文章编号: 1006-9941(2015)12-1221-07

Two new Energetic Ionic Salts with Environmental Protection: Preparation and Thermal Properties of IMI·TNR and 4-AT·TNR

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Abstract: The two kinds of energetic ionic salts IMI·TNR and 4-AT·TNR (IMI=imidazolium, 4-AT=4-amino-1,2,4-triazolium, TNR=2,4,6-trinitro resorcinol) were synthesized. The crystal structures were determined by IR, elemental analysis and X-ray single crystal diffraction. The thermal decomposition mechanisms were investigated with DSC and TG. The non-isothermal reaction kinetic parameters were researched by Kissinger's method and Ozawa's method on the basic of DSC results. The mpact sensitivity, friction sensitivity and flame sensitivity for two ionic salts was measured. Results show that the crystal of IMI · TNR is monoclinic , space group $P2_1/c$ with a density of 1.779 g · cm^{-3} and decomposition temperature of 223.4 ℃ and 4-AT · TNR is triclinic, space group *P*-1 with a density of 1.772 g · cm^{-3} and decomposition temperature of 259.8 ℃. The values of T_b, $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$ are 222.4 ℃, −213.06 J · K^{-1} · mol^{-1}, 302.89 kJ · mol^{-1} and 407.10 kJ · mol^{-1} for IMI · TNR and 257.3 ℃, −221.31 J · K^{-1} · mol^{-1}, 129.66 kJ · mol^{-1} and 243.24 kJ · mol^{-1}, respectively. They are insensitive to impact, friction and flame stimuli.

Key words: azolium cations; energetic materials; explosives; 2, 4, 6-trinitro resorcinol(TNR)

CLC number: TJ55; O62 **Document code**: A **DOI**: 10.11943/j.issn.1006-9941.2015.12.014

1 Introduction

The high energy density materials (HEDMs), especially those materials with excellent performance and environmental compatibility, have been concerned[1-8]. In which, five-azole heterocycles and their derivatives are desired due to their high nitrogen content, enthalpy of formation, density, easily achieved oxygen balance[9-16], among which salts and complexes based on IMI and 4-AT (IMI=imidazolium, 4-AT=4-amino-1,2,4-triazolium) are well researched.

On the other hand, styphnate (2,4,6-trinitro resorcinol, TNR), is the main ingredient of a famous traditional primary explosives lead styphnate, which is utilized as primary explosive, and contribute to an environment in both military and civilian fields. Although energetic styphnate salts may exhibit comparative excellent performance in their designed complexes or salts with PA[17-21], the studies on them are rarely mentioned, and the reports are focused on energetic nitrate, perchlorate or azide salts.

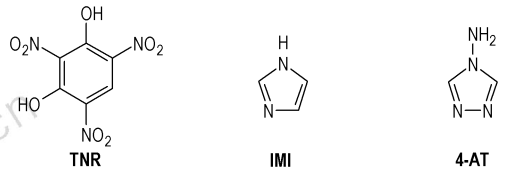
In this contribution, two energetic materials IMI · TNR and 4-AT · TNR based on styphnate (TNR=2,4,6-trinitro resorcinol) (Scheme 1) were obtained and characterized by X-ray diffraction analysis. Both materials were fully characterized by elemental analysis, FT-IR spectroscopy, and their thermal effects, sensitivities and performances were gained.

2 Experimental

2.1 Materials and Physical Techniques

All the reagents and solvents were of analytical grade and used without further purification as commercially obtained.

Elemental analyses were performed on a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra were recorded on a Bruker Equinox 55 infrared spectrometer (KBr pellets) in the range of 4000−400 cm^{-1} with a resolution of 4 cm^{-1}. DSC and TG measurements were carried out by using a Pyris-1 differential scanning calorimeter and a Pyris-1 thermogravimetric analyzer (Perkin Elmer, USA) under dry nitrogen as atmosphere with flowing rate of 20 mL · min^{-1}. The energy of combustion was measured by an oxygen bomb calorimeter (Parr 6200, USA).



TNR IMI 4-AT

Scheme 1 Structural formulas of TNR, IMI, 4-AT

Impact sensitivity was determinedwith a Fall Hammer Apparatus. Salt (30 mg) was placed between two steel poles and was hit by a 5.0 kg drop hammer.

