Preparation and characterization of nitrogen-rich bis-1methylimidazole1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate energetic salt

Liqiong Luo¹ · Bo Jin¹ · Rufang Peng¹ · Yu Shang¹ · Lipengcheng Xiao¹ · Shijin Chu¹

Received: 1 March 2018 / Accepted: 14 June 2018 © Akadémiai Kiadó, Budapest, Hungary 2018

Abstract



A new nitrogen-rich energetic salt of bis-1-methylimidazole 1H, 1'H-5, 5'-bistetrazole-1, 1'-diolate salt, $(1-M)_2$ BTO, was synthesized and characterized (FT-IR, ¹H NMR, ¹³C NMR, elemental analysis, and X-ray single-crystal diffraction). Results indicated that $(1-M)_2$ BTO crystallizes in the triclinic space group *P*-1. The thermal decomposition behavior of $(1-M)_2$ BTO was determined by differential scanning calorimetry (DSC) and thermogravimetric tandem infrared spectroscopy. The decomposition peak temperature of $(1-M)_2$ BTO was 530 K, which suggested that the salt is strong heat resistance. The apparent activation energies were 130.56 kJ mol⁻¹ (Kissinger's method) and 132.50 kJ mol⁻¹ (Ozawa's method), respectively. The enthalpy of formation for the salt was calculated as 917.3 kJ mol⁻¹. The detonation velocity and detonation pressure of $(1-M)_2$ BTO were 7448 m s⁻¹ and 20.7 GPa, respectively, using the Kamlet-Jacobs equation. Furthermore, the sensitivity test results showed that its impact sensitivity is greater than 50 J and friction sensitivity is 180 N, indicating that it has a lower sensitivity.

Keywords Bis-1-methylimidazole $\cdot 1H, 1'H-5, 5'$ -bistetrazole -1, 1'-diolate \cdot Energetic properties \cdot Crystal structure

Introduction

Energetic materials including explosives, propellants, pyrotechnics play an important role in the materials and technology [1, 2], whereas nitramines including RDX, HMX, and CL-20 decompose into a significant mass of toxic products such as nitro- and nitrosoamines after degradation [3–5]. Therefore, exploring environment-friendly and high-energy density materials (HEDMs) insensitive to impact and friction is becoming an intensi-fying endeavor worldwide [6–12]. In pursuit of HEDMs, azole heterocycles and their derivatives circumvent the drawbacks as well as possess high heat of formation, high nitrogen content, high density, excellent thermal stability, and environment friendliness [13–15].

Bo Jin jinbo0428@163.com

Rufang Peng rfpeng2006@163.com

¹ State Key Laboratory of Environmental-friendly Energy Materials, Southwest University of Science and Technology, Mianyang 621010, Sichuan, China

A very promising candidate that fulfills a variety of the desirable properties is 1H,1'H-5,5'-bistetrazole-1,1'-diolate (BTO) since it was firstly reported by Tselinskii in 2001 [16]. Nitrogen content and oxygen balance of BTO are 66.7 and -28.2%, respectively, because two hydroxyl groups are introduced in the tetrazoles. Thus, it can easily form intraor intermolecular hydrogen bonds. The hydroxyl hydrogen of BTO is acidic and makes it easy to separate from the salt. Therefore, BTO is a good candidate of energetic anions [17, 18]. Recently, a series of energetic salts based on BTO anion were synthesized as potential energetic materials, such as diuronium 1H,1'H-5,5'-bistetrazole-1,1'diolate [19], 1,2,4-triazolium, 3-amino-1,2,4-triazolium, 2-methylimidazolium, dicyandiamidine [20], bis(semicarbazide) 5,5'-bistetrazole-1,1'-diolate [21]. The most representative achievement was the synthesis of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50) by Fischer and Klapötke in 2012 [18]. The combination between nitrogen-rich cations and BTO anion are expected to possess excellent energetic properties and perfect sensitivities.

In this study, a new nitrogen-rich energetic salt, $(1-M)_2$ BTO, was synthesized and fully characterized. Its

Scheme 1 Synthesis route of (1-*M*)₂BTO



crystal structure, thermal decomposition, and energetic properties were investigated. The result exhibited that the title salt is an energetic material with favorable thermal stability properties.

