



Preparation, Structure and Kinetic Analysis of the Thermal Behavior of Some Energetic Salts of 3-Hydrazino-4-amino-1,2,4-triazole

Jin-Ting WU, Jian-Guo ZHANG*, Mou SUN, Xin YIN
and Tong-Lai ZHANG

*State Key Laboratory of Explosion Science and Technology,
Beijing Institute of Technology, Beijing 100081, China*

**E-mail: zjgbit@bit.edu.cn*

Abstract: As a key research objective for low melting explosives and propellants, energetic salts have received worldwide attention. 3-Hydrazino-4-amino-1,2,4-triazole (HATr) is an important high-nitrogen compound (73.65% N) with good stability. This paper focuses on the energetic salts which were formed between HATr and picric acid (PA) or 2,4,6-trinitroresorcinol (TNR). Single crystals of HATr·PA and HATr·TNR·H₂O were grown and their crystal structures determined at low temperature. They both belong to the monoclinic system, P2₁/n space group. The thermal characteristics of the two target salts were investigated using DSC and TG-DTG. In addition, the non-isothermal decomposition kinetics, heats of combustion and sensitivity have also been investigated. The detonation pressures (P) and detonation velocities (D) of the salts have been calculated using the K-J equations. The results indicated that both salts have certain potential applications as gunpowder and propellant materials.

Keywords: synthesis, crystal structure, thermal analysis, 3-hydrazino-4-amino-1,2,4-triazole, energetic salts

Introduction

In the search for low melting explosives and propellants, energetic salts have generated widespread interest [1]. Energetic salts are a unique class of highly energetic materials due to their lower vapor pressures and higher densities compared to their atomically similar non-ionic analogs [2]. Their properties can

be carefully tuned via the choice of the component ions, and they are readily optimized and improved through the combination of different cations and anions [3]. Nitrogen-containing heterocycles are one of the sources of energetic salts [4]. Triazole is a high nitrogen-containing ring heterocycle which has a large number N-N and C-N bonds and therefore exhibits a large positive heat of formation [5]. 3-Hydrazino-4-amino-1,2,4-triazole (HATr) is a typical high-nitrogen triazole, with a nitrogen content of 73.65%, and shows good stability.

This paper focuses on the energetic salts which were formed by treating 3-hydrazino-4-amino-1,2,4-triazole (HATr) with picric acid (PA) and 2,4,6-trinitroresorcinol (TNR).

Experimental Section

Caution: *3-Hydrazino-4-amino-1,2,4-triazole and its salts are energetic materials with increased sensitivities towards shock and friction. Therefore, appropriate safety precautions have to be applied whilst synthesizing and handling them.*

Materials and physical techniques

All chemical reagents and solvents were analytically pure, commercial products. Elemental analysis was performed with a Flash EA 1112 fully-automatic trace element analyzer. Infrared spectra were measured using a Bruker Equinox 55 spectrometer with KBr pellets. DSC measurements were carried out with a Pyris-1 differential scanning calorimeter at a linear heating rate of 5 K·min⁻¹. The energies of combustion were measured using a Parr 6200 oxygen bomb calorimeter.

3-Hydrazino-4-amino-1,2,4-triazole di-hydrochloride [HATr·2HCl] was prepared according to the literature [6]. HATr itself was obtained by reacting 3-hydrazino-4-amino-1,2,4-triazole di-hydrochloride with lithium hydroxide.

Synthesis of the energetic salts of HATr

Synthesis of HATr·PA

A solution of HATr (1.140 g, 10 mmol) in water (50 mL) was added with stirring to a suspension of PA (2.291 g, 10 mmol) in water (50 mL) at 338 K. After stirring for 15 min, the solution was cooled to room temperature. The precipitate was collected by filtration, washed with methanol and dried in air to give the desired product as a yellow solid (2.278 g, 66.4%). IR(KBr): $\nu = 3347, 3256, 3087, 1645, 1559, 1432, 1338, 1159, 1080, 913, 786 \text{ cm}^{-1}$; Elemental analysis (%):

found: C 27.94, H 2.65, N 36.76; $C_8H_9N_9O_7$ requires: C 28.00, H 2.64, N 36.73.

