# Synthesis, Characterization, and Thermal Analysis of Two Energetic Ionic Salts Based on 3,4-Diamino-1,2,4-triazole (DATr)

Jin-Ting Wu,<sup>[a]</sup> Jian-Guo Zhang,<sup>\*[a]</sup> Xin Yin,<sup>[a]</sup> Mou Sun,<sup>[a]</sup> and Tong-Lai Zhang<sup>[a]</sup>

Keywords: 3,4-Diamino-1,2,4-triazole; 3-Nitro-1,2,4-triazole-5-one; 2,4,6-Trinitro-resorcinol; Crystal structure; Thermal analysis; Energetic compounds; Sensitivity test

Abstract. Two energetic ionic salts DATr·NTO (2) and DATr·TNR (3) of 3,4-diamino-1,2,4-triazole (DATr) (1) were synthesized by reaction of 3,4-diamino-1,2,4-triazole with either 3-nitro-1,2,4-triazole-5-one (NTO) or 2,4,6-trinitro-resorcinol (TNR) in aqueous solution. Their structures were characterized by FT IR spectroscopy (FT-IR) and X-ray single-crystal diffraction analysis. Their molecular structure and crystal structure were determined. They belong to the monoclinic crys-

# Introduction

Energetic salts as a unique class of high energetic materials due to the lower vapor pressures and higher densities than their atomically similar non-ionic analogues have been widely investigated.<sup>[1–3]</sup> Some of them have attractive energetic properties such as good thermal stability and high density.<sup>[4–6]</sup> The design of energetic materials based on combinations of different ions for a specific purpose provides a powerful methodology.<sup>[7,8]</sup> Triazole is a high nitrogen-containing heterocycle, which leads to high energetic performances arising from an additional energy release upon opening of the strained ring systems during decomposition.<sup>[9,10]</sup>

In this paper, two energetic ionic salts DATr•NTO (2) and DATr•TNR (3) based on 3,4-diamino-1,2,4-triazole (DATr) (1) were synthesized by reacting 3,4-diamino-1,2,4-triazole with either 3-nitro-1,2,4-triazole-5-one (NTO) or 2,4,6-trinitro-resorcinol (TNR) in aqueous solution. Their crystal structures were determined by X-ray single-crystal diffraction analysis and their thermal decomposition characteristics has been investigated using DSC and TG-DTG technologies.

## **Results and Discussion**

# **IR** Spectroscopy

The FT-IR spectra of 2 and 3 are shown in Figure 1. In Figure 1a, the band at 1697 cm<sup>-1</sup> is assigned to the C=O group stretching vibration for NTO of compound 2. In Figure 1b, the

2354 ONLINE LIBRARY

© 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

tal system, space group  $P2_1/c$ . The crystal density is 1.693 g·cm<sup>-3</sup> and 1.738 g·cm<sup>-3</sup>, respectively. The thermal decomposition characteristics of the title compounds were investigated using differential scanning calorimetry (DSC) and thermogravimetry/differential thermogravimetry (TG/DTG) technologies. Furthermore, the sensitivity properties were determined by standard methods.

band of 3348 cm<sup>-1</sup> is predicted for the OH group, and the bands of 1616 cm<sup>-1</sup>, 1565 cm<sup>-1</sup>, 1494 cm<sup>-1</sup>, and 1447 cm<sup>-1</sup> are assigned to the stretching vibration of the benzene cycle of compound **3**. C–N stretching vibrations at 1020–1360 cm<sup>-1</sup> are visible in both spectra of **2** and **3**. In addition, the bands of lower intensity correspond to vibrational modes in the cation and the two compounds show bands in the range of 3400– 3330 and 1295–1145 cm<sup>-1</sup>, which are due to the symmetric stretching of the NH<sub>2</sub> groups and the rocking/twisting vibrational modes of the NH<sub>2</sub> groups, respectively.<sup>[11]</sup>