Results and discussion

Synthesis

As shown in scheme 1,1H,1'H-5,5'-bistetrazole-1,1'-diolate dihydrate (H₂BTO) can be readily obtained by a fourstep reaction from the raw material glyoxal in accordance with a previously reported procedure [17]. The target product $(1-M)_2$ BTO was synthesized after H₂BTO reacted with 1-methylimidazole in water with 1:2 molar quantities.

Crystal structure

A high-quality crystal of $(1-M)_2$ BTO for X-ray singlecrystal diffraction was obtained by slowly evaporating water at room temperature. The parameters of the structural analysis are listed in Table 1. The molecular unit and packing diagram of the salt are shown in Figs. 1 and 2. The selected bond lengths and bond angles of $(1-M)_2$ BTO are summarized in Table 2. The hydrogen bond parameters are given in Table 3.

The salt crystallizes in the triclinic system space group *P*-1 with six H₂O per molecule and exhibits a density of 1.384 g cm⁻³ at 150 K, which is lower than that of H₂BTO (1.811 g cm⁻³) but superior to that of imidazole (1.030 g cm⁻³). As shown in Fig. 1, the energetic salt $(1-M)_2$ BTO can be presented as the form of $(C_2N_8O_2)^{2-}$ ($C_4H_7N_2$)⁺·6H₂O, which is composed of a BTO anion, two 1-methylimidazole cations, and six H₂O formed by the combination of ionic bonds and hydrogen bonds each other. The two hydroxyl H atoms deliver from H₂BTO in the reaction, forming a negative bivalence anion. Although 1-methylimidazole is

Table 1 Crystal data and structure refinement parameters of $(1-M)_2$ BTO

Compound	(1- <i>M</i>) ₂ BTO
Empirical formula	C ₁₀ H ₂₆ N ₁₂ O ₈
Formula mass	442.43
CCDC number	1825802
Size	$0.21 \times 0.20 \times 0.19$
Temperature/K	150(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
a/Å	4.7662(13)
<i>b</i> /Å	8.579(2)
c/Å	13.182(4)
α/°	80.609(3)
β/°	89.133(3)
γ/°	86.337(3)
Cell volume/Å ³	530.7(2)
Ζ	1
$ ho_{ m calcd}/ m g\ m cm^{-3}$	1.384
<i>F</i> (000)	234
R _{int} .	0.0445
Data	1869
Restraints	0
Parameters	136
GOF^a on F^2	1.085
$R_{1}^{\rm b}, [I > 2\sigma \ (I)]$	0.0445
$\omega R_2, [I > 2\sigma (I)]$	0.1062
R_1 , (all data)	0.0532
ωR_2^c , (all data)	0.1109
^{a}GOF goodness of fit, $^{b}R_{1} = 1$	$\sum F_{\rm o} - F_{\rm c} / \sum F_{\rm o} , {}^{\rm c}\omega R_2 =$
$\left[\omega\left(F_{\rm o}^2-F_{\rm c}^2\right)^2/\omega\left(F_{\rm o}^2\right)^2\right]^{1/2}$	

weakly alkaline, its ability to attract protons for N(6) atoms is increased, thereby causing the transfer of proton from BTO to the N(6) position, and subsequently generating the cation. Finally, the energetic salt $(1-M)_2$ BTO is formed by



1-methylimidazole cations and BTO anion through ionic bonds and hydrogen bonds.

In the BTO anion (Table 2), the N–N bond lengths range from 1.310(20) Å for N(2)–N(3) to 1.348(19) Å for N(3)– N(4), which is shorter than the normal N–N bond length (1.454 Å) and longer than the normal N=N bond (1.245 Å) [22]. The C–C bond connecting the two tetrazole moieties are 1.445(29) Å, which is located within the normal range of 1.32 Å for the C=C bond and 1.53 Å for the C–C bond [22]. Additionally, the N–O bond of hydroxyl is 1.321(18) Å, which is found between N–O bond (1.370 Å) and N=O bond (1.205 Å) [23]. These indicate the two pentagons in the BTO are coplanar in the salt. Some multiple bonds show that the $(1-M)_2$ BTO exists as a large π -conjugated system.

