Accepted Manuscript

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PII:	S0022-2860(16)31299-6
DOI:	10.1016/j.molstruc.2016.12.009
Reference:	MOLSTR 23207
To appear in:	Journal of Molecular Structure
Received Date:	19 September 2016
Revised Date:	02 December 2016
Accepted Date:	02 December 2016

Please cite this article as: Yu Shang, Bo Jin, Qiangqiang Liu, Rufang Peng, Zhicheng Guo, Qingchun Zhang, Synthesis, Thermal Behavior, and Energetic Properties of Diuronium 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate Salt, *Journal of Molecular Structure* (2016), doi: 10.1016/j.molstruc. 2016.12.009

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Highlights

- A new energetic salt called diuronium 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate (**DUBTO**) was synthesized successfully and fully characterized.
- The results of the non-isothermal kinetic analysis indicated that the Arrhenius equation of the main exothermic process can be expressed as follows: $lnk = 46.85 218.485 \times 10^3/RT$.
- This salt shows excellent impact sensitivities of >40 J and promising detonation velocity and detonation pressure of **DUBTO** were calculated as 8267 $m \cdot s^{-1}$ and 29.15 GPa, respectively.

Synthesis, Thermal Behavior, and Energetic Properties of Diuronium 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate Salt

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Abstract. A new nitrogen-rich energetic salt called diuronium 1H, 1'H-5, 5'-bistetrazole-1, 1'-diolate (**DUBTO**) was first synthesized by reacting urea with 1H, 1'H-5, 5'-bistetrazole-1, 1'-diolate dihydrate (**H**₂**BTO** 2**H**₂**O**). The structure of this new energetic salt was fully characterized through single-crystal X-ray diffraction, FT-IR, ¹H NMR, ¹³C NMR, and elemental analysis. **DUBTO** was crystallized in the monoclinic space group P21/n. The thermal stability was investigated through differential scanning calorimetry (DSC) and thermogravimetric tandem infrared spectrometry. Results showed that **DUBTO** contained one endothermic process and two exothermic processes. The second exothermic process is mainly intense exothermic decomposition with a mass loss of approximately 69.3 % in the temperature range of 523.8-594.6 K. The non-isothermal kinetic parameters of the main exothermic process were calculated based on methods proposed by Kissinger and Ozawa-Doyle. Based on the Kamlet-Jacobs formula, the detonation velocity and detonation pressure of **DUBTO** were calculated as 8267 m·s⁻¹ and 29.15 GPa, respectively.

Keywords: Diuronium 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate (**DUBTO**); *N*-Oxides; Single crystal; Thermal properties; Energetic properties

1. Introduction

Over the past few decades, considerable effort has focused on the development of nitrogenrich high-energy-density materials (HEDMs) that exhibit a good balance between sensitivity and performance in addition to environmental compatibility.[1-9] Nitrogen-rich energetic salts are among the hottest topics in the field of HEDM.[10] These salts characterized by high energy and low sensitivity play an important role in energetic materials because of their high heat of formation (HOF), density, thermal stability, good oxygen balance, and environmentally friendly properties.[11-14] Considering the requirements of high energy, insensitivity, and stability for energetic materials, several researchers, including Klapötke,[7, 15-20] Shreeve,[21-27] and others[28-33], have synthesized many energetic salts through weak intermolecular interactions.

Tetrazole moiety is a promising energetic building block in this research area because it contains a large number of energetic N–N and C–N bonds, exhibits extensive hydrogen bonding, and decomposes to produce a high percentage of dinitrogen.[34-36] To improve the energetic properties of tetrazoles, several recently published studies showed that introduction of N-oxides yields compounds characterized by higher densityand stability, lower sensitivity, and better oxygen balance.[8, 37-41] 1*H*,1'*H*-5,5'-bitetrazole-1,1'-diol, a typical bitetrazole with *N*-oxides, is strongly acidic and bears two protons that can easily form stable oxygen-rich salts with various nitrogen-rich bases.[42] A series of different 1H,1H-5,5-bitetrazole-1,1-diolates salts were synthesized and actively studied,[42-47] such as dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50), which is one of the most promising energetic materials to replace the

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commonly used military explosive, RDX (1,3,5-trinitro-1,3,5-triazacyclohexane).[44] Uronium is an important nitrogen-rich cation used to construct high-performance energetic materials because of its obvious advantages such as high nitrogen and oxygen percentages, high heat of formation, and low cost.[48] Similar to hydroxylammonium cation, the oxygen of uronium not only increases the oxygen balance but also provides the acceptor character of the hydrogen bond. In this study we present the synthesis and characterization of the new energetic compound **DUBTO**. Furthermore, the thermodynamic analysis, energetic properties, and impact sensitivity were performed to obtain comprehensive data.