Synthesis of $HATr \cdot TNR \cdot H_2O$

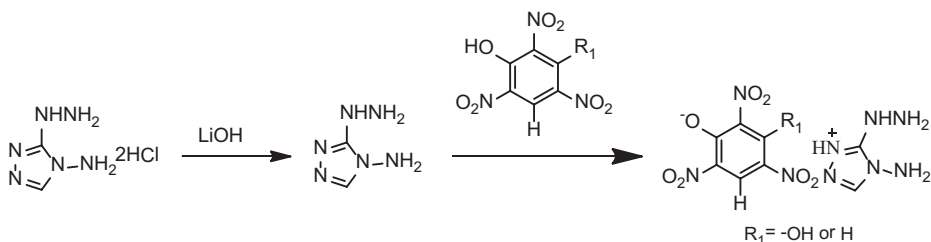
The same method was used as described for $HATr \cdot PA$ to form the product as a yellow solid (2.268 g, 63.1%). IR(KBr): $\nu = 3348, 3040, 2857, 1993, 1643, 1503, 1311, 1369, 1211, 1053, 912, 858 \text{ cm}^{-1}$; Elemental analysis (%): found: C 25.46, H 2.95, N 33.45; $C_8H_{11}N_9O_9$ requires: C 25.47, H 2.94, N 33.42.

X-ray data collection and structure refinement

Collection of X-ray data for $HATr \cdot PA$ and $HATr \cdot TNR \cdot H_2O$ was performed on a Rigaku Saturn 724+ CCD diffractometer (Mo K_α radiation, graphite monochromator). The structure was solved using direct methods and successive Fourier difference syntheses (SHELXS-97) [7], and refined using full-matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97) [8]. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The basic crystallographic data, measurement and refinement details are summarized in Table 1.

Results and Discussion

3-Hydrazino-4-amino-1,2,4-triazole hydrochloride was synthesized according to a literature procedure [6] starting from the reaction of the triaminoguanidinium chloride with formic acid, with hydrochloric acid as catalyst under reflux conditions. Lithium hydroxide was then used to neutralize the salt to obtain 3-hydrazino-4-amino-1,2,4-triazole. $HATr \cdot PA$ and $HATr \cdot TNR \cdot H_2O$ were prepared by reacting an $HATr$ aqueous solution with an aqueous suspension of PA or TNR, respectively. Scheme 1 shows the synthesis route for $HATr \cdot PA$ and $HATr \cdot TNR \cdot H_2O$. Both synthetic routes shown are basically acid-base reactions.



Scheme 1. Synthesis routes for 3-hydrazino-4-amino-1,2,4-triazole and its salts.

X-ray crystallography

Crystals of HATr·PA and HATr·TNR·H₂O that were suitable for X-ray diffraction were obtained by slow, spontaneous crystallization from water at room temperature. Their structures are shown in Figure 1. Crystallographic and structural refinement data are listed in Table 1, and selected bonds lengths and angles are listed in Table 2.

Table 1. X-ray data and parameters

Items	HATr·PA	HATr·TNR·H ₂ O
Empirical formula	C ₈ H ₉ N ₉ O ₇	C ₈ H ₁₁ N ₉ O ₉
Formula mass	343.24	377.26
Temperature (K)	153(2)	153(2)
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Z</i>	4	4
<i>a</i> (Å)	6.8928(17)	15.393(3)
<i>b</i> (Å)	22.670(6)	5.2670(10)
<i>c</i> (Å)	8.460(2)	19.042(4)
β (°)	96.889(4)	111.794(3)
<i>V</i> (Å ³)	1312.3(6)	1433.5(5)
<i>D_c</i> (g·cm ⁻³)	1.737	1.748
μ (M ₀ K α) (mm ⁻¹)	0.71073	0.71073
<i>F</i> (000)	704	776
θ (°)	2.586~29.131	2.139~29.131
Reflection measured	13083	10308
Independent reflection [R _{int}]	2991 [R _{int} =0.0295]	3796 [R _{int} =0.0217]
<i>S</i>	0.998	1.002
<i>R_I</i> , <i>wR₂</i> [<i>I</i> >2σ(<i>I</i>)]	0.0391, 0.0969 ^a	0.0384, 0.0967 ^b
<i>R_I</i> , <i>wR₂</i> (all)	0.0427, 0.1003 ^a	0.0472, 0.1031 ^b
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e·Å ⁻³)	-0.210, 0.043	-0.284, 0.050

^a $w = 1/[\sigma^2(F_o^2) + (0.0526p)^2 + 0.5800p]$, where $p = (F_o^2 + 2F_c^2)/3$.