Friction sensitivity was determined on a MGY-1 pendularfriction sensitivity apparatus by a standard procedure using 20 mg of the sample. When salt was compressed between two steel poles with mirror surfaces at the pressure of 3.92 MPa, and then was hit horizontally with a 1.5 kg hammer fell from 90° angle.

Flame sensitivity was determined by following a standard method, in which the sample was ignited by standard black powder pellet. Salt (20 mg) was compacted to a copper cap under the press of 58.8 MPa and was ignited by standard black powder pellet.

2.2 Synthesis of the compounds

As shown in Scheme 2, the IMI · TNR(1), 4-AT · TNR

Received Date: 2015-04-18; **Revised Date**: 2015-06-30

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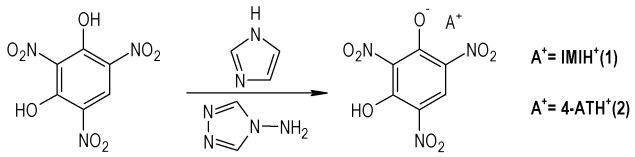
(2) were synthesized by the reactions between the appropriate free bases and styphnate acid in water with 1 : 1 molar quantities.



Scheme 2 Synthesis of the salts of IMI · TNR (1), 4-AT · TNR (2)

IMI(0.14 g, 2 mmol) and TNR (0.49 g, 2 mmol) were dissolved in 30 mL H_2O and stirred for 30 min at 70 ℃. The suspension was stirred for 1 h and filtrated immediately into a cup. The synthesis conditions of 4-AT·TNR are basically the same, but only change IMI to 4-AT in the same mole ratio, two kinds of yellow crystals would be obtained after 1d with yield of 75% and 70%, respectively. IR for IMI·TNR (KBr, ν/cm^{-1}): 3421, 2601, 1632, 1533, 1473, 1415, 1266, 1184, 1102, 904, 840, 790, 705, 630. Anal. calcd for IMI · TNR: C 34.50, N 22.36, H 2.24; found: C 34.42, N 22.29, H 2.31. IR for 4-AT·TNR (KBr, ν/cm^{-1}): 3363, 3139, 2684, 1633, 1574, 1529, 1455, 1380, 1340, 1288, 1187, 1086, 930, 833, 717, 617. Anal. calcd for 4-AT · TNR: C 29.18, N 29.79, H 2.13; found: C 29.11, N 29.69, H 2.19.

2.3 X-ray Crystallography

The crystal data of IMI·TNR(1), 4-AT·TNR(2) were collected with a Bruker Smart CCD diffractometer with graphite monochromatic Mo K_α radiation (λ = 0.71073Å) at 294(2) K using φ and ω scan modes. Their structures were determined and refined by direct methods using SHELXS-97[22] and SHELXL-97[23] programs. All hydrogen atoms were located from difference Fourier electron-density maps and refined isotropically, while all non-hydrogen atoms were obtained from the difference Fourier map and refined anisotropically. The results concerning crystallographic data collection and structure refinements are given in Table 1.

CCDC-951714 and CCDC-951715 contain the supplementary crystallographic data for the title compound (**1**) and (**2**), and these data can be acquired free of charge from the Cambridge Crystallographic Data Centre via www. ccdc. cam. ac. uk/data- request/cif (or through the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-Mail: deposit@ ccdc. cam. ac. uk or http://www. ccdc. cam. ac. uk).

3 Results and Discussion

3.1 Molecular Structures

Fig. 1 shows themolecular structure and packing diagram of IMI · TNR and 4-AT · TNR, respectively. The selected bond lengths and angles are listed in Table 2, and the hydrogen bond lengths and bond angles of IMI · TNR and 4-AT · TNR in Tables 3 and 4, respectively.

IMI · TNR crystallizes in a monoclinic cell, which belongs to space group $P2_1/c$ with cell parameters of a=6.006(1)Å, b=13.170(3)Å and c=14.816(4)Å. For 4-AT · TNR, it is