2. Results and Discussion

2.1 Synthesis

1H, 1'H-5, 5'-bistetrazole-1,1'-diolate dihydrate ($H_2BTO\cdot 2H_2O$) was synthesized in accordance with a previously described procedure.[42] $H_2BTO\cdot 2H_2O$ was synthesized starting from glyoxal, which was treated with hydroxylamine to form glyoxime. Glyoxime was then chlorinated with Cl₂ gas in ethanol; chloro/azido exchange occurred and yielded diazidoglyoxime, which was cyclized under acidic conditions (HCl gas in diethyl ether) to produce 1. The new energetic salt was synthesized after 1 was treated with stoichiometric amounts of urea, as shown in Scheme 1.



Scheme 1. The synthesis of ATHBTO

2.2 Characterization of DUBTO.

The structure of **DUBTO** is supported by FT-IR, ¹H NMR, ¹³C NMR, and elemental analysis. In addition, the crystal structure of **DBUTO** was measured by X-ray diffraction. Figure 1 shows the IR spectrum of **DUBTO**. As shown in Figure 1, the intense broad band at 3447 cm⁻¹ is attributed to the N–H stretching vibrations of **DUBTO**, and the peak at 1665 cm⁻¹ corresponds to the stretching vibrations of C=O.[48] Moreover, the N-oxide of the aromatic tetrazole ring system shows vibrations at 1384–700 cm⁻¹ [ν (NN), ν (NCN), γ (CN), δ aromatic ring], similar to those of other 1*H*,1*H*-5,5-bitetrazole-1,1-diolates salts.[42] Consequently, the infrared spectrum shows good consistency with the structural features of the compound.



Figure 1. IR spectrum of DUBTO

The ¹H NMR and ¹³C NMR spectra also confirmed the correct structure of **DUBTO**. In the ¹H NMR spectrum, the signal for the amino group of salt occurred as a broad singlet at $\delta = 6.99$ ppm (s, 4H, NH₂).[48] In the ¹³C NMR spectrum, the shifts corresponding to the cation and anion in this study are in good agreement with previously recorded shifts for the relevant cation and anion.[42, 48] The signals in the ¹³C NMR [DMSO-*d6*] spectrum of salt were found at δ (ppm) = 160.55 [C=OH⁺] and 135.22 [CN₄O].

A suitable crystal of **DUBTO** was obtained by slowly evaporating water at room temperature, and was then subjected to single crystal X-ray analysis. The X-ray crystallographic analysis data for **DUBTO** show that it crystallizes in the monoclinic space group P21/n with a calculated density of 1.695 g/cm³ (Figure 2) based on two molecules packed in the unit-cell volume of 568.7(2) Å³. The selected data and parameters from their X-ray structures are listed in Table 1. As shown in Figure 2, all of the atoms of **BTO** anion are almost coplanar, with the largest torsion angle of 179.85(16)° in N(2)-N(1)-C(1)-C(1)^{#1}. With bond lengths of 1.3108(18) to 1.3485(18) Å, the distances between the ring atoms of the two tetrazole-oxide rings lie between the length of formal C-N and N-N single and double bonds (C=N: 1.470 Å, C=N: 1.220 Å; N=N: 1.480 Å, N=N: 1.240 Å).[49] Furthermore, the C-C bond connecting the two tetrazole moieties and the N–O bonds are found between a C–C single bond and a C=C double bond $(d(C(1)-C(1)^{\#1}))$ = 1.445(3) Å) and between a N–O single bond and a N=O double bond (d(N(1)-O(1))) =1.3272(15) Å), respectively [42] Selected bond lengths and angles of **DUBTO** are presented in Table 2. This result demonstrates the conjugation of the negative charge throughout the aromatic Meanwhile, all the torsion angles [i.e., O(1)-N(1)-C(1)-N(4) (-176.79(12)°), O(1)-N(1)rings. $C(1)-C(1)^{\#1}$ (3.0(3)°)] are close to $\pm 180^{\circ}$ and 0°, which illustrates that the atoms of anion are strictly coplanar. The packing structure of **DUBTO** viewed along the c axis is built up by hydrogen bonding. The extensive hydrogen-bonding interactions between cations and anions form a complex 3D network (Figure 3). Further details are provided in Table 3.



Figure 2. Ball-and-stick molecular structure of DUBTO

Compound	DUBTO	
Empirical formula	C ₄ H ₁₀ N ₁₂ O ₄	
Formula weight	290.24	
CCDC number	1487783	
Crystal size [mm ³]	0.21 x 0.20 x 0.19	
Crystal system	Monoclinic	
Space group	P21/n	
<i>a</i> [Å]	3.6802(8)	
<i>b</i> [Å]	17.688(4)	
<i>c</i> [Å]	8.7803(19)	
α [°]	90	
β [°]	95.758(2)	
γ [°]	90	
V [Å ³]	568.7(2)	
Ζ	2	
$\rho_{\text{calcd}} \left[\text{g} \cdot \text{cm}^{-3} \right]$	1.695	
<i>T</i> [K]	100(2)	
F(000)	300	
$R_{\rm int.}$	0.0214	
Data	1011	
Restraints	1	
parameters	91	
$GOF^{[a]}$ on F^2	1.05	
$R_{1}^{[b]}(I \ge 2\sigma(I))$	0.0328	
$\omega R_2 (I > 2\sigma (I))$	0.0859	
$R_1(\text{all data})$	0.0361	
$\omega R_2^{[c]}$ (all data)	0.0884	