In the energetic salt, the 1-methylimidazole cations and BTO anion are interconnected with each other via hydrogen bonds. And the hydrogen bond is an important factor in

Table 2 Bond lengths/Å and bond angles/° for $(1-M)_2BTO$

Bond	Length/Å	Bond	Angle/°
O(1)–N(1)	1.321(18)	H(1 WB)-O(1W)-H(1WA)	98.08
N(1)-N(2)	1.344(18)	H(2 WB)-O(2W)-H(2WA)	102.47
N(1)–C(1)	1.345(20)	H(3 WB)-O(3W)-H(3WA)	112.69
N(2)–N(3)	1.310(20)	O(1)-N(1)-N(2)	121.88(12)
N(3)–N(4)	1.348(19)	O(1)–N(1)–C(1)	129.85(13)
N(4)–C(1)	1.328(22)	N(2)–N(1)–C(1)	108.26(14)
N(5)–C(4)	1.316(23)	N(3)–N(2)–N(1)	106.49(12)
N(5)–C(3)	1.369(22)	N(2)-N(3)-N(4)	110.76(13)
N(5)–C(5)	1.462(22)	C(1)-N(4)-N(3)	106.01(14)
N(6)–C(4)	1.312(24)	C(4)–N(5)–C(3)	108.31(16)
N(6)-C(2)	1.357(24)	C(4)–N(5)–C(5)	126.30(16)
$C(1)-C(1)^{a}$	1.445(29)	C(3)–N(5)–C(5)	125.39(16)
C(2)–C(3)	1.344(28)	C(4)–N(6)–C(2)	109.28(17)
		N(4)-C(1)-N(1)	108.48(13)
		$N(4)-C(1)-C(1)^{a}$	127.01(19)
		$N(1)-C(1)-C(1)^{a}$	124.49(19)
		C(2)-C(3)-N(5)	107.05(16)
		N(6)-C(4)-N(5)	108.66(16)

 $x^{a} - x, -y + 1, -z + 1$

 Table 3 Hydrogen bonds for (1-M)2BTO

D–H…A	Length (D–H)	Length (H…A)	Length (D…A)	Angle (D– H…A)
O(1 W)– H(1WB)····O(2 W) ^a	0.859	1.973	2.801	161.54
O(1 W)– H(1WA)····O(3 W) ^b	0.863	1.966	2.819	169.94
O(2 W)– H(2WB)…O(1 W) ^c	0.865	1.924	2.770	165.37
O(2 W)- H(2WA)····O(3 W) ^d	0.861	1.991	2.843	169.89
O(3 W)–H(3 WB)…O(1)	0.867	1.918	2.776	170.58
O(3 W)-H(3WB)…N(1)	0.867	2.690	3.516	159.62
$O(3W)-H(3WA)\cdots O(1)^{e}$	0.861	1.950	2.807	173.24
$N(6)-H(6A)\cdots O(1)^{f}$	0.880	2.166	2.891	139.33
N(6)-H(6A)···N(4)	0.880	2.293	2.950	131.50
$a^{a}[-x-1, -y, -z], b[-x]{d}[-x-1, -y+1, -z+1], e^{a}$	x = 1, -y, -y, -z	-z+1],], ^f [-x, -z]	c[-x-x+1,-z]	(-2, -y, -z] + 1]

stabilizing the crystal structure. Table 3 further lists details about the hydrogen bonds. In addition, Fig. 2 shows the extensive hydrogen-bonding interactions between cations and anions from a complex 3D network along the a-, b-, and c-axes. The 1-methylimidazole cation is an H-bond donor, and the BTO anion is a H-bond acceptor. The N(6) atoms from 1-methylimidazole cation and O(1), N(4) atoms from the BTO anion are involved in the N(6)– $H(6A)\cdots O(1)$ hydrogen bond and N(6)– $H(6A)\cdots N(4)$



Fig. 3 IR spectrum of $(1-M)_2$ BTO



Fig. 4 DSC curve of $(1-M)_2$ BTO at 10 K min⁻¹

hydrogen bond, which connect tightly between the 1-methylimidazole cations and BTO anion.

Characterization of (1-M)₂BTO

The structure of $(1-M)_2$ BTO was supported further by its corresponding FT-IR, ¹H NMR, ¹³C NMR, and elemental analysis. FT-IR spectrum of $(1-M)_2$ BTO (Fig. 3) reveals that the intense broad bands at 3434, 3152, and 2919 cm⁻¹ are attributed to the N–H, =C–H, and –CH₃ stretching vibrations of $(1-M)_2$ BTO, respectively. The sharp peak at 1404 cm⁻¹ is ascribed to the bending vibration of –CH₃. In addition, the peak at 732 cm⁻¹ is caused by the out-of-plane bending vibration of =C–H. Consequently, the *N*-oxide of the aromatic tetrazole ring system generates vibrations at 1384–700 cm⁻¹ [17]. Thus, the FT-IR spectrum was suggested that $(1-M)_2$ BTO was successfully prepared.



