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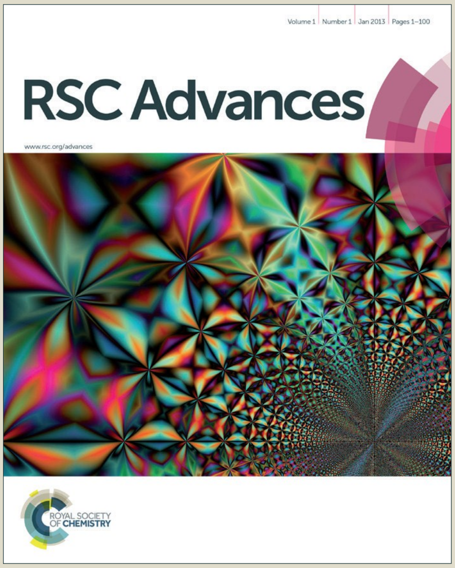

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Nitrogen-rich Energetic Salts of 1*H*,1′*H*-5,5′-Bistetrazole-1,1′-diolate: Synthesis, Characterization, and Thermal Behaviors

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Abstract: A series of nitrogen-rich heterocyclic 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate salts, namely, 1,2,4-triazolium (**2**), 3-amino-1,2,4-triazolium (**3**), 4-amino-1,2,4-triazolium (**4**), 3,5-diamino-1,2,4-triazolium (**5**), 2-methylimidazolium (**6**), imidazolium (**7**), pyrazolium (**8**), 3-amino-5-hydroxypyrazolium (**9**), dicyandiamidine (**10**), and 2,4-diamino-6-methyl-1,3,5-triazin (**11**), was synthesized with cations. These energetic salts were fully characterized through FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The structures of **2**, $\mathbf{3\cdot7H_2O}$, $\mathbf{6\cdot2H_2O}$, **8**, and $\mathbf{10\cdot4H_2O}$ were further confirmed through single crystal X-ray diffraction. Their thermal stabilities were investigated through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Results indicated that all of the salts possess excellent thermal stabilities with decomposition temperatures ranging from 225.7 °C to 314.0 °C. On the basis of Kamlet–Jacobs formula, we carefully calculated their detonation velocity and detonation pressure. All of the salts, except **11**, exhibit promising detonation performances with a detonation pressure of 20.23–28.69 GPa and a detonation velocity of 7050–8218 m s^{-1}. These values are much higher than those of TNT. The impact sensitivities of the compounds were determined via Fall hammer test. All of the compounds show excellent impact sensitivities of >50 J, and this finding is higher than that of TATB (50 J). Therefore, these ionic salts with excellent energetic properties could be applied as new energetic materials.

Introduction

Energetic materials, including explosives, propellants, and pyrotechnics, are widely used in various military and civilian fields.[1-3] To satisfy the requirements of improved energetic materials, researchers synthesized high-energy-density materials with decreased sensitivity to thermal shock and friction and with enhanced detonation performances, including detonation velocity and detonation pressure.[4] Nitrogen-rich energetic salts with high energy and low sensitivity play an important role in energetic materials because of their high heat of formation (HOF), density, thermal stability, good oxygen balance, and environmental greenness.[5-14]

Tetrazole moiety is a promising energetic building block in this research area because it contains a large number of energetic N–N and C–N bonds, exhibits extensive hydrogen bonding, and decomposes to produce a high percentage of dinitrogen.[15-18] The introduction of *N*-oxides to tetrazoles and bitetrazoles results in greater energetic performances, such as high densities and low sensitivities, than the introduction of tetrazoles without *N*-oxides does.[12, 19-21] Thomas M. Klapötke[22] reported that 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (**BTO**) is a good energetic building block that presents various properties. **BTO** exhibits excellent thermal stabilities but shows comparative insensitivity, although it contains a very high amount of nitrogen that reaches 66.7%. Therefore, **BTO** is a good candidate of energetic anions. Recently, a family of energetic salts based on BTO salts were synthesized as potential energetic materials [22-26]. Triazolium , limidazolium and dicyandiamidine cations are important nitrogen-rich cations used to construct high-performance energetic materials[27-33]. The combination of the nitrogen-rich cations and BTO anion would be expected to possess both high nitrogen concomitant high energetic properties and desired remarkable sensitivities.

Herein, we aimed to design and synthesize bitetrazole-derived compounds based on **BTO** with a high percentage of nitrogen content and thus develop powerful and eco-friendly energetic materials with enhanced thermal stability. In this study, a series of energetic salts was designed and synthesized (Scheme 1) on the basis of **BTO**. These salts were fully characterized through multinuclear NMR spectroscopy, IR spectroscopy, elemental analysis (EA), differential scanning