Table 1 Crystal data and structure refinements for IMI · TNR and 4-AT · TNR

compound	IMI · TNR	4-AT · TNR
CCDC No.	951714	951715
formula	$C_9H_7N_5O_8$	$C_8H_7N_7O_8$
formula mass /g · mol^{-1}	313.20	329.21
crystal system	monoclinic	triclinic
space group	$P2_1/c$	P-1
crystal size/mm	0.33 × 0.32 × 0.29	0.53 ×0.53 × 0.19
Z	4	2
a/Å	6.006(1)	8.157(2)
b/Å	13.170(3)	8.2047(19)
c/Å	14.816(4)	10.159(3)
α /(°)	–	78.844(9)
β/(°)	93.818(4)	89.602(11)
γ/(°)	–	68.005(7)
volume/Å^3	1169.4(5)	616.9(3)
ρ_c/g · cm^{-3}	1.779	1.772
μ (Mo K_α)/mm^{-1}	0.159	0.160
F(0 0 0)	640.0	336.0
θ/ (°)	6.32–58.26	5.4–58.22
reflection collected /unique	10192/3091	7561/3230
R_1, wR_2[$I > 2\sigma(I)$]	0.0412/0.1069	0.0451/0.1237
R_1, wR_2(all data)	0.0522/0.1156	0.0564/0.1334
GOF onF_2	1.001	0.999
largest diff. peak and hole/e · Å^{-3}	0.32/–0.23	0.76/–0.27

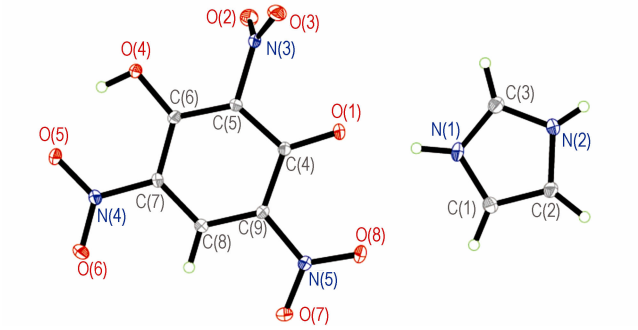
triclinic, space group P-1 with a density of 1.772 g · cm^{-3} and cell parameters of a = 8.157(2) Å, b = 8.2047(19) Å and c=10.159(3) Å.

In IMI anions, the C—N bond lengths range from 1.321(2) Å[N(1)—C(3)] to 1.375(2)Å[N(1)—C(1)] with an average value of 1.351 Å, which is longer than the normal C = N bond length (1.270Å) and shorter than the normal C—N bond length (1.450 Å). In 4-AT anions, the C—N bond lengths range from 1.307(2) Å[N(1)—C(1)] to 1.362(2) Å[N(3)—C(1)] with an average value of 1.328Å, which is longer than the normal C = N bond length (1.270 Å) and shorter than the normal C—N bond length (1.450 Å)[24]. There are two N—N bond[N(1)—N(2), 1.369(2) Å and N(3)—C(4), 1.412(2)Å], longer than the normal N = N bond length of 1.252 Å and shorter than the normal N—N bond length of 1.470 Å.[24]

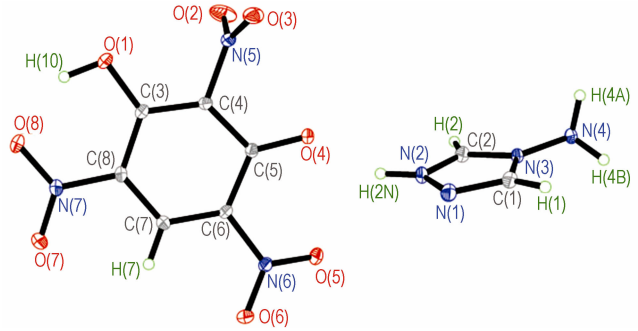
In IMI · TNR molecule, there is only one ionic bond between every IMI anion and TNR cation. Plane of the imidazole ring and the phenyl ring are not in one plane but parallel substantially to each other (Angle between the two planes is 1.696(59)°). Conversely, in 4-AT · TNR the benzene and triazole ring lie in different planes, which are angulated by 75.212(56)° towards each other.

As shown in Fig. 1c, each TNR anion within the crystal structure is surrounded by five TNR anions linked by hydrogen bonds to oxygen atoms on the phenolic hydroxyl and nitro and some van der Waals forces. The hydrogen bonds′ length of the crystal structure are from 2.5684 Å to 3.4641 Å, only one