Fig. 5 TG-DTG curve of $(1-M)_2$ BTO at 10 K min⁻¹



Fig. 6 FT-IR spectra of gas products of $(1-M)_2$ BTO during decomposition at individual temperatures

The ¹H NMR and ¹³C NMR spectra also confirmed the correct structure of $(1-M)_2$ BTO. In the ¹H NMR spectrum, the signal for the methyl of salt occurred as a singlet at $\delta/$ ppm = 3.76 [*s*, CH₃]. The signals in the ¹³C NMR [DMSO- d^6] spectrum of salt was found at $\delta/$ ppm = 34.67 [CH₃], and $\delta/$ ppm = 135.55 [CN₄O].

Thermal analysis of (1-M)₂BTO

Thermal behavior of energetic materials is a signification factor to evaluate their practical safety and storage. Therefore, differential scanning calorimetry (DSC) and thermogravimetry-derivative thermogravimetry (TG-DTG) were used to investigate the thermal behavior of the new energetic salt. The DSC and TG-DTG curves with a linear heating rate of 10 K min⁻¹ in flowing high-purity nitrogen were obtained and were shown, respectively, in Figs. 4 and 5. Endothermic and exothermic processes both occur in the DSC curve (Fig. 4). The intense endothermic peak appeared at a temperature of 412 K, indicating that the salt began to melt. The strong exothermic decomposition stage was shown in the DSC curve, and the peak was observed at 530 K. Thermal behavior of (1-M)₂BTO was further investigated by TG-DTG (Fig. 5), which revealed a severe mass loss step of 80.2% in the range of 481-558 K.

Thermogravimetric analysis tandem infrared spectrum (TGA-IR) was used to identify the constituents of the thermal decomposition gas and understand the thermal decomposition mechanism of $(1-M)_2$ BTO (Fig. 6). The results showed that main decomposition products were likely H₂O (3750 cm⁻¹), N₂O (2240, 2204, 1300, and 714 cm⁻¹), NH₃ (964 and 930 cm⁻¹), and NO (1912 cm⁻¹) [24]. When the temperature increased to 582.7 K, infrared signals were hardly observed, which indicated that $(1-M)_2$ BTO is completely decomposed. Therefore, the salt was decomposed into H₂O, NH₃, NO_x, and a small amount of residue. Based on the discussion above, a possible mechanism for the thermal decomposition of $(1-M)_2$ BTO has been proposed as follows and illustrated in Fig. 7.

Thermal decomposition kinetics of (1-M)₂BTO

The effects of $(1-M)_2$ BTO on the thermal decomposition kinetics were investigated by DSC at different heating rates of 5, 10, 15, 20 K min⁻¹ (Fig. 8). The methods of Kissinger's [25] and Ozawa-Doyle's method [26, 27] were applied to obtain kinetic parameters, the apparent activation energy (E_a) and pre-exponential factor (A). The





Fig. 8 DSC curves of the main exothermic decomposition of (1- $M)_2$ BTO at different heating rates

Kissinger Eq. (1) and Ozawa-Doyle Eq. (2) are as follows, respectively:

$$\ln\left(\frac{\beta}{T_{\rm p}^2}\right) = \ln\left(\frac{AR}{E_{\rm a}}\right) - \frac{E_{\rm a}}{RT_{\rm p}} \tag{1}$$

$$\lg \beta = C - 0.4567 E_{\rm a}/RT \tag{2}$$

where T_p is the peak temperature (K), A is the pre-exponential factor (s⁻¹), E_a is the apparent activation energy (kJ mol⁻¹), R is the gas constant (8.314 J mol⁻¹ K⁻¹), β is the linear heating rate (K min⁻¹), and C is a constant.

Table 5 Calculation of the parameters using Kamlet-Jacobs equation

$M/g \text{ mol}^{-1}$	$\rho/{\rm g}~{\rm cm}^{-3}$	$N/\text{mol g}^{-1}$	$\overline{M}/g \text{ mol}^{-1}$	$\Delta H_{\rm f}^{\theta}/{\rm kJ}~{\rm mol}^{-1}$
442.43	1.384	0.0429	17	917.3

The kinetic parameters of E_a and A basing on the methods of Kissinger and Ozawa-Doyle are derived from the slope and the intercept of the linear dependence between T_p and β according to Eqs. (1) and (2). The results are listed in Table 4.