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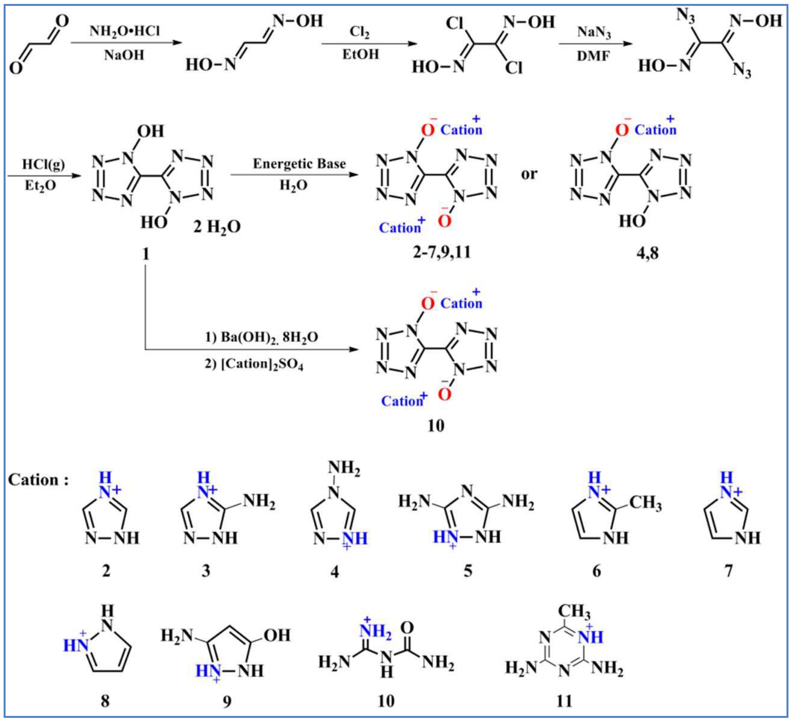
calorimetry (DSC), and thermogravimetric analysis (TGA). As expected, several ionic salts exhibited potentially useful thermal stabilities, detonation properties, and low sensitivities; therefore, these salts can be applied as energetic materials.

Results and Discussion

Syntheses

1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (**BTO**) was synthesized in accordance with a previously described procedure.[22] **BTO** was synthesized starting from glyoxal, which was treated with hydroxylamine to form glyoxime. Glyoxime was then chlorinated with Cl_2 gas in ethanol; chloro/azido exchange occurred and yielded diazidoglyoxime, which was cyclized under acidic conditions (HCl gas in diethyl ether) to produce **1**. All of the compounds except dicyandiamidine salt **10** were synthesized after **1** was treated with stoichiometric amounts of the respective free base. Dicyandiamidine salt **10** was isolated from a reaction mixture containing the barium salt of **1** and dicyandiamidine sulfate after the poorly soluble barium sulfate was removed through filtration. The formation of nitrogen-rich salts (**2**–**11**) is straightforward, as shown in Scheme 1.



Scheme 1. Synthesis of energetic salts based on 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (BTO).

Spectroscopy

The structures of these prepared energetic compounds are supported by their corresponding FT-IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The data are listed in the Experimental Section. In the IR spectra, the investigated compounds reveal a number of bands between 1540 and 700 cm^{-1}; the bands show a characteristic pattern of ν(NN), ν(NCN), γ(CN), and aromatic ring vibrations of the tetrazole in the vibrational spectra[22]. The characteristic absorption of N–H bonds was observed in all of the compounds at 3100–3500 cm^{-1}; the bands at 3300–3500 cm^{-1} are attributed to the amino group of the energetic salts. In the ^{13}C NMR spectra, all of the signals, except a signal associated with the anion at δ = 134.84–135.69 ppm, are assigned to the energetic cations.

X-ray crystallography

Suitable crystals (**2**, **3·7H$_2$O**, **6·2H$_2$O**, **8**, and **10·4H$_2$O**) were obtained by slowly evaporating water at room temperature and then subjected to single crystal X-ray analysis. The selected crystallographic data are summarized in Table 1. The structures of **2**, **6·2H$_2$O**, and **8** are displayed in Figs. 1–3. The structures of **3·7H$_2$O** and **10·4H$_2$O** are presented in

Figs. S1 and S2.† Additional information regarding crystal-structure determinations are provided in ESI.† In this paper, only three examples of the determined crystal structures are discussed. The solid-state structures of the remaining compounds are described in Supporting Information.

Table 1. Crystal data and structure refinement parameters of **2**, **3·7H$_2$O**, **6·2H$_2$O**, **8** and **10·4H$_2$O**.

Compound	**2**	**3·7H$_2$O**	**6·2H$_2$O**	**8**	**10·4H$_2$O**
Empirical formula	$C_6H_8N_{14}O_2$	$C_{30}H_{63}N_{80}O_{17}$	$C_{10}H_{18}N_{12}O_4$	$C_5H_6N_{10}O_2$	$C_6H_{20}N_{16}O_6$
Formula weight	308.26	1816.60	370.36	238.20	412.38
CCDC number	1435484	1444741	1435485	1435486	1441695
Crystal size [mm^3]	0.65×0.25×0.15	0.80×0.70×0.20	0.20×0.19×0.12	0.20×0.18×0.12	0.21×0.20×0.19
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	C2/c	P2$_1$/c	P-1	P2$_1$/c	P1
a [Å]	15.2410(12)	19.0634(3)	5.3860(5)	10.042(2)	3.5356(14)
b [Å]	10.5185(8)	11.83085(18)	7.2676(6)	13.882(2)	13.300(5)
c [Å]	7.7546(7)	32.1874(7)	11.1149(11)	6.7012(12)	18.164(7)
α[°]	90	90	106.362(7)	90	72.222(4)
β[°]	100.767(8)	95.3131(17)	92.344(13)	98.155(4)	87.207(4)
γ[°]	90	90	104.613(9)	90	86.316(4)
V [Å^3]	1221.26(18)	7228.2(2)	401.00(6)	924.8(3)	811.3(6)
Z	8	4	1	4	2
ρ_{calcd}[g·cm^{-3}]	1.688	1.670	1.534	1.711	1.688
T[K]	293	293K	113	113(2)	100(2)
F(000)	640.0	3756.0	194.0	488	432
$R_{int.}$	0.0329	0.0291	0.0147	0.0483	0.0327
Data	1093	12900	1800	2122	5081
Restraints	0	1	5	3	9
parameters	108	1189	133	163	506
R1 ($I > 2\sigma$ (I))	0.0474	0.0637	0.0313	0.0422	0.0927
ωR_2 ($I > 2\sigma$ (I))	0.1247	0.1790	0.0893	0.1191	0.2447
R_1(all data)	0.0522	0.0886	0.0329	0.0442	0.0955
ωR_2(all data)	0.1331	0.2054	0.0904	0.1213	0.2473