^b $w = 1/[\sigma^2(F_o^2) + (0.0561p)^2 + 0.3600p]$, where $p = (F_o^2 + 2F_c^2)/3$.

Compound HATr·PA: in the PA anion, the C-C bond lengths range from 1.37 to 1.45 Å, which is longer than a C=C bond length (1.34 Å) and shorter than a normal C-C bond length (1.54 Å), maintaining the characteristics of a benzene ring. For the triazole ring, the angle of C1-N1-C2 is 106.71(11)°, and the angles of N1-C1-N2 and N1-C2-N3 are 106.15(11)° and 111.92(12)°, respectively. Additionally, the benzene and triazole rings lie in different planes (Figure 2a),

which are inclined at 68.54° .

Compound $\text{HATr} \cdot \text{TNR} \cdot \text{H}_2\text{O}$: the structure consists of one HATr cation, one TNR anion and one crystal-water molecule. In contrast to the $\text{HATr} \cdot \text{PA}$ crystal, the planes of the benzene and triazole rings are almost parallel, with an angle of inclination of 2.2° (Figure 2b).

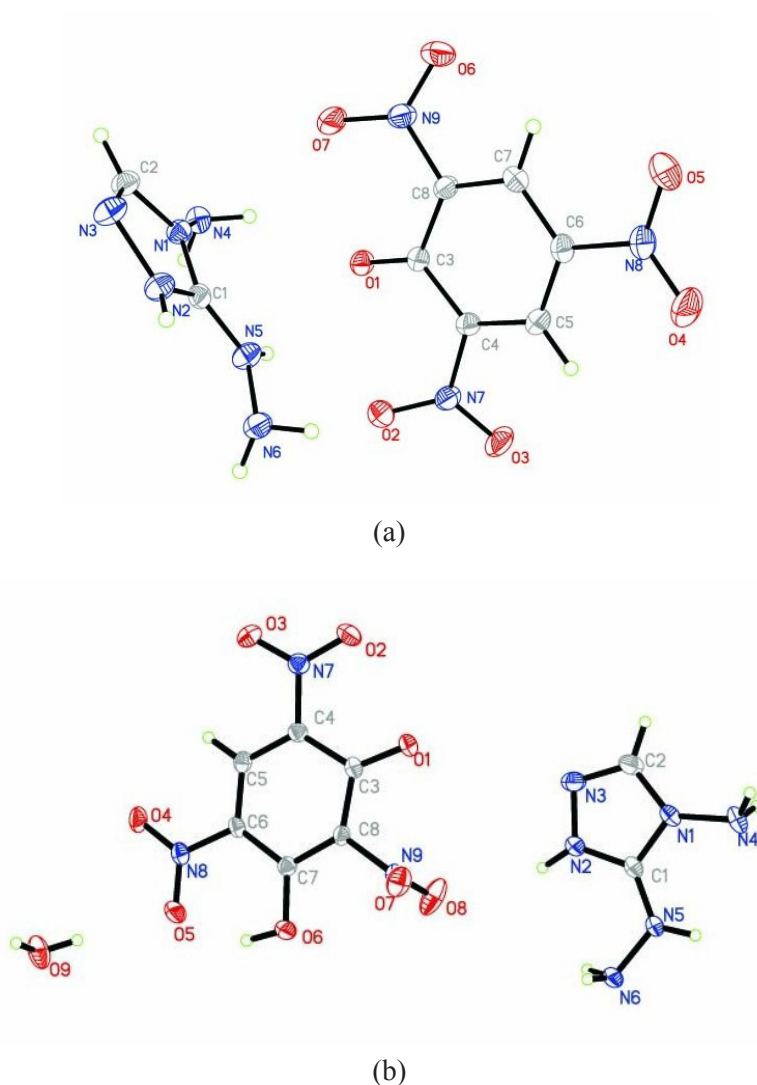
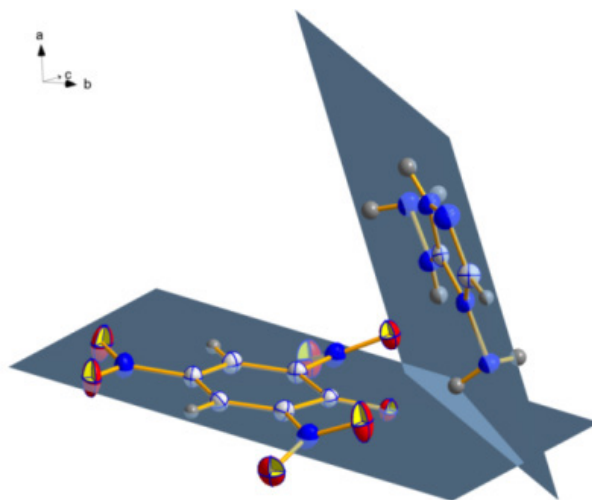


Figure 1. Molecular unit of (a) $\text{HATr} \cdot \text{PA}$ and (b) $\text{HATr} \cdot \text{TNR} \cdot \text{H}_2\text{O}$. Thermal ellipsoids are set to 50% probability.

