(551)
N(1)-N(2)-C(2)	106.301(539)	N(1)-C(1)-O(1)	128.255(517)
C(1)-N(3)-C(2)	109.000(787)	N(3)-C(1)-O(1)	128.958(617)
C(1)-N(3)-N(4)	121.054(746)	N(2)-C(2)-N(3)	109.285(637)

Conclusions

3,3'-Diamino-4,4'-azo-1,2,4-triazole cation was obtained through the protonation of compound **1**; based on the cation, a series of oxygen-rich poly-nitrogen energetic salts were synthesized, which were fully characterized with IR, and NMR spectrum, DSC, and elemental analysis. All the salts except for the nitroformate exhibited excellent thermal stabilities (209.7 to 275.4 °C). And the densities of these salts measured using an ULTRAPYC 1200e v4.01 machine fell in the range from 1.71 to 1.99 g cm^{-3}, which places them in a class of relatively dense compounds. Meanwhile, with the EXPLO5 v6.01 program, the detonation properties were calculated: most salts exhibited high detonation velocities (about 9500 m s^{-1}); notably, these salts exhibited very high specific impulses (265 to 301 s), which were attributed to the high enthalpy of formation and high nitrogen content. Moreover, all these salts exhibited reasonable impact sensitivities (8-40 J) and friction sensitivities (90-360 N), and none of them exhibited sensitivity towards electrostatic discharge of approximately 20 kV and. Compared with the neutral substrate **1**, the densities and oxygen balance of these salts improved a lot, which contribute to the promoting of the detonation properties. Based on the high detonation properties, high thermal stabilities and applicable sensitivities, these salts have potential as high performance energetic materials. In brief, the N,N'-azo-triazole was proved to be an excellent backbone for constructing novel energetic salts.

Experimental Section

General methods

Crystals of **2**, **3**, **4** and **10** were mounted on a Rigaku RAXIX RSPID IP diffractometer equipped with a graphite-monochromatized MoK*α* radiation (λ = 0.71073 Å). Data for **2**, **3**, **4** and **10** were collected at 93(2) K, 293(2) K, 273(2) K and 153(2) K, respectively, using an Oxford Cobra low temperature device to maintain the temperature. Data collection was performed, and the unit cell was initially refined using APEX2 [v2.1-0].[48] Data reduction was performed using SAINT [v7.34A][49] and XPREP [v2005/2].[50] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2004/1].[51] The structures were solved and refined with the aid of the programs in the SHELXTL-plus [v6.12] system of programs.[52] The structures of **2**, **3** and **10** were solved by direct methods with SHELXS-97,[53] and structure of **4** was solved by direct methods with SHELXS-2013, and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were determined with theoretical calculations and refined with an isotropic vibration factor.

CCDC 963404 (**2**), CCDC 976507 (**3**), CCDC 979523 (**4**) and CCDC 978800 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Theoretical study

Calculations were carried out using the Gaussian 03 suite of programs. The geometric optimization of the structures and frequency analysis were carried out using B3LYP functional with the 6-31+G** basis set, and single point energies were calculated at the MP2/6-31+G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

The heat of formation of the cation was computed by using isodesmic reaction, and the heats of formation of the anion were referred to literatures. The enthalpy of an isodesmic reaction is obtained by combining the MP2/6-31+G** energy difference for the reaction, the scaled zero point energies (B3LYP/6-31+G**), and other thermal factors (B3LYP/6-31+G**). Thus, the heats of formation of the cation and anions being investigated can be extracted readily. With the values of the heats of formation and densities of the compounds, the detonation pressures (*P*), detonation velocities (*D*) and specific impulses (I_{sp}) were calculated using EXPLO5 v6.01.

3,3'-diamino-4,4'-azo-1,2,4-triazole (1): T_{decomp}: 283.1 °C. ^{1}H NMR (DMSO-d$_6$) δ: 9.15, 8.63 ppm; IR (KBr): 3288, 3107, 2988, 2759, 1676, 1628, 1594, 1497, 1429, 1308, 1183, 1101, 995, 939, 816, 783, 720, 702, 560 cm^{-1}; elemental analysis calcd (%) for $C_4H_6N_{10}$ (194.16): C 24.74, H 3.11, N 72.14; found: C 24.66, H 3.20, N 72.14.

3,3'-diamino-4,4'-azo-1,2,4-triazole chloride (2): 3,3'-diamino-4,4'-azobis-1,2,4-triazole (1.82g, 9 mmol) was solved in 30 mL methanol, then 3 mL concentrated hydrochloric acid was added to the solution with constant stirring for 2 h. The solution was filtered to give a yellow filtrate, which was evaporated to produce a yellow product, followed by recrystallization in water. Yield: 1.02 g, 41%. *Mp*: 154.5 °C. T_{decomp}: 244.7 °C. IR (KBr): 3391, 3228, 3051, 1690, 1559, 1466, 1307, 1255, 1204, 952, 786, 605 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 9.17, 8.65 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 131.2, 141.8 ppm; elemental analysis calcd (%) for $C_4H_8N_{10}Cl_2$ (267.08): C 17.99, H 3.02, N 52.44; found: C 18.21, H 3.04, N 52.61.