The calculated results by Kissinger and Ozawa-Doyle methods are similar, and they all fall within the normal range of the kinetic parameters for the thermal decomposition reaction of solid materials [28]. From Table 4, the exothermic peak T_p shifts to higher temperatures as the heating rate increasing and the linear correlation coefficients are extremely close to 1 demonstrating that the results are credible. The Arrhenius equation can be expressed using the obtained E_a (the average of E_k and E_o) and $\ln A_k$ values: $\ln k = 29.18 - 131.53 \times 10^3 / RT$.

Energetic properties

Detonation parameters including detonation velocity (D) and detonation pressure (P) are critical parameters for energetic materials. The empirical Kamlet-Jacobs equations [29] were applied to estimate detonation velocity and detonation pressure for $(1-M)_2$ BTO as shown in the following equations:

Table 4 Peak temperatures of the exothermic stage at different	$\beta/\mathrm{K} \mathrm{min}^{-1}$	$T_{\rm p}/{\rm K}~{\rm min}^{-1}$	Kissinger's method			Ozawa–Doyle's method	
heating rates and kinetic parameters			$\overline{E_{\rm k}/{\rm kJ}~{\rm mol}^{-1}}$	ln A/s ⁻¹	r _k	$E_{\rm o}/{\rm kJ}~{\rm mol}^{-1}$	r _o
	5	516.5	130.56	29.18	0.994	132.50	0.995
	10	528.3					
	15	533.3					
	20	540.1					





Table 6 Energetic properties of (1-*M*)₂BTO compared with TNT, RDX, TATB

Sample	$ ho^{\rm a}/{ m g~cm^{-3}}$	$T_{\rm dec}^{\rm b}/{\rm K}$	$N + O^{c} / \%$	$\Delta H_{\rm f}^{\rm d}/{\rm kJ}~{\rm mol}^{-1}$	P ^e /GPa	$D^{\rm f}/{\rm m~s^{-1}}$	IS ^g /J
(1- <i>M</i>) ₂ BTO	1.384	530	70.14	917.3	20.7	7448	> 50
TNT^h	1.648	568	18.50	95.3	19.5	6881	15
RDX^h	1.806	503	37.84	83.8	34.9	8748	7.5
TATB ⁱ	1.930	597	69.74	- 139.7	31.1	8114	50

^aCalculated density, ^bdecomposition peak temperature, ^cnitrogen and oxygen content, ^dcalculated molar formation enthalpy of the salts, ^edetonation pressure, ^fdetonation velocity, ^gimpact sensitivity, ^hRef. [33]. ⁱRef. [34]

$$D = 1.01 \left(N \overline{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.3\rho)$$
(3)

$$P = 1.558\rho^2 N \overline{M}^{1/2} Q^{1/2}$$
(4)

where *D* is the detonation velocity (km s⁻¹), *P* is the detonation pressure (GPa), *N* is the explosive detonation that generated gas moles per gram (mol g⁻¹), \overline{M} is the gaseous product of the average molecular weight (g mol⁻¹), *Q* is the explosive detonation chemical energy (kJ g⁻¹) per gram, and ρ is the density (g cm⁻³). The value of *Q* should be calculated firstly to calculate the values of *D* and *P*. The *Q* is determined by heat of formation ($\Delta H_{\rm f}^{\theta}$) of the detonation reactants and products.

Basing on Born-Haber's [30] (*m*, *n*, *o*, and *p* stand for the factor of C, H₂, N₂, O₂, respectively) energy cycle (Fig. 9), the standard heat of formation ($\Delta H_{\rm f}^{\theta}$) of a salt can be simplified in the formula (5):

$$\Delta H_{\rm f}^{\theta}(\text{ionic salt}, 298 \,\text{K}) = \Delta H_{\rm f}^{\theta}(\text{anion salt}, 298 \,\text{K}) + \Delta H_{\rm f}^{\theta}(\text{cation salt}, 298 \,\text{K}) - \Delta H_{\rm L}$$
(5)

where $\Delta H_{\rm L}$ is the lattice energy of salt and can be predicted using the formula suggested [31]. The calculated standard enthalpy of formation for the 1-methylimidazole and BTO²⁻ was 126.0 kJ mol⁻¹ [32] and 587.7 kJ mol⁻¹ [6, 17], respectively. Detonation parameters in the Kamlet-Jacobs equation are shown in Table 5.