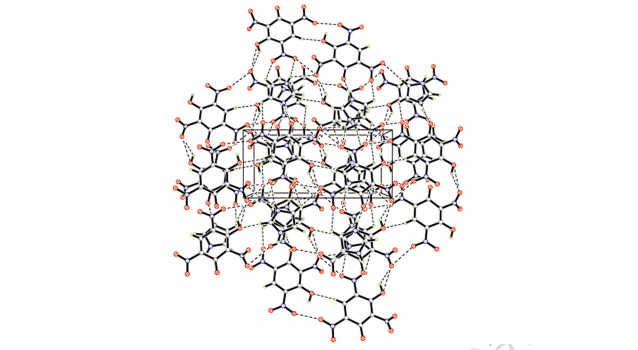
strong hydrogen bonds connected O4, which results in a smaller crystal density, D_c=1.779 g·cm^{-3}. In Fig.1d, each 4-AT anion connected with three TNR cations through four hydrogen bonds[N(2)—H(2)N···O(4), N(2)—H(2)N···O(5), N(4)—H(4)B···O(3), N(4)—H(4B)···O(7)]. The hydrogen bonds' lengths of the crystal structure are from 2.5843 Å to 3.3896 Å.



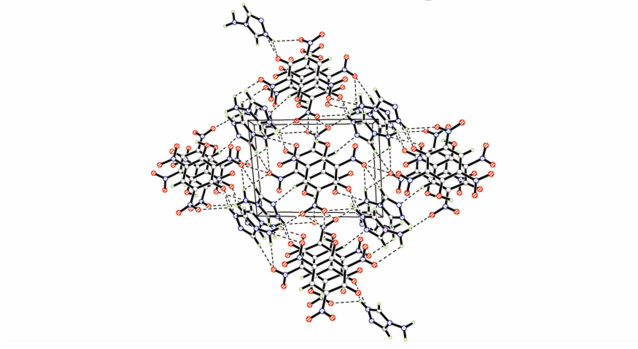
a. molecular structure of IMI · TNR



b. molecular structure of 4-AT · TNR



c. packing diagram of IMI · TNR



d. packing diagram of 4-AT · TNR's

Fig. 1 Molecular structure and packing diagram of IMI · TNR and 4-AT·TNR

Table 2 Selected bond lengths and bond angles

IMI · TNR		4-AT · TNR	
bond	length /Å	bond	length /Å
O(4)—C(6)	1.332(2)	O(1)—C(3)	1.339(1)
O(4)—H(4)O	0.84(2)	O(1)—H(1)O	0.94(3)
O(6)—N(4)	1.232(1)	O(2)—N(5)	1.218(2)
O(1)—C(4)	1.248(1)	O(3)—N(5)	1.224(2)
O(5)—N(4)	1.250(1)	O(4)—C(5)	1.256(2)
N(3)—O(3)	1.229(2)	O(5)—N(6)	1.232(2)
N(3)—O(2)	1.225(2)	O(6)—N(6)	1.235(2)
N(3)—C(5)	1.463(2)	O(7)—N(7)	1.232(2)
O(7)—N(5)	1.226(1)	O(8)—N(7)	1.254(2)
N(5)—C(9)	1.452(2)	N(5)—C(4)	1.462(2)
N(5)—O(8)	1.224(2)	N(6)—C(6)	1.453(1)
IMI · TNR		**4-AT · TNR**	
bond	angle/(°)	bond	angle /(°)
C(6)—O(4)—H(4)O	106(2)	C(3)—O(1)—H(1)O	104(2)
O(3)—N(3)—O(2)	123.7(1)	O(2)—N(5)—O(3)	123.8(1)
O(3)—N(3)—C(5)	117.9(1)	O(2)—N(5)—C(4)	118.1(1)
O(2)—N(3)—C(5)	118.4(1)	O(3)—N(5)—C(4)	118.1(1)
O(7)—N(5)—C(9)	118.3(1)	O(5)—N(6)—O(6)	123.4(1)
O(7)—N(5)—O(8)	122.2(1)	O(5)—N(6)—C(6)	118.8(1)
C(9)—N(5)—O(8)	119.5(1)	O(6)—N(6)—C(6)	117.8(1)
N(5)—C(9)—C(8)	116.8(1)	O(7)—N(7)—O(8)	121.6(1)
N(5)—C(9)—C(4)	120.9(1)	O(7)—N(7)—C(8)	120.1(1)
C(8)—C(9)—C(4)	122.3(1)	O(8)—N(7)—C(8)	118.3(1)
N(3)—C(5)—C(4)	115.8(1)	O(1)—C(3)—C(4)	118.1(1)