Compound **2** crystallizes in the monoclinic space group C2/c with a calculated density of 1.688 g cm^{-3}. Fig. 2 shows that the molecular unit of crystalline **2** consists of one anion and two 1,2,4-triazolium cations. The selected data and parameters from their X-ray structures are listed in Table 1. All of the atoms of **BTO** anion are almost coplanar, and the largest torsion angle is 179.6(2)°. This angle is located at N006-N002-C009-C009^1. The N–N bond lengths in the tetrazolate of BTO anion vary from 1.304(2) Å to 1.340(2) Å, which are between N–N single bonds (1.454 Å) and N=N double bonds (1.245 Å).[34] Furthermore, the C–C bond connecting the two tetrazole moieties and the N–O bonds are found between a C–C single bond and a C=C double bond (d(C0090-C009^1) = 1.437(3) Å) and between a N–O single bond and a N=O double bond (d(O001-N002) = 1.3209(17) Å), respectively. This finding indicates the conjugation of the negative charge throughout the aromatic rings, as seen in other tetrazolate salts.[35, 36] One bis(tetrazole-1-oxide) anion, whose packing is affected by several strong hydrogen bonds, is coordinated by four additional 1,2,4-triazolium cations. Strong hydrogen bonds between N003-H003···O001 (1.830 Å) and N004-H004···O001 (1.616 Å) are also illustrated in Fig. 1(a). The packing structure of **2** was built and linked to a 2D layer by various hydrogen bonds. After the layer was assembled, further interlinking of the 2D layers to 3D supramolecules was stimulated by π-stacked or other weak interactions, as shown along the *b* axis in Fig. 1(b).

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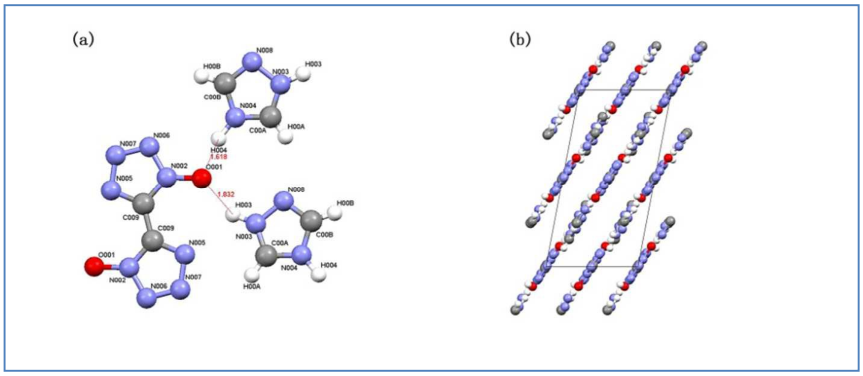

Figure 1. Molecular structure (a) and packing diagram in the unit cell (b) of **2**.

Compound **6·2H$_2$O** crystallizes in the triclinic space group P-1 with two H$_2$O per molecule and exhibits a density of 1.534 g cm^{-3} at 113 K. Its crystallographic data are summarized in Table 1. As shown in Fig. 2(a), all of the atoms of **BTO** anion are almost coplanar, with the largest torsion angle of 179.73(8)° in O(1)-N(1)-N(2)-N(3). The bond lengths, bond angles, and torsion angles of anions are similar to those of compound **2**. For example, the bond lengths of C–C, which connects two tetrazole moieties, range from 1.437(3) Å to 1.4393(19) Å; this value indicates a delocalization effect. This length is significantly shorter than that of a typical C–C single bond of 1.54 Å. Hydrogen bond interactions between cations and anions are provided in ESI.† In Fig. 2(a), one anion is coordinated by two 2-methylimidazolium cations and two hydrate water molecules to form four strong intermolecular hydrogen bonds [N(6)-H(6) ··N(4)#2 (1.978 Å), O(2)-H(2B) ··O(1)#5 (1.855 Å)]. The 2D layer structure is formed by intermolecular hydrogen bonds, and the 2D layer stacks are parallel to the crystallographic *c* axis in Fig. 2(b).