Table 2. Selected bond lengths and angles

HATr·PA		HATr·TNR·H ₂ O	
Bond lengths (Å)			
O1-C3	1.2585(16)	O1-C3	1.2525(14)
N3-C2	1.2924(19)	N1-C2	1.3738(18)
N5-N6	1.4121(17)	N2-N3	1.3907(15)
N1-N4	1.4031(16)	N7-C4	1.4465(16)
N2-N3	1.3927(16)	C3-C4	1.4530(17)
N9-C8	1.4563(17)	N1-N4	1.4002(16)
Bond angles (°)			
C1-N1-C2	106.71(11)	C1-N1-C2	106.89(11)
C2-N3-N2	104.18(11)	C2-N1-N4	131.36(11)
N5-C1-N2	127.98(13)	O8-N9-C8	119.24(10)
O3-N7-C4	118.28(12)	N5-C1-N1	124.49(12)
N2-C1-N1	106.15(11)	C8-C3-C4	112.28(10)
O6-N9-C8	117.95(12)	O1-C3-C8	120.39(11)



(a)

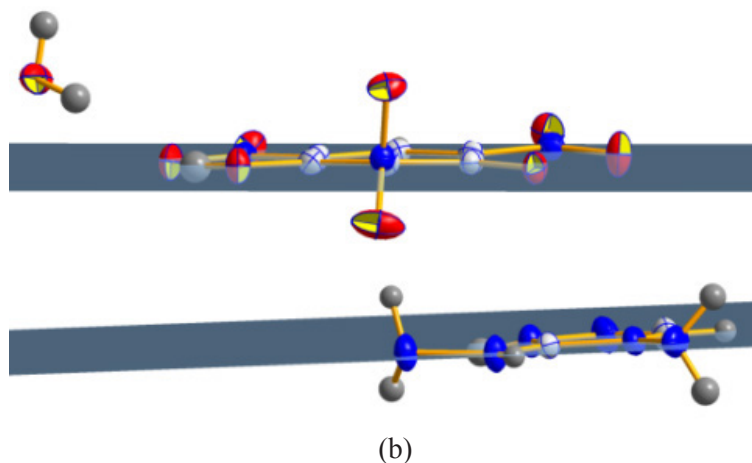


Figure 2. Plane view of (a) HATr·PA and (b) HATr·TNR·H₂O in unit cell.

Thermal decomposition

In order to investigate the thermal behavior of the two salts, DSC and TG-DTG curves at a linear heating rate of 5 K·min⁻¹ were recorded in a nitrogen atmosphere (Figures 3 and 4).

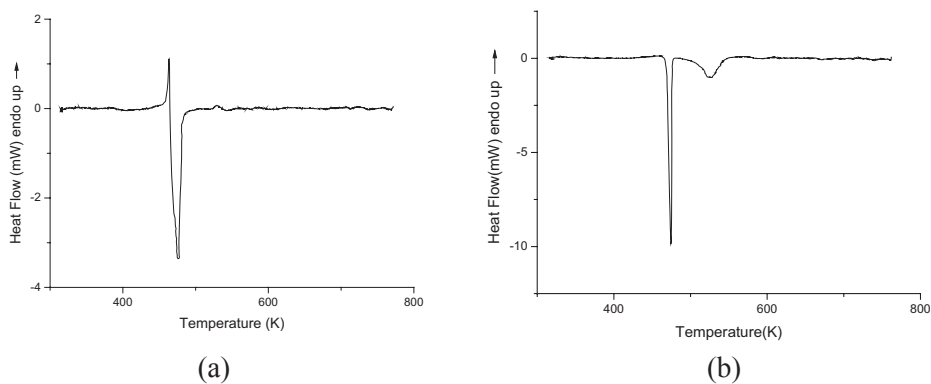


Figure 3. DSC curves of (a) HATr·PA and (b) HATr·TNR·H₂O at 5 K·min⁻¹.