Table 3 Hydrogen bond lengths and bond angles for IMI · TNR

D—H···A	d(D—H) / Å	d(H···A) / Å	d(D···A) / Å	∠D—H···A /(°)
N(1)—H(1)N···O(1)[a]	0.9100	1.7700	2.6666	169.00
N(2)—H(2)N···O(6)[b]	0.8000	2.4100	3.1733	161.00
N(2)—H(2)N···O(2)[c]	0.8000	2.5600	3.0966	126.00
O(4)—H(4)O···O(2)[d]	0.8500	2.4300	2.8766	114.00
O(4)—H(4)O···O(5)	0.8500	1.8300	2.5684	145.00
O(4)—H(4)O···N(4)	0.8500	2.4300	2.9069	116.00
C(1)—H(1)···O(8)[a]	0.9500	2.5600	3.0848	115.00

Note: Symmetry operators: (a) 1-*x*,1/2+*y*,1/2-*z*; (b) -1+*x*,*y*,*z*; (c) -*x*,1/2+*y*,1/2-*z*; (d) 1+*x*,*y*,*z*.

Table 4 Hydrogen bond lengths and bond angles for 4-AT · TNR

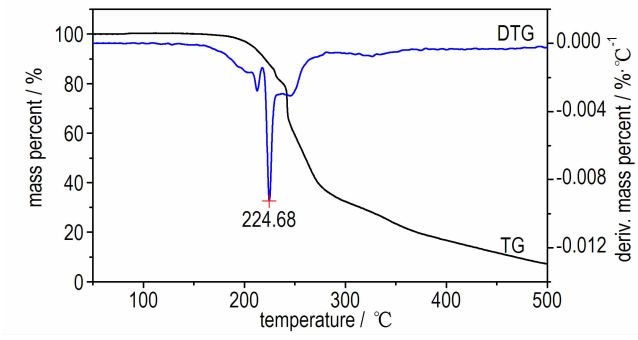
D—H···A	d(D—H) / Å	d(H···A) / Å	d(D···A) / Å	∠D—H···A /(°)
O(1)—H(1)O···O(5)[a]	0.9400	2.3900	2.9419	117.00
O(1)—H(1)O···O(8)	0.9400	1.7500	2.5843	147.00
O(1)—H(1)O···N(7)	0.9400	2.3900	2.9307	116.00
N(2)—H(2)N···O(4)[a]	0.9000	1.7900	2.6255	153.00
N(2)—H(2)N···O(5)[a]	0.9000	2.4000	3.0317	127.00
N(4)—H(4)A···O(6)[b]	0.9600	2.1900	3.1443	173.00
N(4)—H(4)B···O(3)	0.9100	2.5300	3.0263	114.00

Note: Symmetry operators: (a) -1+*x*,1+*y*,*z*; (b) -1+*x*,1+*y*,-1+*z*.

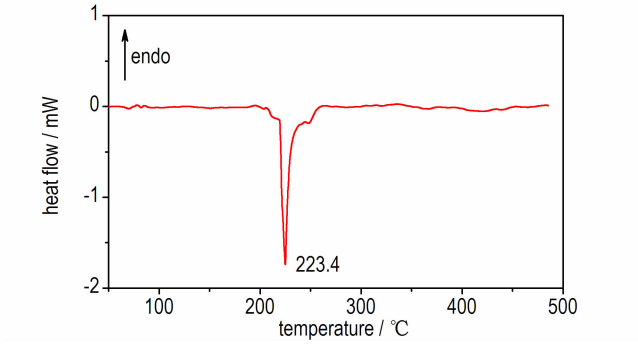
3.2 Thermal decomposition

The thermal behavior, DSC and TG-DTG curves of IMI · TNR and 4-AT · TNR at a linear heating rate of 10 ℃ · min^{-1}, recorded in a nitrogen atmosphere separately, are given in Fig. 2 and Fig. 3.

Fig. 2b shows that there are three exothermic peaks (the first and last small exothermic peaks are overshadowed in the middle of quickly sharp exothermic peak) with the main peak temperature of 223.4 ℃ of IMI·TNR, and there is the mass loss of 62.5% corresponding to this temperature range in Fig. 2a. The mass of the final residue is 6.5% at 500 ℃.