#### Molecular Structure

There are one 3-nitro-1,2,4-triazole-5-one anion or 2,4,6-trinitro-resresorcinol anion and one 3,4-diamino-1,2,4-trizolium in 2 and 3, respectively, which are connected by electrostatic attraction. The molecular structures of compounds 2 and 3 are shown in Figure 2. One proton from one NTO molecule transfers to a molecule of 1 (N2 accepts the proton). There exist two planes in the molecular structure of compound 2, as shown in Figure 2a. The first one is the NTO anion plane (A): 0.087x + 0.468y - 0.879z = -0.0827, and the second one is the structure plane (B) from 1: 0.196x - 0.007y - 0.980z = -4.164. The angle between A and B is 28.86°. The C1-O1 bond length is 1.27 Å, which is 0.06 Å longer than the normal C=O bond length (1.21 Å) and 0.18 Å shorter than the normal C-O bond length (1.45 Å), which indicates that the carbonyl bonds have a certain degree of distortion due to the loss of the hydrogen atom on the adjacent N3 atom. This is mainly due to the  $\pi$ bond of the triazole ring; the electronegativity is enhanced such that the oxygen atom of the carbonyl bond is excluded while the intensity of the carbonyl group is reduced.

In the molecular structure of compound 3, a proton from one hydroxyl group of the TNR molecule transfers to 1 and

<sup>\*</sup> Prof. Dr. J.-G. Zhang Fax: +86-10-68918038

E-Mail: zjgbit@bit.edu.cn

 <sup>[</sup>a] State Key Laboratory of Explosion Science and Technology Beijing Institute of Technology Beijing 100081, P. R. China



a: DATr·NTO (2)

b: DATr·TNR (3)

Figure 1. FT-IR spectra of (a) DATr·NTO (2) and (b) DATr·TNR (3).



Figure 2. Molecular structure of (a) DATr·NTO (2) and (b) DATr·TNR (3).

two nitrogen atoms accept protons. There exist three planes in the molecular structure of **3**: the benzene ring plane (C): 0.8226x + 0.5486y - 0.1498z = 1.8984, another plane is the 3,4-diamino-1,2,4-triazolium unit (D): 0.8328x - 0.0607y - 0.4402z = -2.2520. The angle between C and D is  $42.76^{\circ}$ . The benzene ring structure remains of its original nature, where six carbon atoms are still coplanar, but the interior angles of benzene ring have already changed due to the external groups. The angle of C5–C6–C7 has the least impact (120.46°), whereas the angles of C7–C8–C3 (126.44°) and C8–C3–C4 (112.72°) have the large change.

The packing diagram of 2 shows that the intermolecular arrangement of 3,4-diamino-1,2,4-triazolium consists of regular stacking, the intermolecular arrangement of 3-nitro-1,2,4-triazole-5-one anion consists of mutual intersecting and staggering; while the packing diagram of 3 indicates a similar arrangement (see Figure 3). The kind of arrangement improves the degree of disorder of the entire unit cell, increasing the entropy of the molecule as a whole, so the stability of the molecule increased.

#### Thermal Decomposition

The DSC and TG-DTG curves of compounds 2 and 3 with a linear heating rate of 10 K·min<sup>-1</sup> are shown in Figure 4 and Figure 5, respectively.

For compound **2**, the DSC curve shows a sharp exothermic process starting at 231.1 °C with a peak temperature of 236.7 °C. Corresponding to the exothermic decomposition, a sharp mass loss (58.4%) was found in the TG-DTG curves, afterwards there is a further slow process of thermal decomposition with continuous mass loss and a great amount of heat and gases were released in the total decomposition process and left nothing.

For compound **3**, the DSC curve shows that there are two processes: one endothermic process occurs at 201.4 °C and one exothermic process with a top at 261.9 °C. At the same time, the TG-DTG curves indicate two stages in the process of thermal decomposition. The first mass loss stage occurs at 272.0 °C, the first stage of mass loss of 59.2% of the initial mass for **3**. The second stage is a slow process of thermal decomposition with continuous mass loss, and left nothing.

The constant-volume combustion heats  $(Q_v)$  of DATr·NTO (2) and DATr·TNR (3) were  $-10.3417 \text{ MJ·kg}^{-1}$  and  $-10.5384 \text{ MJ·kg}^{-1}$ , respectively, which were measured with a Parr company 1104 oxygen bomb calorimeter in an oxygen atmosphere. The data indicate that both of them release large amounts of energy upon decomposing. The combustion equation of the compounds is as follows:

# ARTICLE



Figure 3. Views of stacking unit cell for packing for (a) DATr·NTO (2) and (b) DATr·TNR (3).