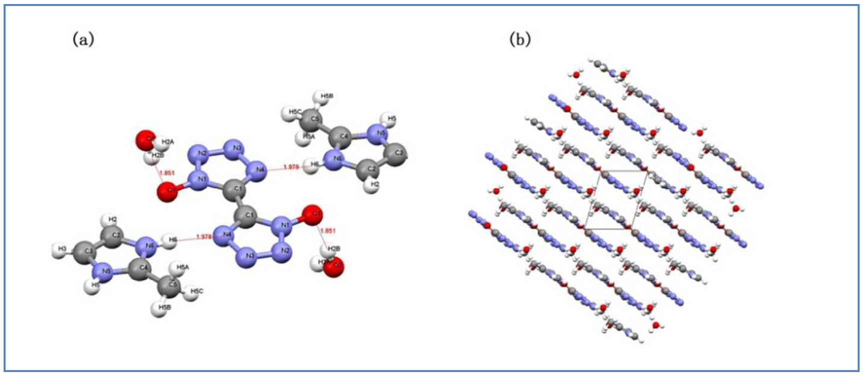

Figure 2. Molecular structure (a) and packing diagram in the unit cell (b) of **6·2H$_2$O**.

In Table 1, **8** crystallizes in the monoclinic space group P2$_1$/c with four molecules per unit cell and exhibits a crystal density of 1.711 g cm^{-3} at 113 K. Fig. 3(a) shows the presence of two asymmetric units. Each unit contains one **BTO** anion and one limidazolium cation. For the anion, a small torsion angle of the two tetrazole-oxide rings at N(1)-C(1)-C(2)-N(8) of −8.6(2)° is detected. The bond lengths are similar to those of compound **2** and **6·2H$_2$O**. The N–N bond lengths in the tetrazolium ring range from 1.3027(15) Å to 1.35 594(15) Å, which are between the lengths of N–N single bonds (1.454 Å) and N=N double bonds (1.24 Å). The C–N bond lengths in the tetrazolium ring vary from 1.3311(15) Å to 1.3448(14) Å, which are between the lengths of C–N single bonds (1.470 Å) and C=N double bonds (1.220 Å). This result also demonstrates the conjugation of the negative charge throughout the aromatic rings. Among the bonds in the crystals of **8**, the intermolecular hydrogen bonds of tetrazole [O(2)-H(2) ··O(1)#1 (1.637 Å), N(9)-H(9) ··O(1) (1.945 Å)] are the strongest. Hydrogen bond interactions between cations and anions are provided in ESI.† In Fig. 3(b), the supercell consisting of layers of **8** are arranged in a wave-like layer structure along the *a* axis.

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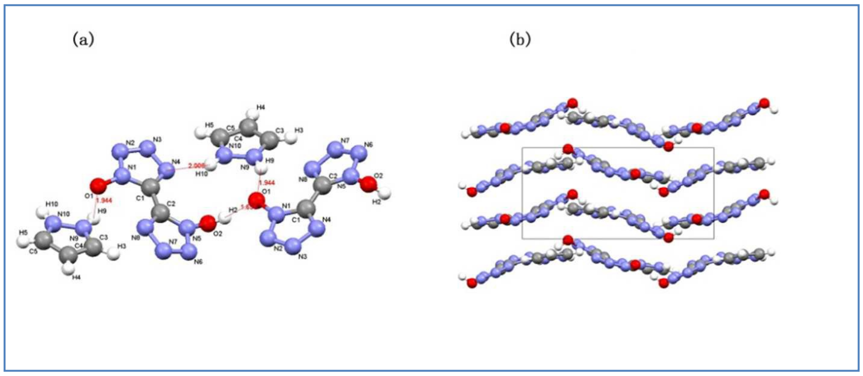

Figure 3. Molecular structure (a) and packing diagram in the unit cell (b) of **8**.

Thermal behavior

Thermal stability is a key factor of energetic materials because unacceptable thermal stabilities strictly limit their applications. Compounds **2**–**11** were examined through DSC and TGA at a heating rate of 10 °C/min in flowing high purity nitrogen (ESI,† Figs. S1–S10). In Table 2, the decomposition peak temperatures (T_d) of the compounds are higher than that of RDX (230.0 °C) except compound **8** (T_d = 228 °C); T_d of some compounds (**5**,**11**) is even higher than that of TNT (295.0 °C). T_d of all of the products range from 228 °C (**8**) to 413 °C (**11**); this value indicates that these compounds are promising energetic materials that exhibit good thermal stability. In all of the salts, the exothermic temperature range agrees with that of weight loss. In these energetic materials, the least mass loss of 53.7% can be observed in the exothermic temperature range of **3**; this phenomenon can be attributed to its low oxygen content. In particular, salt **2** decomposes with the highest mass loss of 90.8% at the exothermic temperature range.

Energetic Properties

The heat of formation (HOF) is an important parameter used to evaluate the performance of energetic compounds; this parameter was calculated by using Gaussian 09 program [37]. The calculated HOFs are summarized in Table 2. All of the compounds exhibit positive HOFs ranging from 120.1 kJ/mol (**10·4H$_2$O**) to 1385.3 kJ/mol (**9**), which are higher than those of HMX (104.8 kJ/mol), TNT (95.3 kJ/mol), and RDX (83.8 kJ/mol).