3,3'-diamino-4,4'-azo-1,2,4-triazole nitrate (3): Compound **3** was prepared from the anions exchange reaction of compound **2** (0.83 g, 3 mmol) with silver nitrate (1.02 g, 6 mmol) in water as a light yellow powder 0.82 g, yield: 82%. T_{decomp}: 238.5 °C. IR (KBr): 3405, 3221, 3136, 3091, 1695, 1558, 1466, 1384, 1326, 1278, 1184, 930, 863, 828, 783, 544 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 11.17, 9.17, 8.65 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 131.2, 141.8 ppm; elemental analysis calcd (%) for $C_4H_8N_{12}O_6$ (320.18): C 15.00, H 2.52, N 52.50; found: C 15.18, H 2.60, N 52.67.

3,3'-diamino-4,4'-azo-1,2,4-triazole perchlorate (4): Compound **4** was prepared from the anions exchange reaction of compound **2** (0.45 g, 1.6 mmol) with silver perchlorate (0.66 g, 3.2 mmol) in water as a white powder 0.56 g, yield: 84%. T_{decomp}: 275.4 °C. IR (KBr): 3390, 3242, 3170, 3138, 3093, 1692, 1571, 1473, 1310, 1253, 1200, 1147, 1112, 936, 785, 626, 549 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 11.17, 9.17, 8.65 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 131.2, 141.8 ppm; elemental analysis calcd (%) for $C_4H_8N_{12}O_6Cl_2$ (395.07): C 12.16, H 2.04, N 35.45; found: C 12.34, H 2.10, N 35.61.

3,3'-diamino-4,4'-azo-1,2,4-triazole dinitramide (5): Compound **5** was prepared from the anions exchange reaction of compound **2** (0.91 g, 3 mmol) with ammonium dinitramide (0.74 g, 6 mmol) in ethanol as a white powder 1.22 g, yield: 88%. T_{decomp}: 231.2 °C. IR (KBr): 3149, 3060, 3032, 2958, 2926, 2855, 1696, 1532, 1457, 1400, 1308, 1194, 1121, 1027, 946, 872, 829, 762, 724, 693, 608, 544 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 11.17, 9.22, 8.65 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 131.2, 141.8 ppm; elemental analysis calcd (%) for $C_4H_8N_{16}O_8$ (408.21): C 11.77, H 1.98, N 54.90; found: C 11.91, H 2.02, N 55.14.

3,3'-diamino-4,4'-azo-1,2,4-triazole nitroformate (6): Compound **6** was prepared from the anions exchange reaction of compound **2** (0.66 g, 2.5 mmol) with silver nitroformate (1.29 g, 5 mmol) in water as a yellow powder 0.78 g, yield: 64%. T_{decomp}: 80.2 °C. IR (KBr): 3421, 3329, 3269, 3161, 1701, 1562, 1544, 1479, 1415, 1383, 1310, 1259, 1195, 1148, 1066, 943, 871, 820, 790, 730, 684, 547 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 11.17, 9.65, 8.89 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 136.8, 134.0 ppm; elemental analysis calcd (%) for $C_6H_8N_{16}O_{12}$ (496.23): C 14.52, H 1.62, N 45.16; found: C 14.74, H 1.68, N 45.32.

3,3'-diamino-4,4'-azo-1,2,4-triazole 5-nitrotetrazolate (7): Compound **7** was prepared from the anions exchange reaction of compound **2** (0.80 g, 3 mmol) with silver 5-nitrotetrazolate (1.33 g, 6 mmol) in water as a white powder 0.74 g, yield: 58%. *Mp*: 159.2 °C, T_{decomp}: 209.7 °C. IR (KBr): 3511, 3379, 3286, 3017, 2962, 2760, 1707, 1641, 1588, 1547, 1500, 1458, 1434, 1327, 1303, 1261, 1212, 1160, 1093, 948, 883, 838, 795, 747, 700, 665, 614, 558 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 11.17, 9.16, 8.97 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 155.2 ppm; elemental analysis calcd (%) for $C_4H_8N_{12}O_6$ (424.26): C 16.99, H 1.90, N 66.03; found: C 17.18, H 1.92, N 65.97.

4-amino-1,2,4-triazole chloride (9): ^{1}H NMR (DMSO-d$_6$) δ: 10.31, 9.19, 7.27 ppm; IR (KBr): 3455, 3220, 3118, 3085, 3039, 3002, 1609, 1565, 1404, 1330, 1208, 1170, 1090, 1066, 991, 973, 867, 729, 654, 611, 455 cm^{-1}.

3,3'-dione-4,4'-azo-1,2,4-triazole (10): Acetic acid (5 mL) was added to a solution of sodium dichloroisocyanurate (SDIC) (5.09 g, 23 mmol) in water (40 mL) with vigorous stirring at 30 °C for 1 h; then, 4-amino-1,2,4-triazole chloride (3.09 g, 23 mmol) was added to the solution. The reaction was kept at 25 °C for 2 h. The mixture was filtered to give the yellow filtrate. After evaporating the water, a light yellow solid was obtained. Yield: 1.22 g, 47%. T_{decomp}: 258.1 °C. IR (KBr): 3428, 3158, 3065, 2945, 1711, 1539, 1431, 1403, 1387, 1348, 1274, 1257, 1206, 987, 816, 723, 616, 602 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ: 8.74, 3.45 ppm; ^{13}C NMR (DMSO-d$_6$) δ: 150.72, 127.83, 32.47 ppm; elemental analysis calcd (%) for $C_6H_8N_8O_2$ (224.18): C 32.15, H 3.60, N 49.98; found: C 32.38, H 3.62, N 50.17.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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A new family of high performance nitrogen-rich energetic salts containing N,N'-azo linkage were synthesized through the protonation of 3,3'-diamino-4,4'-azobis-1,2,4-triazole