Figure 4. DSC curves of (a) DATr·NTO (2) and (b) DATr·TNR (3) at a heating rate of 10 K·min<sup>-1</sup>.



a: DATr·NTO (2)

b: DATr·TNR (3)

-678.5 kJ·mol<sup>-1</sup>, respectively.

Figure 5. TG-DTG curves of (a) DATr NTO (2) and (b) DATr TNR (3) at a heating rate of 10 K min<sup>-1</sup>.

 $C_{a}H_{b}O_{c}N_{d} + (a + 0.25b - 0.5c)O_{2} \rightarrow aCO_{2} + 0.5bH_{2}O + 0.5dN_{2} \quad (1) \qquad \Delta_{f}H^{o}_{298}(R) = \Delta_{f}H^{o}_{298}(P) - \Delta_{r}H^{o}_{298}(R) = \Delta_{f}H^{o}_{298}(R) + 0.5dN_{2} \quad (1) \qquad \Delta_{f}H^{o}_{298}(R) = \Delta_{f}H^{o}_{29}(R) + 0.5dN_{2} \quad (1) \qquad \Delta_{f}H^{o}_{29}(R) = \Delta_{f}H^{o}_{29}(R) + 0.5dN_{2} \quad (1) \qquad \Delta_{f}H^{o}_{29}(R) = \Delta_{f}H^{o}_{29}(R) \quad (1) \qquad \Delta_{f}$ 

The energy of combustion is calculated by the formula:  

$$\Delta H = Q_{p} = Q_{V} + \Delta nRT$$
(2)

The enthalpies of the compounds can be calculated from the energy of combustion on the basis of Equation (1) and the Hess's law as applied in thermochemical Equation (3).

With the known enthalpies of the formation of carbon dioxide  $[\Delta_f H^o{}_{298}(\text{CO}_2, g) = -393.5 \text{ kJ} \cdot \text{mol}{}^{-1}]$  and water  $[\Delta_f H^o{}_{298}(\text{H}_2\text{O}, 1) = -285.8 \text{ kJ} \cdot \text{mol}{}^{-1}]$ , the enthalpy of the for-

mation of 2 and 3 can be calculated with  $-214.6 \text{ kJ} \cdot \text{mol}^{-1}$  and

(3)



#### **Physicochemical Properties**

The detonation parameters were calculated by equations proposed by *Keshavarz*.<sup>[12]</sup> Table 1 shows that for compounds **2** and **3** the calculated detonation pressures (*P*) are 17.1 and 19.5 GPa, which are comparable to that of TNT (19.5 GPa).<sup>[13]</sup> The detonation velocities (*D*) are 6320 m·s<sup>-1</sup> (**2**) and 6699 m·s<sup>-1</sup> (**3**) comparable to TNT (6881 m·s<sup>-1</sup>) and RDX (8977 m·s<sup>-1</sup>).<sup>[13,14]</sup>

**Table 1.** Physicochemical Properties of DATr·NTO (2) and DATr·TNR(3).

	DATr·NTO (2)	DATr•TNR (3)
$\overline{T_{\rm m}^{\ a)}}$	-	203.6
$T_{\rm d}^{\rm b)}$	236.7	261.9
OB <sup>c)</sup>	-59.4	-55.8
N <sup>d)</sup>	55.0	32.5
P <sup>e)</sup>	17.1	19.5
$D^{(f)}$	6320	6699

a) Melting point/DSC endothermic peak. b) Thermal degradation/DSC main exothermic peak. c) Oxygen balance. d) Nitrogen content /%. e) Detonation pressure /GPa. f) Detonation velocity /m·s<sup>-1</sup>.

#### Sensitivity Tests

On the basis of the Chinese standard,<sup>[15]</sup> the impact and friction sensitivities as well as the flame sensitivity were determined. The results of the sensitivity tests of DATr·NTO (2) and DATr·TNR (3) are listed in Table 2.