On the basis of the calculated density and calculated HOFs, we determined the detonation properties of **2**–**11** by using the empirical Kamlet–Jacobs (K–J) equations. In Table 2, the detonation pressures of the salts ranged from 19.76 GPa (**11**) to 28.69 Gpa (**4**), which are comparable to those of TNT (19.5 GPa) and RDX (34.9 GPa). Their detonation velocities range from 6820 m/s (**11**) to 8218 m/s (**4**), which are also comparable to those of TNT (6881 m/s) and RDX (8748 m/s). The detonation velocities of the salts except **11** were higher than that of TNT. These properties suggest that these energetic salts may be used as environmentally friendly and nitrogen-rich energetic materials.

Sensitivity should be extensively investigated because this parameter is closely linked with the safety of handling and applying explosives. In this work, the impact sensitivities were determined using a BAM Fallhammer apparatus with a 10 kg drop weight. These sensitivities were >50 J (Table 2). This result indicates that all of the energetic salts are more sensitive than RDX (7.4 J), HMX (7 J), TNT (15 J), and TATB (50 J).

Table 2. Properties of compounds 2-11 compared with TNT/RDX

	T_{dec}[a] [°C]	ρ[b] [g/cm^3]	N+O[c] [%]	$\Delta_f H_{cation}$[d] [kJ/mol]	$\Delta_f H_{anion}$[e] [kJ/mol]	ΔH_L[f] [kJ/mol]	$\Delta_f H_{salt}$[g] [kJ/mol]	P[h] [GPa]	vD[i] [m/s]	IS[j] [J]
2	246.7	1.688	74.00	838.5	587.7	1301.70	956.00	24.49	7577	> 60
3·7H$_2$O	282.7	1.670	75.71	802.0	587.7	643.027	1548.67	21.05	7050	> 50
4	243.0	1.667	79.38	936.3	420.7	472.00	885.00	28.69	8218	> 50
5	303.0	1.650	77.15	764.0	587.7	1209.49	906.21	23.05	7405	> 50
6·2H$_2$O	269.0	1.534	62.67	672.4	587.7	1173.72	751.13	20.23	7142	> 60

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7	262.0	1.715	65.33	723.0	587.7	1316.05	717.64	22.03	7151	> 50
8	225.7	1.711	72.24	821. 5	420.7	491.02	751.13	25.45	7693	> 50
9	273.0	1.702	70.62	1010.7	587.7	1223.81	1385.29	28.48	8151	> 60
10·4H$_2$O	254.0	1.688	78.05	350.6	587.7	1168.85	120.05	25.41	7720	> 50
11	314.0	1.678	67.59	648.0	587.7	1130.96	752.74	19.76	6820	> 60
TNT[k]	295.0	1.648	18.50	-	-	-	95.3	19.5	6881	15
RDX[k]	230.0	1.806	37.84	-	-	-	83.8	34.9	8748	7.5
TATB[l]	324.0	1.930	69.74	-	-	-	-139.7	31.15	8114	50

[a] Decomposition peak temperature. [b] Calculated density. [c] Nitrogen and Oxygen content. [d] Calculated enthalpy of formation of cations, Reference. [32, 38][e] Calculated molar enthalpy for the formation of the anion, Reference.[22] [f] The lattice energy of the ionic salts. [g] Calculated molar enthalpy for the formation of the salts. [h] Detonation pressure. [i] Detonation velocity. [j] Impact sensitivity. [k] Reference.[38] [l] Reference.[9]

Conclusions

A series of BTO-based nitrogen-rich energetic salts were synthesized and fully characterized through multinuclear NMR spectroscopy, IR spectroscopy, elemental analysis (EA), DSC, and TGA. The structures of **2**, **3·7H$_2$O**, **6·2H$_2$O**, **8**, and **10·4H$_2$O** were further confirmed through single-crystal X-ray diffraction characterization. The DSC results revealed that all of the energetic salts exhibit excellent thermal stabilities with decomposition temperatures ranging from 225.7 (**8**) °C to 314 °C (**11**). All of the salts are insensitive to impact (>50 J); as such, these salts can be safely handled and can be applied to specific areas. Furthermore, the calculated detonation parameters of the new energetic compounds yield detonation pressures and velocities ranging from 19.76 GPa (**11**) to 28.69 GPa (**4**) and from 6820 m/s (**11**) to 8218 m/s (**4**), respectively. On the basis of reasonable detonation properties, excellent impact sensitivities, and superior stabilities, we can use these compounds as potential “green” energetic materials in commercial applications.

Experimental Section

Safety Precautions! Although we experienced no difficulties in the synthesis and characterization of these materials, small-scale syntheses are strongly encouraged. All of the compounds should be handled with extreme care, and eye protection and gloves must be worn at all times.

General Methods: Chemical reagents and solvents were purchased from Aladdin (Shanghai, China) and used as supplied without further purification. ^{1}H NMR and ^{13}C NMR spectra were obtained using a JEOL GSX 600 MHz nuclear magnetic resonance (NMR) spectrometer in a DMSO solution by using tetramethylsilane as an internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet-5700 FTIR spectrometer by using pressed KBr pellets to evaluate the chemical bonding of the samples from 4000 cm^{-1} to 400 cm^{-1}. Elemental analyses (C, H, and N) were conducted using a Vario EL CUBE device. DSC was performed by a Q200 DSC instrument (TA Instruments, United States) at a heating rate of 10 °C/min in flowing high-purity nitrogen. TGA was performed with an SDT Q600 TGA instrument (TA Instruments, United States) at a heating rate of 10 °C/min in flowing high-purity nitrogen.