The *Q* estimated through $\Delta H_{\rm f}^{\theta}$ was 917.3 kJ g⁻¹, and the theoretically computed detonation velocity (*D*) and detonation pressure (*P*) were determined as 7448 m s⁻¹ and 20.7 GPa, which show superior detonation performance than those of TNT (6881 m s⁻¹, 19.50 GPa) and lower than those of RDX (8478 m s⁻¹, 34.9 GPa), respectively, (Table 6).

Sensitivity must be seriously considered in the research because it is closely related to the safety of handling and storage of explosives. For initial safety testing, impact and friction sensitivities are measured using the fall hammer test with approximately 30 mg of samples (10 kg drop hammer). The result presents that $(1-M)_2$ BTO has low impact sensitivity (> 50 J) and low friction sensitivity (180 N), so it may be applied as insensitive energetic materials owing to their high nitrogen content, low mechanical sensitivity, good stability, and environmental compatibility.

Conclusions

In summary, the energetic salt, $(1-M)_2$ BTO was synthesized successfully and its structure was confirmed by single-crystal X-ray diffraction and other spectroscopic analysis. Furthermore, thermal stability analysis and thermal decomposition kinetics suggested that $(1-M)_2$ BTO exhibits good resistance to thermal decomposition of up to 530 K, and incurred 80.2% mass loss in the temperature range of 481–558 K. The apparent activation energies obtained through the methods of Kissinger and Ozawa are 130.56 and 132.50 kJ mol⁻¹, respectively, with pre-exponential factor of ln A(s⁻¹) = 29.18. The enthalpy of formation for the salt was calculated as 917.3 kJ mol⁻¹. Based on the Kamlet-Jacobs equation, the detonation velocity and detonation pressure of $(1-M)_2$ BTO are 7448 m s⁻¹ and 20.7 GPa, respectively.

Experimental

Caution!

Although we experienced no difficulties in the synthesis and characterization of the salt, small-scale syntheses are strongly encouraged. All of compounds should be handled extremely with care by using the best safety equipment and the correct experimental manipulation.

General

All chemicals and solvent were purchased commercially from Aladdin (Shanghai China) and used as received. Fourier-transform infrared spectroscopy (FT-IR) was recorded with a Nicolet-5700 FT-IR spectrometer using pressed KBr pellet in the range from 4000 to 400 cm⁻¹. ¹H NMR and ¹³C NMR spectra of $(1-M)_2$ BTO were performed on a JEOL GSX 600 MHz nuclear magnetic resonance (NMR) spectrometer in a d^6 -DMSO solution by using tetramethylsilane as an internal standard. X-ray singlecrystal diffraction analysis was collected by a Bruker Smart APEX II CCD diffractometer. DSC was performed by a Q200 DSC instrument (TA Instruments, USA) in flowing high-purity nitrogen at a heating rate of 5, 10, 15, and 20 K min⁻¹. TGA was performed with an SDT Q600 TGA instrument (TA Instruments, USA) at a heating rate of 10 K min⁻¹ in flowing high-purity nitrogen.

Synthesis of 1H, 1'H-5, 5'-bistetrazole-1, 1'-diolate dihydrate (H₂BTO)

 H_2BTO was synthesized by a four-step reaction from the raw material glyoxal in accordance with a previously reported procedure [17]. Firstly, glyoxal was treated with hydroxylamine to form glyoxime. Glyoxime was then chlorinated with Cl_2 gas in ethanol. And then chloro/azido exchange occurred and yielded diazidoglyoxime. Diazidoglyoxime was cyclized under acidic conditions (HCl gas in diethyl ether) to produce H_2BTO .