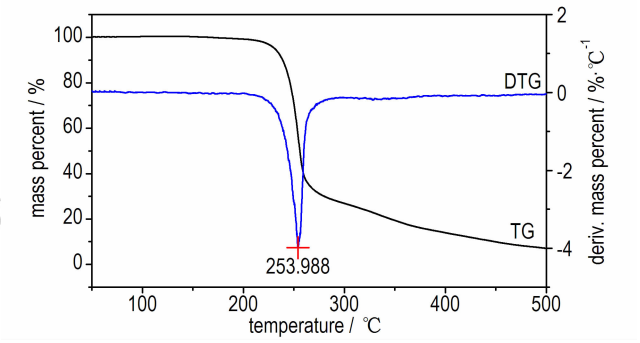
a. TG-DTG curve



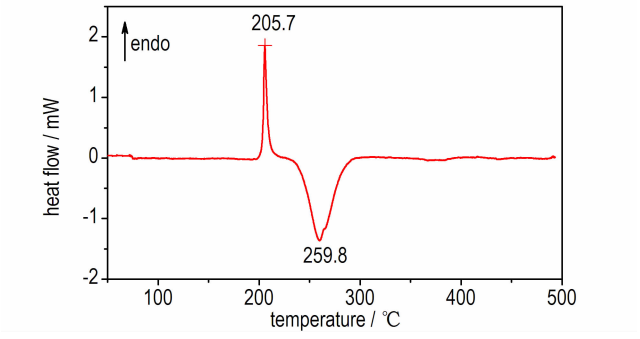
b. DSC curve

Fig. 2 TG-DTG and DSC curves of IMI · TNR in a nitrogen atmosphere at heating rate of 10 ℃ · min^{-1}

Moreover, Fig. 3b exhibits two sharp peaks. One is endothermic melting peak, and another is rapidly decomposed peak. The first endothermic process starts from 195.2 ℃ and gained a peak temperature at 205.7 ℃. Following is an exothermic process, which indicates that the product immediately decomposes after melting. The decompose temperature ranges from 230.8 ℃ to 297.3 ℃ with the peak temperature at 259.8 ℃. Fig. 3a shows that the compound loses mass 70% in this process, and remains 7.5% finally. After the rapid decomposition the products of the two compounds are H_2O, CO_2, N_2 and a small amount of residue.



a. TG-DTG curve



b. DSC curve

Fig. 3 TG-DTG and DSC curves of 4-AT · TNR in a nitrogen atmosphere at a heating rate of 10 ℃ · min^{-1}

3.3 Energy of combustion and enthalpy of formation

We used Kissinger's method[25] and Ozawa's method[26] to study the kinetic parameters of the rapidly exothermic process of title compounds, based on the DSC curves obtained under the condition of static air at heating rates of 5, 10, 15 ℃ · min^{-1} and 20 ℃ · min^{-1}. The peak temperatures (T_p) of the exothermic process at different heating rates, the apparent activation energy (E_a), the pre-exponential factor (A) and the linear correlation coefficient of two compounds were determined and listed in Table 5 and Table. 6. The calculated results with two methods, are similar and all in the normal range (40–400 kJ · mol^{-1})[27].

Table 5 Peak temperatures of the first main exothermic stage at different heating rates and kinetic parameters for IMI · TNR with different method

β /℃ · min^{-1}	T_p /℃	Kissinger's method				Ozawa's method			
		E/kJ · mol^{-1}	ln(A/s^{-1})	r	S	E/kJ · mol^{-1}	ln(A/s^{-1})	r	S
5	219.6	310.65	75.62	−0.9904	0.0992	303.27	–	−0.9909	0.0431
10	223.4								
15	225.7								
20	228.7								

Note: β is the heating rate, r is the linear correlation coefficient.

Table 6 Peak temperatures of the first main exothermic stage at different heating rates and kinetic parameters for 4-AT · TNR with two method

β /℃ · min^{-1}	T_p /℃	Kissinger's method				Ozawa's method			
		E/kJ · mol^{-1}	ln(A/s^{-1})	r	S	E/kJ · mol^{-1}	ln(A/s^{-1})	r	S
5	249.7								
10	259.8	132.97	29.41	−0.9912	0.0912	134.89	–	−0.9923	0.0395
15	265.6								
20	273.4								

3.4 Calculation of the Thermal Explosion Properties

According to the formula group[28] as follow, the corresponding critical temperatures of thermal explosion (T_b), entropies of activation ($\Delta S^{\neq}$), enthalpies of activation ($\Delta H^{\neq}$), and free energies of activation ($\Delta G^{\neq}$) of the decomposition reaction are obtained, and listed in Table 7.