X-ray Crystallography: The single crystals of **2**, **3·7H$_2$O**, **6·2H$_2$O**, **8**, and **10·4H$_2$O** were cultured via a slow solvent evaporation method. Data were collected using a three-circle Bruker platform diffractometer equipped with a SMART APEX II CCD detector. All calculations were performed using the Crystal Structure[39] crystallographic software package except for refinement, which was performed using SHELXL2014[40]. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The details of the data collection and refinement are presented in Table 1.

Computational details: Computations were performed in Gaussian 09 Suite.[37] The structures were geometrically optimized and the frequency was analyzed using a B3LYP function with a 6-31+G** basis set[41]. Single-point energies were

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calculated at the MP2(full)/6-311++G** level. All of the optimized structures were characterized as true local energy minima on the potential-energy surface without imaginary frequencies.

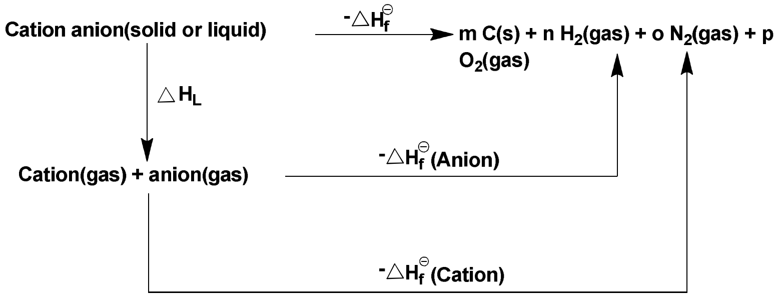

Figure 4. Born–Haber circle of ionic salt

According to the Born–Haber[42] (m, n, o, and p respectively stand for the factor of C, H_2, N_2, and O_2) energy cycle (Figure 4), the standard HOF of a salt can be simplified in Eq. (1):

$$\Delta_f H^0(Salt, 298K) = \Delta_f H^0(Cation, 298K) + \Delta_f H^0(Anion, 298K) - \Delta H_L \quad (1)$$

where ΔH_L is the lattice energy of the salts, which can be predicted by the formula proposed by Jenkins et al.[42, 43] [Eq. (2)]

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

where n_M and n_X depend on the nature of the ions M^{p+} and X^{q-}, respectively; these parameters are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. Lattice potential energy (U_{POT}) is expressed as follows [Eq. (3)]

$$U_{POT}/\text{kJ}\cdot\text{mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

where ρ_m is the density, M_m is the chemical formula mass of the ionic material, and γ and δ are coefficients, whose values are described in previous studies.[42, 43]

HOF is an important parameter that represents the energy content of a material. Positive values correspond to enhanced detonation properties. The enthalpies of BTO^- and BTO^{2-} are 420 and 587.7 kJ/mol, respectively. The HOF of the gas phase of the selected cations were obtained through isodesmic reactions.[44, 45] The representative reactions are shown in Scheme 2. The calculated total energy (E_0), zero-point energy (ZPE), and other thermal factors are obtained in ESI.† The HOFs of the cations and the anion are listed in Table 2.

Detonation velocity (D) and detonation pressure (P) were evaluated by the empirical K–J equations, as shown in Eqs. (4) and (5):[43,46,47]

$$D = 1.01(N\overline{M}^{1/2}Q^{1/2})^{1/2}(1+1.3\rho) \quad (4)$$

$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2} \quad (5)$$

where D is the detonation velocity (km/s), P is the detonation pressure (GPa), N is the explosive detonation that generates gas moles per gram (mol/g), $\overline{M}$ is the gaseous product with an average molecular weight (g·mol^{-1}), Q is the explosive detonation chemical energy (kJ/g) per gram, and ρ is the density (g·cm^{-3}). Q should be calculated before D and P are determined. Q is also determined by ΔH_f of the detonation reactant and product. In this study, N, $\overline{M}$, and Q are calculated on the basis of the chemical composition of each explosive.[47]

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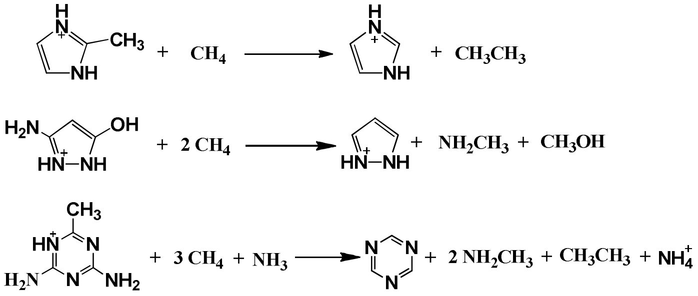

Scheme 2. Isodesmic reaction schemes for selected compounds

Synthesis of 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate Dihydrate: 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate was synthesized according to a procedure reported in the literature.[22]

Bis-1,2,4-triazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (2): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 5 mL distilled water, and 1,2,4-triazolium (138.1 mg, 2 mmol), previously dissolved in 3 ml water was added. The mixture was heated and filtered. After cooling to room temperature, **2** crystallized as colorless blocks to yield 249.4 mg (0.81 mmol, 81%). DSC (10 °C/min): 227 °C (m.p), 246.7 °C (dec.). IR (KBr) ν/cm^{-1}: 3495 (vs), 3412 (vs), 3140 (s), 2923 (s), 1891 (w), 1636 (w), 1570 (w), 1428 (s), 1384 (m), 1227 (s), 1166 (w), 1040 (s), 951 (w), 906 (s), 730 (m), 637 (w), 520 (m). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 8.89. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 145.39, 135.63. elemental analysis (%) calcd for $C_6H_{10}N_{14}O_2$ (308.17): C, 23.38; H, 2.62; N, 63.62; found: C, 23.26; H, 2,51; N, 63.62.