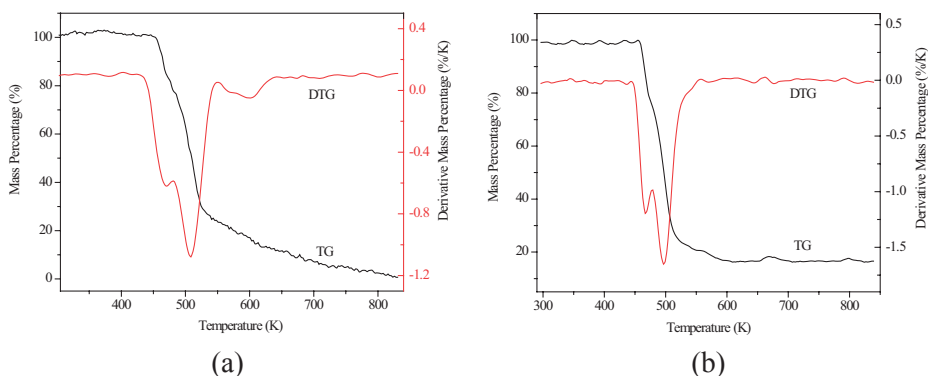


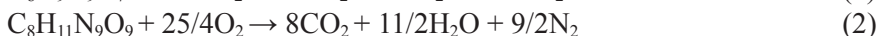
Figure 4. TG-DTG curves of (a) HATr·PA and (b) HATr·TNR·H₂O at 5 K·min⁻¹.

For HATr·PA, the DSC curve shows two processes: one endotherm at 449.1 K, and one exotherm commencing at 464.6 K with a peak temperature of 476.2 K, whilst the TG-DTG curves indicate three stages in the process of thermal decomposition. The first mass loss (15.7%) occurs at 445.7 K. The second mass loss (53.3%) occurs at 523.2 K. The final stage is a slow process of thermal decomposition with continuous mass loss and no residue remaining.

For HATr·TNR·H₂O, the DSC curve shows that there are two decomposition processes: one sharp exotherm occurs at 461.8 K, with a further broad exotherm at 524.7 K (maximum). The TG-DTG curves also indicate two mass loss stages and one slow loss in the process of thermal decomposition. The first mass loss (22.4%) occurs at 457.6 K. The second mass loss (50.6%) occurs at 474.1 K. The final stage is a slow process of thermal decomposition with continuous mass loss and almost no residue remaining.

The heats of combustion and formation are significant characteristics for the assessment of the energetic properties of a new compound. The constant-volume heats of combustion (Q_v) of HATr·PA and HATr·TNR·H₂O were -11.5237 MJ·kg⁻¹ and -10.2348 MJ·kg⁻¹, respectively, as measured by oxygen bomb calorimetry under O₂.

The bomb equations are as follows (Eqs. 1 and 2):



The energies of combustion are as follows (Eqs. 3 and 4) (Q_p : constant-pressure energy of combustion):

$$\Delta H[\text{HATr}\cdot\text{PA}] = Q_p = Q_v + \Delta nRT = -3941.149 \text{ kJ}\cdot\text{mol}^{-1} = -11.4822 \text{ MJ}\cdot\text{kg}^{-1} \quad (3)$$

$$\Delta H[\text{HATr}\cdot\text{TNR}\cdot\text{H}_2\text{O}] = Q_p = Q_v + \Delta nRT = -3845.696 \text{ kJ}\cdot\text{mol}^{-1} = -10.1938 \text{ MJ}\cdot\text{kg}^{-1} \quad (4)$$

Non-isothermal kinetic analyses

Kissinger's method [9] and Ozawa-Doyle's method [10] are widely used to determine an apparent activation energy [11]. Using the first exothermic peak temperatures measured at four different heating rates (5, 10, 15, 20 K·min⁻¹), Kissinger's and Ozawa-Doyle's methods were applied to obtain the kinetic parameters for the two salts. The Kissinger (Eq. 5) and Ozawa (Eq. 6) equations are as follows, respectively:

$$\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R} \quad (5)$$

$$\log \beta + \frac{0.4567E_a}{RT_p} = C \quad (6)$$

where: T_p is the peak temperature, K; R is the gas constant, 8.314 kJ·mol⁻¹·K⁻¹; β is the linear heating rate, K·min⁻¹; C is a constant.