**Table 2.** Results of sensitivity tests on DATr•NTO (2) and DATr•TNR(3).

	DATr·NTO (2)	DATr·TNR (3)
Friction sensitivity /%	70	50
Impact sensitivity /cm	40.5	35.2
Flame sensitivity, $h_{50}$ /cm	18.43	13.2

The sensitivity measurement results for DATr·NTO showed that the 50% firing height ( $h_{50}$ ) for flame sensitivity was 18.43 cm and the friction sensitivity firing rate was 70% with a 1 kg hammer, 90° angle, and 1.96 MPa pressure. The impact sensitivities of the compounds were determined with a fall-hammer apparatus. The compound was compressed between two steel poles and hit with a 0.8 kg hammer. The test results showed that the 50% firing height is 40.5 cm (3.18 J) for **2**, and 35.2 cm (2.76 J) for **3**, comparable to TNT (15 J) and RDX (7.5 J).<sup>[13,14]</sup>

In other words, both of the ionic salts are sensitive and can be regarded as potential energetic materials.

#### Conclusions

Two energetic ionic salts based on 3,4-diamino-triazole were prepared and characterized by FT-IR spectroscopy and X-ray single-crystal diffraction analysis. Thermal analysis illustrated that a rapid exothermic process occurs in very short time and a great number of gases was produced, and left finally nothing of the two energetic ionic salts. According to the thermal and sensitivity analysis, both of the two ionic salts have potential application as energetic materials and gas generating-agent components used in military and civilian fields.

# **Experimental Section**

**Synthesis:** 3,4-Diamino-1,2,4-triazolium chloride was synthesized according to a literature method<sup>[16]</sup> starting from the reaction of the diaminoguanidinium chloride with formic acid, and hydrochloric acid as catalytic agent under reflux conditions. Equal potassium hydroxide was used to neutralize and to get 3,4-diamino-1,2,4-triazole (1). Scheme 1 shows the synthesis route of the two energetic ionic salts.



Scheme 1. Syntheses of 3,4-diamino-1,2,4-triazole and its salts 2 and 3.

Table 3. Crystal data and structure refinement parameters for 2 and 3.

	DATr·NTO (2)	DATr·TNR (3)
Empirical formula	C <sub>4</sub> H <sub>7</sub> N <sub>9</sub> O <sub>3</sub>	C <sub>8</sub> H <sub>8</sub> N <sub>8</sub> O <sub>8</sub>
Formula mass	229.19	344.22
Temperature /K	153(2)	153(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	P2(1)
Z	4	2
a /Å	10.323(6)	10.087(3)
b/Å	6.186(4)	6.019(2)
c /Å	14.080(8)	11.036(4)
βI°	91.047(6)	100.974(4)
Cell volume /Å <sup>3</sup>	899.0(9)	657.7(4)
Density, calculated /g·cm <sup>-3</sup>	1.693	1.738
Absorption coefficient /mm <sup>-1</sup>	0.71073	0.71073
F(000) /Å	472	352
$\Theta$ Range for data collection /°	2.468-31.502	2.51-31.50
h, k, and l range	-15 < h < 14	-14 < h < 12
	-9 < k < 8	-8 < k < 8
	-20 < l < 20	-16 < l < 16
Reflection measured	8406	8154
Independent reflection $(R_{int})$	2949 $[R_{int} = 0.0333]$	4167 $[R_{int} = 0.0223]$
Refinement method	1.001	0.999
Final $R_1$ and $wR_2 [I > 2\sigma(I)]$	$R_1 = 0.0460$	$R_1 = 0.0351$
	$wR_2 = 0.1079^{\text{ a}}$	$wR_2 = 0.0757^{\text{b}}$
$R_1$ and $wR_2$ indices (all data)	$R_1 = 0.0606$	$R_1 = 0.0386$
	$wR_2 = 0.1175^{\text{a}}$	$wR_2 = 0.0776^{\text{b}}$
Largest diff. peak and hole /e·Å <sup><math>-3</math></sup>	0.259, -0.235	0.244, -0.174

a)  $w = 1/[\sigma^2(F_o^2) + (0.0748P)^2 + 0.1090P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ . b)  $w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.0000P]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

# ARTICLE

DATr•NTO (2) and DATr•TNR (3) were prepared by reacting 3,4-diamino-1,2,4-triazole (1) with an aqueous solution of 3-nitro-1,2,4-triazole-5-one (NTO) or 2,4,6-trinitro-resresorcinol (TNR), respectively. The mixtures were kept stirring over 15 min at 50 °C. The two title salts were obtained by slow spontaneous crystallization, filtered off, and washed three times with methanol.