Bis-3-amino-1,2,4-triazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (3): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 3 mL distilled water, and 3-amino-1,2,4-triazole (168.2 mg, 2 mmol), previously dissolved in 4 ml water was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **3** crystallized as colorless needles, yield 256.9 mg (0.76 mmol, 76%). DSC (10 °C/min): 282.7 °C (dec.). IR (KBr) ν/cm^{-1}: 3400 (s), 3151 (s), 2698 (w), 1808 (w), 1696 (s), 1630 (w), 1571 (w), 1506 (w), 1419 (m), 1360 (w), 1319 (w), 1234 (m), 1173 (w), 1064 (w), 948 (m), 784 (w), 717 (w), 519 (w). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 7.91. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 154.67, 143.81, 135.61. elemental analysis (%) calcd for $C_{30}H_{64}N_{80}O_{17}$ (338.20): C, 21.31; H, 2.98; N, 66.25; found: C, 21.06; H, 3.01; N, 66.20.

4-amino-1,2,4-triazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (4): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was suspended in a few milliliters of water, and 4-amino-1,2,4-triazole (168.2 mg, 2 mmol) was added. After boiling and stirring the mixture for a few minutes, **4** precipitated as thin, colorless plates upon cooling the solution to room temperature, yield 174.1 mg (0.64 mmol, 64%). DSC (10 °C/min): 213 °C (m.p.) 243 °C (dec.). IR (KBr) ν/cm^{-1}: 3497 (s), 3408 (s), 3178 (w), 3129 (w), 2926 (w), 1637 (w), 1424 (w), 1365 (w), 1271 (vw), 1241 (w), 1072 (w), 1031 (w), 668 (w). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 9.19, 7.57. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 144.62, 135.63, 119.08. elemental analysis (%) calcd for $C_4H_8N_{12}O_3$ (272.1): C, 17.65; H, 2.94; N, 61.77; found: C, 17.91; H, 2.37; N, 61.44.

Bis-3,5-diamino-1,2,4-triazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (5): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 3 mL distilled water, and 3,5-diamino-1,2,4-triazole (198.2 mg, 2 mmol), previously dissolved in 4 ml water was added dropwise resulting in the formation of a white precipitate at room temperature. The solution was stirred for a few minutes, and then filtered, washed with cold water and dried in vacuo to afford 331.4 mg of **5** as a white powder in a yield of 90%. DSC (10 °C/min): 303 °C (dec.). IR (KBr) ν/cm^{-1}: 3418 (vs), 3117 (m), 1700 (m), 1652 (s), 1419 (m), 1230 (w), 1169 (vw), 1050 (w), 1010 (w), 733 (w). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 7.15. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 155.07, 135.55. elemental analysis (%) calcd for $C_6H_{12}N_{18}O_2$ (368.2): C, 19.57; H, 3.261; N, 68.48; found: C, 19.73; H, 3.17; N, 69.28.

Bis-2-methylimidazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (6): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was suspended in a few milliliters of water, and 2-methylimidazole (164.2 mg, 2 mmol) was added. After boiling and stirring the mixture for a few minutes, After cooling, the precipitate was collected by filtration, and then 315 mg of **6** was obtained as white solid in a yield of 85%. DSC (10 °C/min): 240 °C (m.p.) 269 °C (dec.). IR (KBr) ν/cm^{-1}: 3430 (s), 3129 (s), 2917 (s), 2713 (s), 1955 (w), 1621 (m), 1420 (s), 1406 (s), 1349 (w), 1330 (w), 1303 (w), 1230 (s), 1168 (m), 1116 (w), 1086 (w), 1051 (w), 999 (w), 890 (w), 769 (m), 665 (w), 501 (m). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 7.29, 2.45. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 144.33, 135.31, 119.89, 12.41. elemental analysis (%) calcd for $C_{10}H_{18}N_{12}O_4$ (370.29): C, 32.42; H, 4.90; N, 45.38; found: C,32.30; H, 4.92; N, 45.40.

Bis-imidazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (7): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 3 mL distilled water, and imidazole (136.2 mg, 2 mmol), previously dissolved in 4 ml water was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, **7** crystallized as colorless needles, yield 233 mg (0.76 mmol, 76%). DSC (10 °C/min): 258 °C (m.p.) 262 °C (dec.). IR (KBr) ν/cm^{-1}: 3410 (s), 3145 (m), 1631 (m), 1574 (w), 1425 (m), 1288 (w), 1169 (w), 1080 (m), 927 (w), 757 (m), 627 (w). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 9.09, 7.70. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 135.62, 119.77. elemental analysis (%) calcd for $C_8H_{10}N_{12}O_2$ (306.20): C, 31.38; H, 3.29; N, 54.88; found: C,31.30; H, 3.32; N, 54.79.