From the original data, the apparent activation energies E_k and E_o , the pre-exponential factor A_k and the linear coefficients R_k and R_o were determined and are listed in Table 3 (k and o means Kissinger's method and Ozawa-Doyle's method, respectively).

Table 3. Peak temperatures of the first exothermic stage at different heating rates, and the kinetic parameters, for HATr·PA and HATr·TNR·H₂O

β [K·min ⁻¹]	T_p of HATr·PA	T_p of HATr·TNR·H ₂ O
5	476.2	474.3
10	483.3	483.6
15	494.4	496.7
20	501.5	507.8
Kissinger's method E_k [kJ·mol ⁻¹], $\ln A_k$, R_k	95.145, 5.035, 0.9428	71.663, 4.181, 0.9358
Ozawa-Doyle method E_o [kJ·mol ⁻¹], R_o	98.208, 0.9512	75.909, 0.9480

The calculated results using both methods correspond well with each other, and they are all in the normal range of kinetic parameters for the thermal decomposition of solid materials [12]. The apparent activation energy for

HATr·TNR·H₂O is almost 23 kJ·mol⁻¹ lower than that for HATr·PA. This reveals that the energy barrier encountered for decomposition of HATr·TNR·H₂O is smaller and thus this salt is more easily decomposed, which is in agreement with the DSC curves.

The Arrhenius equations for the two compounds can be expressed as follows:

$$\ln k = 5.035 - 96.302 \times 10^3 / (RT) \quad \text{for HATr·PA}$$

$$\ln k = 4.181 - 73.202 \times 10^3 / (RT) \quad \text{for HATr·TNR·H}_2\text{O}$$

Calculation of the critical temperature for thermal explosion, ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger

Using Eq. (7) [13], the value of the peak temperature (T_{p0}), corresponding to $\beta \rightarrow 0$, was obtained, where a , b and c are coefficients.

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^3 \quad (7)$$

The corresponding critical temperature of thermal explosion (T_b) is obtained using Eq. (8) [13], where R is the gas constant, and E is the value of E_k by Kissinger's method.

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{p0}}}{2R} \quad (8)$$

The entropy of activation (ΔS^\ddagger), the enthalpy of activation (ΔH^\ddagger) and the free energy of activation (ΔG^\ddagger) of the decomposition reaction corresponding to $T = T_{p0}$, $E_a = E_k$ and $A = A_k$ (obtained by Kissinger's method) were obtained using Eqs. (9), (10) and (11) [13].

$$A = \frac{k_B T}{h} e^{\Delta S^\ddagger / R} \quad (9)$$

$$\Delta H^\ddagger = E - RT \quad (10)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (11)$$

where k_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$) and h is Planck's constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}$). The calculated critical temperature of thermal explosion and the thermodynamic parameters are listed in Table 4.

Table 4. Calculated critical temperature of thermal explosion and thermodynamic parameters

	T_{P0} (K)	T_b (K)	ΔH^\ddagger (kJ·mol ⁻¹)	ΔG^\ddagger (kJ·mol ⁻¹)	ΔS^\ddagger (J·K ⁻¹ ·mol ⁻¹)
HATr·PA	481.1	484.9	93.41	135.05	-200.06
HATr·TNR·H ₂ O	474.6	479.3	69.98	111.69	-206.89

The value of the critical temperature of thermal explosion for HATr·PA was a little higher than that for HATr·TNR·H₂O. The thermodynamic parameters followed the same pattern as with the thermal explosion, indicating that HATr·TNR·H₂O has a greater tendency for the occurrence of an explosion.

Sensitivity tests

The impact and friction sensitivities, as well as the flame sensitivity, were determined according to Chinese Standards [14]. The results of these tests on HATr·PA and HATr·TNR·H₂O are listed in Table 5.

Table 5. Results of sensitivity tests on HATr·PA and HATr·TNR·H₂O

	HATr·PA	HATr·TNR·H ₂ O
Friction sensitivity (%)	60	0
Impact sensitivity, h_{50} (cm)	31.45	0
Flame sensitivity, h_{50} (cm)	12.41	18.24

The results showed that HATr·PA is more sensitive than HATr·TNR·H₂O to the three kinds of stimulus.