**Instruments and Determination Conditions:** The infrared spectra were recorded by Fourier transform techniques with a Bruker Equinox 55 spectrometer with KBr pellets. Differential scanning calorimeter (DSC) and thermo-gravimetric analysis (TGA) were carried out with a model Pyris-1 differential scanning calorimeter and a model Pyris-1 thermogravimetric analyzer in a dry oxygen-free nitrogen atmosphere with a flow rate of 20 mL·min<sup>-1</sup>. The amount of compound used for testing DSC and TGA was 0.5 mg, but because of a thermal explosion of compound **2** (0.5 mg) during TG test, we repeated the TGA test with only 0.3 mg of **2** (Figure 5a).

The single crystals of **2** and **3** were cultured by slowly solvent evaporation method. Collection of X-ray diffractions data of **2** and **3** was performed with a Rigaku Saturn 724+ CCD diffractometer (Mo- $K_{\alpha}$  radiation, graphite monochromator). The structure was solved using the direct methods and successive Fourier difference syntheses (SHELXS-97)<sup>[17]</sup> refined using full-matrix least-squares on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97).<sup>[18]</sup> Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. Detailed information concerning crystallographic data collection and structure refinement are summarized in Table 3.

# 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 (Nos. QNKT11–06 and ZDKT12–03).

## References

- [1] H. Xue, H. Gao, B. Twamley, J. M. Shreeve, *Chem. Mater.* **2006**, *18*, 4007.
- [2] Y. Huang, H. X. Gao, B. Twamley, J. M. Shreeve, Eur. J. Inorg. Chem. 2008, 16, 2560.
- [3] L. He, G. H. Tao, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* 2010, 16, 5736.
- [4] H. X. Gao, C. F. Ye, O. D. Gutpa, J. C. Xiao, M. A. Hiskey, J. M. Shreeve, *Chem. Eur. J.* 2007, *13*, 3853.
- [5] N. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Z. Anorg. Allg. Chem. 2012, 638, 302.
- [6] N. Fischer, T. M. Klapötke, J. Stierstorfer, Propellants Explos. Pyrotech. 2011, 36, 225.
- [7] T. Fendt, N. Fischer, T. M. Klapötke, J. Stierstorfer, *Inorg. Chem.* 2011, 50, 1447.
- [8] K. Wang, D. A. Parrish, J. M. Shreeve, Chem. Eur. J. 2011, 17, 14485.
- [9] L. E. Fried, M. R. Manaa, P. F. Pagoria, R. L. Simpson, Annu. Rev. Mater. Res. 2001, 31, 291.
- [10] H. X. Gao, J. M. Shreeve, Chem. Rev. 2011, 111, 7377.
- [11] N. B. Colthup, L. H. Daly, S. E.Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., Academic Press, **1990**.
- [12] M. H. Keshavarz, J. Hazard. Mater. 2009, 135, 1296.
- [13] Y. Q. Zhang, Y. Guo, Y. H. Joo, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* 2010, 16, 10778.
- [14] D. D. Diaz, S. Punna, P. Holzer, A. K. Mcpherson, K. B. Sharpless, V. V. Fokin, M. G. Finn, J. Polym. Sci. Part A 2004, 42, 4392.
- [15] Z. T. Liu, Y. L. Lao, *Initiation Explosive Experimental*. Beijing Institute of Technology, P. R. China, **1995**.
- [16] K. Emilsson, K. Luthman, H. Selander, Eur. J. Med. Chem. 1986, 21, 235.
- [17] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Göttingen, Germany, 1997.
- [18] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement from Diffraction Data, University of Göttingen, Germany, 1997.
- [19] A. Becke, J. Chem. Phys. 1993, 98, 5648.
- [20] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.

Received: May 16, 2013 Published Online: July 23, 2013