Bis-1-methylimidazole 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate salt (1-*M*)₂BTO

H₂BTO (206 mg, 1 mmol) was dissolved in 5 mL of distilled water. Then, 0.16 mL 1-methylimidazole was added dropwise to the above solution with magnetic stirring. The mixed solution was refluxed for 10 min. After cooling to room temperature, $(1-M)_2$ BTO crystallized as a solid. The samples were filtered and were dried under vacuum, yield 287 mg (0.65 mmol, 76%). ¹H NMR (600 MHz, [D₆]DMSO, 25 °C) δ /ppm = 8.37, 7.41, 7.30, 3.76. 13C NMR (150 MHz, [D₆]DMSO, 25 °C) δ /ppm = 137.18, 135.55, 124.06, 122.38, 34.67. IR (KBr) v cm⁻¹: 3434, 3152, 2919, 2850, 1631, 1404, 1356, 1282, 1234, 1165, 1057, 999, 732, 626, 503. Elemental analysis (EA): Found/%: C 27.12, H 5.88, N 37.97; Calculated/%: C 27.15, H 5.92, N 37.99.

Acknowledgements This work was supported by the financial support received from the Science Challenge Project (Project No. TZ2018004), the National Natural Science Foundation of China (Project No. 51372211), the China Academy of Engineering Physics Research Institute (Project No. 18zh0079) and Open Project of State Key Laboratory Cultivation Base for Nonmetal Composites and Functional (Project No. 14tdfk05).

References

- Badgujar DM, Talawar MB, Asthana SN, Mahulikar PP. Advances in science and technology of modern energetic materials: an overview. J Hazard Mater. 2008;151:289–305.
- Cumming A. Energetic materials and the environment. Propellants Explos Pyrot. 2017;42:5–6.
- 3. Bachmann WE, Sheehan JC. A new method of preparing the high explosive RDX. J Am Chem Soc. 1949;71:1842–5.
- 4. Monteilrivera F, Paquet L, Halasz A, Montgomery MT, Hawari J. Reduction of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine by zerovalent iron: product distribution. Environ Sci and Technol. 2005;39:9725–31.

- Simini M, Checkai RT, Kuperman RG, Phillips CT, Kolakowski JE, Kurnas CW, Sunahara GI. Reproduction and survival of *Eisenia fetida* in a sandy loam soil amended with the nitroheterocyclic explosives RDX and HMX. The 7th international symposium on earthworm. Ecology. 2003;47:657–62.
- 6. Wang RH, Xu HY, Guo Y, Sa RJ, Shreeve JM. Bis[3-(5-nitroimino-1,2,4-triazolate)]-based energetic salts: synthesis and promising properties of a new family of high-density insensitive materials. J Am Chem Soc. 2010;132:11904–5.
- Yin P, Zhang QH, Zhang JH, Parrish DA, Shreeve JM. *N*-trinitroethylamino functionalization of nitroimidazoles: a new strategy for high performance energetic materials. J Mater Chem A. 2013;1:7500–10.
- Feng YY, Liu XY, Duan LQ, Yang Q, Wei Q, Xie G, Chen SP, Yang XW, Gao SL. In situ synthesized 3D heterometallic metalorganic framework (MOF) as a high-energy-density material shows high heat of detonation, good thermostability and insensitivity. Dalton Trans. 2015;44:2333–9.
- 9. He L, Tao GH, Parrish DA, Shreeve JM. Impact insensitive dinitromethanide salts. Chem Commun. 2013;49:10329–31.
- Zhang WQ, Zhang JH, Deng MC, Qi XJ, Nie FD, Zhang QH. A promising high-energy-density material. Nat Commun. 2017;8:181.
- Feng YG, Bi YG, Zhao WY, Zhang TL. Anionic metal-organic frameworks lead the way to eco-friendly high-energy-density materials. J Mater Chem A. 2016;4:7596–600.
- Talawar MB, Sivabalan R, Mukundan T, Muthurajan H, Sikder AK, Gandhe BR, Rao AS. Environmentally compatible next generation green energetic materials (GEMs). J Hazard Mater. 2009;161:589–607.
- 13. Zhang JH, Zhang QH, Vo TT, Parrish DA, Shreeve JM. Energetic salts with π -stacking and hydrogen-bonding interactions lead the way to future energetic materials. J Am Chem Soc. 2015;137:1697–704.
- Klapoetke TM, Preimesser A, Stierstorfer J. Energetic derivatives of 4,4',5,5'-tetranitro-2, 2'-bisimidazole (TNBI). Z Anorg Allg Chem. 2012;638:1278–86.
- Klapoetke TM, Martin FA, Mayr NT, Stierstorfer J. Synthesis and characterization of 3,5-diamino-1,2,4-triazolium dinitramide. Z Anorg Allg Chem. 2010;636:2555–64.
- Tselinskii IV, Mel'nikova SF, Romanova TV. Synthesis and reactivity of carbohydroximoyl azides: I. Aliphatic and aromatic carbohydroximoyl azides and 5-substituted 1-hydroxytetrazoles based thereon. Russ J Org Chem. 2001;37:430–6.
- Fischer N, Klapoetke TM, Reymann M, Stierstorfer J. Nitrogenrich salts of 1H,1'H-5,5'-bitetrazole-1,1'-diol: energetic materials with high thermal stability. Eur J Inorg Chem. 2013;2013:2167–80.
- Fischer N, Fischer D, Klapoetke TM, Piercey DG, Stierstorfer J. Pushing the limits of energetic materials: the synthesis and characterization of dihydroxylammonium 5,5'-bistetrazole-1,1'diolate. J Mater Chem. 2012;22:20418–22.
- Shang Y, Jin B, Liu QQ, Peng RF, Guo ZC, Zhang QC. Synthesis, thermal behavior, and energetic properties of diuronium 1H,1'H-5,5'-bistetrazole-1,1'-diolate salt. J Mol Struct. 2017;1133:519–25.
- 20. Shang Y, Jin B, Peng RF, Guo ZC, Liu QQ, Zhao J, Zhang QC. Nitrogen-rich energetic salts of 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate: synthesis, characterization, and thermal behaviors. RSC Adv. 2016;6:48590–8.
- Zhang ZB, Yin L, Yin X, Zhang JG. Preparation, crystal and properties of nitrogen-rich energetic salt of bis(semicarbazide)5,5'-bitetrazole-1,1'-diolate. Crystals. 2016;6:76075–83.
- 22. Fischer N, Izsák D, Klapoetke TM, Rappenglüeck S, Stierstorfer J. Nitrogen-rich 5,5'-bistetrazolates and their potential use in