Conclusions

Two energetic salts HATr·PA and HATr·TNR·H₂O were synthesized and characterized. Their crystal structures were determined at low temperature. Thermal analysis indicated that there was either no or one endothermic process and one or two exothermic processes, with no residue left at 850 K. The energies of combustion of HATr·PA and HATr·TNR·H₂O are -11.4822 MJ·kg⁻¹ and -10.1938 MJ·kg⁻¹, respectively. Non-isothermal kinetic analysis indicated that the Arrhenius equation for HATr·PA and HATr·TNR·H₂O can be expressed as follows:

$$\ln k = 5.035 - 96.302 \times 10^3 / (RT) \quad (\text{for HATr·PA})$$

$$\ln k = 4.181 - 73.202 \times 10^3 / (RT) \quad (\text{for HATr·TNR·H}_2\text{O})$$

Moreover, the values of the critical temperature for thermal explosion, ΔS^\ddagger , ΔH^\ddagger and ΔG^\ddagger are 484.9 K, 93.41 kJ·mol⁻¹, 135.05 kJ·mol⁻¹, -200.06 J·K⁻¹·mol⁻¹ respectively for HATr·PA, and 479.3 K, 69.98 kJ·mol⁻¹, 111.69 kJ·mol⁻¹, -206.89 J·K⁻¹·mol⁻¹, respectively for HATr·TNR·H₂O. The flame sensitivity measurements showed that the 50% flame heights were 12.41 cm and 18.24 cm for HATr·PA and HATr·TNR·H₂O, respectively. Above all, the results indicate that these two compounds have certain potential applications as gunpowder and propellant materials.

Acknowledgements

We gratefully acknowledge the Program for New Century Excellent Talents in University (No. NCET-09-0051), the project of State Key Laboratory of Science and Technology (No. QNK11-06 and ZDK12-03).

References

- [1] a) Drake G.W., Hawkins T.M., Boatz J., Hall L., Vij A., Experimental and Theoretical Study of 1,5-Diamino-4-H-1,2,3,4-tetrazolium Perchlorate, *Propellants Explos. Pyrotech.*, **2005**, 30(2), 156-163; b) Drake G.W., Hawkins T.M., Brand A., Hall L., McKay M., Energetic, Low-melting Salts of Simple Heterocycles, *Propellants Explos. Pyrotech.*, **2003**, 28(4), 174-180; c) Xue H., Twamley B., Shreeve J.M., Energetic Azolium Azolate Salts, *Inorg. Chem.*, **2005**, 44, 5068-5072; d) Gao H., Ye C.F., Twamley B., Shreeve J.M., Energetic Bicyclic Azolium Salts, *Chem. Eur. J.*, **2006**, 12, 9010-9018.
- [2] a) Smiglak M., Reichert W.M., Holbrey J.D., Wilkes J.S., *et al.*, Combustible Ionic Liquids by Design: is Laboratory Safety Another Ionic Liquid Myth?, *Chem. Commun.*, **2006**, 24, 2554-2556; b) Huang Y.G., Gao H.X., Twamley B., Shreeve J.M., Nitroamino Triazoles: Nitrogen-rich Precursors of Stable Energetic Salts, *Eur. J. Inorg. Chem.*, **2008**, 16, 2560-2568; c) He L., Tao G.H., Parrish D.A., Shreeve J.M., Liquid Dinitromethanide Salts, *Inorg. Chem.*, **2010**, 50, 679-685.
- [3] a) Gao H., Ye C., Gupta O.D., Xiao J.C., Hiskey M.A., 2,4,5-Trinitroimidazole-based Energetic Salts, *Chem. Eur. J.*, **2007**, 13, 3853-3860; b) Fischer N., Klapötke T.M., Stierstorfer J., Explosives Based on Diaminourea, *Propellants Explos. Pyrotech.*, **2011**, 36, 225-232; c) Fischer N., Klapötke T.M., Piercey D.G., Stierstorfer J., Hydroxylammonium 5-Nitriminotetrazolates, *Z. Anorg. Allg. Chem.*, **2012**, 638(2), 302-310.
- [4] a) Crawford M.J., Klapötke T.M., Martin F.A., Sabaté C.M., Energetic Salts of the Binary 5-Cyanotetrazolate Anion ([C₂N₅]⁻) with Nitrogen-Rich Cations, *Chem. Eur. J.*, **2012**, 17, 1683-1695; b) Klapötke T.M., Sabaté C.M., *Cent. Eur. J. Energ. Mater.*, **2010**, 7(2), 161-173; c) Fischer N., Klapötke T.M., Stierstorfer J., Less