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^2 + d\beta^2$$

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{p0}}}{2R}$$

$$A = \frac{k_B T}{h} e^{\Delta S^{\neq}/R}$$

$$\Delta H^{\neq} = E - RT$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$$

Among them, a, b, c and d are constant coefficients, and T_{pi} is the peak temperature of the exothermic process at different heating rates. The k_B is the Boltzmann constant, 1.381×10^{-23} J · K^{-1} and h is the Planck constant, 6.626×10^{-34} J · s, $T = T_{p0}$ and $A = A_k$ (Kissinger's method).

Table 7 Calculated T_b, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$

substance	T_{p0} /K	T_b /K	$\Delta S^{\neq}$ /J · K^{-1} · mol^{-1}	$\Delta H^{\neq}$ / kJ · mol^{-1}	$\Delta G^{\neq}$ /kJ · mol^{-1}
IMI · TNR	489.1	495.5	−213.06	302.89	407.10
4-AT · TNR	513.2	530.4	−221.31	129.66	243.24

3.5 Physicochemical properties

The impact and friction sensitivities as well as the flame sensitivity were determined on the basic of the China National Military Standard (CNMS)[29-31]. The impact sensitivities for title compounds, RDX, HMX and TNT are shown in Table 8. The results show that the title compounds are insensitive to friction sensitivity (misfire under the condition of pressure 3.92 MPa, hammer angle 90°) and flame sensitivity (do not fire when the distance between agents and the black powder pellet<6 cm). Meanwhile, they misfire in the impact sensitivities measurement even the drop height was above 80 cm. It reveals that the two compounds have low impact sensitivity, friction sensitivity and flame sensitivity.

Table 8 Physicochemical properties of IMI · TNR, 4-AT · TNR, RDX, HMX and TNT

substance	T_m /℃	T_d /℃	ρ /g · cm^{-3}	ΔU_c /kJ · kg^{-1}	ΔH_c /kJ · kg^{-1}	ΔH_f /kJ · mol^{-1}	OB /%	N /%	S_i /%	S_f /%	S_F /cm
IMI · TNR	Dec.	223	1.78	−14329	−14366.6	−42.18	−68.96	22.36	/	/	/
4-AT · TNR	205	260	1.77	−11313	−11356.3	−409.69	−55.89	29.78	/	/	/
RDX[28]	Dec.	230	1.91	−9600	/	/	−21.6	37.84	80	76±8	/
HMX[28]	Dec.	287	1.82	−9880	/	/	−21.6	37.84	100	100	/
TNT[28,32]	81	300	1.65	−15220	/	/	−74.0	18.50	4–8	4–6	/

Note: T_m is the melting point (peak). T_d is the peak temperature. ρ is the calculated density. ΔU_c is the energy of combustion. ΔH_c is the enthalpy of combustion of cation. ΔH_f is the molar enthalpy of formation. OB is the oxygen balance (O-2C-H/2-Z) ×1600/M; O, the number of oxygen atoms; C, the number of carbon atoms; H, the number of hydrogen atoms; Z, the number of metal atoms; M, the molecular mass of the compound. N is the nitrogen content. S_i denotes the impact sensitivity, firing rate with 10.0 kg drop hammer. S_f denotes the friction sensitivity, firing rate at the pressure of 3.92 MPa with a 1.5 kg hammer from 90° angle. S_F denotes the flame sensitivity, the maximum height of 100% ignition.

Compared with RDX, HMX and TNT, some physicochemical properties of the twotitle compounds are shown in Table 8. Obviously, physicochemical properties of IMI · TNR and 4-AT · TNR (T_d=223, 260 ℃, ΔU_c=−14329, −11313 kJ · kg^{-1}, ρ=1.77, 1.78 g · cm^{-3}) are both not lower than RDX (T_d = 230 ℃, ΔU_c = −9600 kJ · kg^{-1}) and close to HMX (T_d = 287 ℃, ΔU_c = −9880 kJ · kg^{-1}), whose densities are even higher than that of TNT (ρ=1.65 g · cm^{-3}).

3.6 Calculation of Detonation Parameters

In accordance with the Brinkley-Wilson rule[28], the detonation reaction equations of title compounds are given in Scheme 3.