propellant systems: a comprehensive study. Chem Eur J. 2012;18:4051-62.

- Huang HF, Zhou ZM, Liang LX, Song JH, Wang K, Cao D, Bian CM, Sun WW, Xue M. Nitrogen-rich energetic dianionic salts of 3,4-bis(1*H*-5-tetrazolyl)furoxan with excellent thermal stability. Z Anorg Allg Chem. 2012;638:392–400.
- Niu H, Chen SS, Jin SH, Li LJ, Jing BC, Jiang ZM, Ji JW, Shu QH. Thermolysis, nonisothermal decomposition kinetics, calculated detonation velocity and safety assessment of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate. J Therm Anal Calorim. 2016;126:473–80.
- 25. Kissinger HE. Reaction kinetics in differential thermal analysis. Anal Chem. 1957;29:1702–6.
- 26. Doyle C. Kinetic analysis of thermogravimetric data. J Appl Polym Sci. 1961;5:285–92.
- Ozawa T. A new method of analyzing thermogravimetric data. B Chem Soc Jpn. 1965;38:1881–6.
- 28. Li ZM, Xie SH, Zhang JG, Feng JL, Wang K, Zhang TL. Two high nitrogen content energetic compounds: 3,6-diguanidino-

1,2,4,5-tetrazine and its diperchlorate. J Chem Eng Data. 2012;57:729–36.

- Kamlet MJ, Jacobs SJ. Chemistry of detonations. I. A simple method for calculating detonation properties of C-H-N-O explosives. J Chem Phys. 1968;48:23–35.
- Jenkins HDB, Tudela D, Glasser L. Lattice potential energy estimation for complex ionic salts from density measurements. Inorg Chem. 2002;41:2364–7.
- Sućeska M. Calculation of the detonation properties of C-H-N-O explosives. Propellants, Explos, Pyrotech. 1991;16:197–202.
- Verevkin SP, Zaitsau DH, Emel'yanenko VN, Paulechka YU, Blokhin AV, Bazyleva AB, Kabo GJ. Thermodynamics of ionic liquids precursors: 1-methylimidazole. J Phys Chem B. 2011;115:4404–11.
- Tang YX, Gao HX, Parrish DA, Shreeve JM. 1,2,4-Triazole links and *N*-azo bridges yield energetic compounds. Chem Eur J. 2015;21:11401–7.
- Gao HX, Shreeve JM. Azole-based energetic salts. Chem Rev. 2011;111:7377–436.