- Sensitive Transition Metal Salts of the 5-Nitrotetrazolate Anion, *Z. Anorg. Allg. Chem.*, **2011**, 637, 1273-1276; d) Xue H., Twamley B., Shreeve J.M., Energetic Quaternary Salts Containing bi(1,2,4-triazoles), *Inorg. Chem.*, **2005**, 44, 7009-7013.
- [5] a) Xue H., Gao H., Twamley B., Shreeve J.M., Energetic Salts of 3-Nitro-1,2,4-triazole-5-one, 5-Nitroaminotetrazole, and other Nitro-substituted Azoles, *Chem. Mater.*, **2007**, 19, 1731-1739; b) Schmidt M.W., Gordon M.S., Boatz J.A., Triazolium-based Energetic Ionic Liquids, *J. Phys. Chem. A*, **2005**, 109, 7285-7295; c) Wang Q., Li J.Z., Yu H.J., Fu X.L., Fan X.Z., Ji P.Y., Review on Azotetrazolate Nonmetal Salts, *Chin. J. Energ. Mater.*, **2010**, 5, 592-598; d) Singh R.P., Verma R.D., Meshri D.T., Shreeve J.M., Energetic Nitrogen-rich Salts and Ionic Liquids, *Angew. Chem. Int. Ed.*, **2006**, 45, 3584-3601.
- [6] Cardillo P., Dellavedova M., Gigante L., Lunghi A., Synthesis, Spectroscopic and Thermal Characterization of Azido-1,2,4-triazoles: A Class of Heteroarenes with a High Nitrogen Content, *Eur. J. Org. Chem.*, **2012**, 6, 1195-1201.
- [7] Sheldrick G.M., SHELXS-97, *Program for Crystal Structure Determination*; University of Göttingen: Germany, **1997**.
- [8] Sheldrick G.M., SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.
- [9] Kissinger H.E., Reaction Kinetics in Differential Thermal Analysis, *Anal. Chem.*, **1957**, 18, 1702-1706.
- [10] Ozawa T.A., A New Method of Analyzing Thermo-gravimetric Data, *Bull. Chem. Soc. Jpn.*, **1965**, 38, 1881-1886.
- [11] Zhang Y.Q., Guo Y., Joo Y.H., Parrish D.A., Shreeve J.M., 3,4,5-Trinitropyrazole-Based Energetic Salts, *Chem. Eur. J.*, **2010**, 16, 10778-10784.
- [12] a) Li Z.M., Xie S.H., Zhang J.G., Feng J.L., Wang K., Two High Nitrogen Content Energetic Compounds: 3,6-Diguanidino-1,2,4,5-Tetrazine and Its Dipercchlorate, *J. Chem. Eng. Data*, **2012**, 57, 729-736; b) Wu B.D., Zhang J.G., Zhang T.L., Yang L., Zhou Z.N., Two Environmentally Friendly Energetic Compounds, [Mn(AZT)₄(H₂O)₂](PA)₂·4H₂O and [Co(AZT)₂(H₂O)₄](PA)₂, Based on 3-Azido-1,2,4-triazole (AZT) and Picrate (PA), *Eur. J. Inorg. Chem.*, **2012**, 1261-1268; c) Wu B.D., Wang S.W., Yang L., Zhang T.L., Zhang J.G., Preparation, Crystal Structures, Thermal Decomposition and Explosive Properties of Two Novel Energetic Compounds M(IMI)₄(N₃)₂ (M = Cu(II) and Ni(II), IMI = Imidazole): The New High-Nitrogen Materials (N > 46%), *Eur. J. Inorg. Chem.*, **2011**, 2616-2623.
- [13] Diaz D.D., Punna S., Holzer P., Mcpherson A.K., Sharpless K.B., Fokin V.V., Finn M.G., Click Chemistry in Materials Synthesis. 1. Adhesive Polymers from Copper-catalyzed Azide-alkyne Cycloaddition, *J. Polym. Sci., Part A: Polym. Chem.*, **2004**, 42, 4392-4403.
- [14] Zhang T.L., Hu R.Z., Xie Y., *et al.*, The Estimation of Critical-temperatures of Thermal-explosion for Energetic Materials using Nonisothermal DSC, *Thermochim. Acta*, **1994**, 244, 171.
- [15] Liu Z.T., Lao Y.L., *Initiation Explosive Experimental*, Beijing Institute of Technology, China, **1995**.