Pyrazolium 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (8): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 3 mL distilled water, and 1,2-diazole (138.16 mg, 2 mmol), previously dissolved in 4 ml water was added dropwise resulting in the formation of a white precipitate at room temperature. The solution was stirred for a few minutes, and then filtered, washed with cold water and dried in vacuo to afford 207 mg of **8** as a white powder in a yield of 87%. DSC (10 °C/min): 225.7 °C (dec.). IR (KBr) ν/cm^{-1}: 3496 (s), 3410 (s), 3145 (s), 3090 (s), 1624 (m), 1533 (m), 1413 (m), 1395 (m), 1356 (m), 1312 (w), 1218 (s), 1176 (s), 1128 (m), 1097 (s), 1064 (m), 1015 (w), 996 (w), 806 (m), 612 (w), 774 (m), 486 (m). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25°C) δ/ppm: 14.11, 8.14, 6.62. ^{13}C NMR (150 MHz, ([D$_6$]DMSO, 25°C) δ/ppm: 135.69, 134.13. elemental analysis (%) calcd for $C_5H_6N_{10}O_2$ (238.13): C, 25.22; H, 2.54; N, 58.81; found: C, 25.10; H, 2.56; N, 58.90.

Bis-3-amino-5-hydroxypyrazole 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (9): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 3 mL distilled water, and 3-amino-5-hydroxypyrazole (198.2 mg, 2 mmol), previously dissolved in 4 ml water was added. After boiling and stirring the mixture for a few minutes, water was removed by filtrate, and then 316.68 mg of **9** was obtained as light yellow solid in a yield of 86%. DSC (10 °C/min): 233 °C (m.p.) 273 °C (dec.). IR (KBr) ν/cm^{-1}: 3411 (s), 3198 (s), 2308 (vw), 1635 (w), 1401 (s), 1231 (m), 1165 (w), 1046 (w), 998 (w), 727 (w), 501 (w). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 12.76, 7.03, 4.90. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 160.76, 155.01, 135.52, 74.41. elemental analysis (%) calcd for $C_8H_{12}N_{14}O_4$ (368.23): C, 26.10; H, 3.28; N, 53.24; found: C, 25.870; H, 3.56; N, 53.90.

Bis-dicyandiamidine 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (10): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate(206 mg, 1 mmol) was suspended in a few milliliters of water. $Ba(OH)_2{\cdot}8H_2O$ (316 mg, 1 mmol) was added to the clear solution, and the mixture was heated until boiling to obtain a white, poorly soluble deposit. The white barium salt was filtered off under vacuum and dried. The substance was proved to be anhydrous by elemental analysis. Afterwards, the white powder was suspended in water to mix it with dicyandiamidine sulfate (504.54 mg, 2 mmol). $BaSO_4$ was filtered off and water was removed by evaporating the filtrate, and then 313 mg of **10** was obtained as white solid in a yield of 76%. DSC (10 °C/min): 230 °C (m.p.) 254 °C (dec.). IR (KBr) ν/cm^{-1}: 3368 (vs), 1750 (m), 1700 (m), 1606 (m), 1420 (m), 1354 (w), 1241 (w), 1084 (w), 625 (w), 458 (w). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 8.04, 7.18. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 156.30 155.63,134.84. elemental analysis (%) calcd for $C_6H_{20}N_{16}O_6$ (412.38): C, 17.48; H, 4.89; N, 54.35; found: C, 17.30; H, 4.90; N, 54.50.

Bis-2,4-diamino-6-methyl-1,3,5-triazin 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate (11): 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate dihydrate (206 mg, 1 mmol) was dissolved in 3 mL distilled water, and 2,4-diamino-6-methyl-1,3,5-triazin (250.26 mg, 2

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mmol), previously dissolved in 4 ml water was added dropwise resulting in the formation of a white precipitate at room temperature. The solution was stirred for a few minutes, and then filtered, washed with cold water and dried in vacuo to afford 378.3 mg of **11** as a white powder in a yield of 90%. DSC (10 °C/min): 314 °C (dec.). IR (KBr) ν/cm^{-1}: 3291 (s), 3116 (s), 2324 (vw), 1685 (s), 1623 (m), 1550 (w), 1463 (w), 1398 (m), 1241 (m), 1174 (w), 1104 (w), 1065 (w), 1006 (w), 906 (w), 792 (w), 742 (m), 552 (m). ^{1}H NMR (600 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 7.44, 2.18. ^{13}C NMR (150 MHz, [D$_6$]DMSO, 25 °C) δ/ppm: 171.03, 164.28, 135.60,23.39. elemental analysis (%) calcd for $C_{10}H_{16}N_{18}O_2$ (420.29): C, 28.57; H, 3.81; N, 60.00; found: C, 29.02; H, 4.19; N, 60.15.

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A series of nitrogen-rich heterocyclic 1*H*,1′*H*-5,5′-bistetrazole-1,1′-diolate salts was synthesized. Results indicated that all of the salts possess excellent thermal stabilities with decomposition temperatures ranging from 225 °C to 314 °C. All of the compounds show excellent impact sensitivities of >50 J and promising detonation performances with a detonation pressure of 20.23–28.69 GPa and a detonation velocity of 7050–8218 m/s. Therefore, these ionic salts with excellent energetic properties could be applied as new energetic materials.