Using method of literature[33-34], the heat of detonation (Q_V), detonation temperature (T_B), detonation pressure (p_{CJ}), detonation velocity (D) of two materials were calculated, and results are shown in Table 9. Compared with conventional explosives, explosion heat and detonation temperature of IMI · TNR are close to RDX (Q_V=1266.08 kJ · mol^{-1},

$$C_9H_7N_5O_8 \longrightarrow 3.5\,H_2O + 2.5\,N_2 + 4.5\,CO + 4.5\,C$$

$$C_8H_7N_7O_8 \longrightarrow 3.5\,H_2O + 3.5\,N_2 + 4.5\,CO + 3.5\,C$$

Scheme 3 Detonation reaction equations of the title compounds

Table 9 Detonation parameters of the title compounds

substance	Q_V /kJ · mol^{-1}	T_B /K	p_{CJ} /GPa	D /km · s^{-1}
IMI · TNR	1327.38	3279.14	16.33	5.97
4-AT · TNR	963.35	2321.10	20.88	6.76

T_B =3700 K), while explosion pressure and detonation velocity of 4-AT · TNR are comparable to that of TNT (p_{CJ} = 19.1 GPa, D=6.92 km · s^{-1})[28].

4 Conclusions

Two styphnate salts, with IMI and 4-AT cations were preparedwith a ratio 1 ∶ 1 in water solution. As characterized by X-ray diffraction, IMI · TNR is monoclinic, space group $P2_1/c$ with a density of 1.779 g · cm^{-3} and 4-AT · TNR is triclinic, space group P-1 with a density of 1.772 g · cm^{-3}. IMI · TNR and 4-AT · TNR are stabilized by a variety of hydrogen bonds in their crystals. In addition, the high decompose point are 224.4 ℃ and 259.8 ℃, and their activation energies are 306.96 kJ · mol^{-1} and 133.93 kJ · mol^{-1}. The sensitivity measuring shows that the two compounds are insensitive energetic materials confirming with their calculated results of detonation parameters. Compared with conventional explosives, heat of detonation and detonation temperature of IMI · TNR are close to RDX (Q_V = 1266.08 kJ · mol^{-1}, T_B = 3700 K), while the detonation pressure and detonation velocity of 4-AT · TNR are comparable to that of TNT (p_{CJ} = 19.1 GPa, D=6.92 km · s^{-1}).

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两种新型环保含能离子盐：IMI·TNR 和 4-AT·TNR 的制备和热性能

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摘 要：制备了两种含能离子盐 IMI·TNR 和 4-AT·TNR（IMI=咪唑，4-AT=4-氨基-1,2,4-三唑，TNR=2,4,6-三硝基间苯二酚）。采用 IR、元素分析和 X 射线单晶衍射确定了晶体结构。用差示扫描量热法（DSC）和热重分析（TG），分析了热分解机理。基于 DSC 的结果，采用 Kissinger 法和 Ozawa 法获得非等温反应的动力学参数。测定了两种离子盐的撞击感度、摩擦感度和火焰感度。结果表明，IMI·TNR 为单斜晶系，空间群为 $P2_1/c$，晶体密度为 1.779 g·cm^{-3}，分解温度为 223.4 ℃；4-AT·TNR 为三斜晶系，空间群为 P-1，晶体密度为 1.772 g·cm^{-3}，分解温度为 259.8 ℃。它们的 T_b、$\Delta S^{\neq}$、$\Delta H^{\neq}$ 和 $\Delta G^{\neq}$ 值分别为 222.4 ℃，−213.06 J·K^{-1}·mol^{-1}，302.89 kJ·mol^{-1} 和 407.10 kJ·mol^{-1}（IMI·TNR）和 257.3 ℃，−221.31 J·K^{-1}·mol^{-1}，129.66 kJ·mol^{-1} 和 243.24 kJ·mol^{-1}（4-AT·TNR）。它们对冲击、摩擦和火焰的刺激不敏感。

关键词：唑类阳离子；含能材料；炸药；2,4,6-三硝基间苯二酚（TNR）
中图分类号：TJ55；O62 **文献标志码**：A **DOI**：10.11943/j.issn.1006-9941.2015.12.014

读者·作者·编者

向作者致谢

近年，《含能材料》得到了广大作者的大力支持，为表达我们深深的谢意，特向 2014～2015 两年来发表两篇以上论文的作者（第一作者）赠送 2016 年全年《含能材料》。本刊期望在新的一年能继续得到广大作者更多的关心！欢迎赐稿！

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《含能材料》编辑部
二〇一五年十二月