 Table 1. Crystal data and structure refinement parameters of DUBTO

^[a] GOF= Goodness of Fit. ^[b] $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$. ^[c] $\omega R_2 = [(\omega (F_0^2 - F_c^2)^2) / \omega (F_0^2)^2]^{1/2}.$



Figure 3. Ball-and-stick packing diagram of **DUBTO** viewed down the c axis. Dashed lines indicate hydrogen bonding

Table 2. Bond Lengths [Å] and angles [°] for DUBTO					
bond	Length/Å	bond	Angle/°		
N(1)-O(1)	1.3272(15)	O(1)-N(1)-N(2)	121.51(11)		
N(1)-N(2)	1.3335(17)	O(1)-N(1)-C(1)	129.32(11)		
N(1)-C(1)	1.3459(18)	N(2)-N(1)-C(1)	109.10(11)		
N(2)-N(3)	1.3108(18)	N(3)-N(2)-N(1)	105.96(11)		
N(3)-N(4)	1.3485(18)	N(2)-N(3)-N(4)	111.08(12)		
N(4)-C(1)	1.3269(19)	C(1)-N(4)-N(3)	105.83(12)		
N(6)-C(2)	1.3137(19)	C(2)-N(6)-H(6A)	120		
N(6)-H(6A)	0.88	C(2)-N(6)-H(6B)	120		
N(6)-H(6B)	0.88	H(6A)-N(6)-H(6B)	120		

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N(7)-C(2)	1.3146(19)	C(2)-N(7)-H(7A)	120
N(7)-H(7A)	0.88	C(2)-N(7)-H(7B)	120
N(7)-H(7B)	0.88	H(7A)-N(7)-H(7B)	120
O(2)-C(2)	1.2895(18)	C(2)-O(2)-H(2C)	116.6
O(2)-H(2C)	0.9659	N(4)-C(1)-N(1)	108.03(12)
C(1)-C(1)#1	1.445(3)	N(4)-C(1)-C(1)#1	127.47(16)
		N(1)-C(1)-C(1)#1	124.51(15)
		O(2)-C(2)-N(6)	117.30(13)
		O(2)-C(2)-N(7)	121.39(13)
		N(6)-C(2)-N(7)	121.31(13)
Symmony dunsion	Table 3. Hydroge	en bonds for DUBTO	x · 2, y · 1, 2 · 5
D-HA	d(D-H)	d(HA)	d(DA)
N(6)-H(6A)O(1)#1	0.88	2.153	2.977
N(6)-H(6B)O(2)#2	0.88	2.421	2.949
N(6)-H(6B)N(2)#3	0.88	2.523	3.18
N(7)-H(7A)N(4)#4	0.88	2.208	2.989
N(7)-H(7B)N(3)	0.88	2.166	3.031
O(2)-H(2C)O(1)#5	0.966	1.511	2.472
O(2)-H(2C) = N(1)#5	0 966	2,395	3 308

Symmetry transformations used to generate equivalent atoms: #1 [x-3/2, -y+3/2, z-1/2]; 2# [x+1/2, -y+3/2, z+1/2]; 3# [x-1, y, z]; 4# [-x+1, -y+1, -z+2]; 5# [x-1, y, z-1]

2.3 Thermal stability analysis of DUBTO

To investigate the thermal behavior of **DUBTO**, we analyzed it through differential scanning calorimetry (DSC) and thermogravimetry–derivative thermogravimetry (TG–DTG), with a linear heating rate of 10 K/min in flowing high-purity nitrogen. The data curves from these analyses are shown in Figures 4 and 5. In the DSC curve, three processes occur: one endothermic and two exothermic. The endothermic process starts at 451.4 K and shows a peak temperature of 460.6 K. Subsequently, **DUBTO** becomes unstable and begins to decompose. The first exothermic decomposition stage is exhibited in the DSC data, and the peak is observed at 465.3 K. The second exothermic process is a main process with peak temperature of 561.2 K. In addition, TG-DTG curves showed two main mass loss processes during the decomposition of **DUBTO**. The first mass loss occurred at 456.2 K and ended at 479.2 K, accompanied by a mass loss of 10.8 % and a summit peak located at 466.2 K in the DTG curve. The second stage occurred at 523.8 K and ended at 594.6 K, along with 69.3 % mass loss and the summit peak in the DTG curve at 562.3 K.



Figure 4. DSC curve of DUBTO



Figure 5. TG-DTG curve of DUBTO

To improve our understanding of the thermal decomposition behavior of **DUBTO**, thermogravimetric analysis tandem infrared spectrum was used to rapidly identify the constituents of the thermal decomposition gas. Figure 6 depicts the FT-IR spectra of the thermal decomposition of **DUBTO** also exhibits two stages, a characteristic that is consistent with the TG/DTG results. The first decomposition occurred at approximately 455.2 K. From Figure 6, we can deduce that the main decomposition products are H₂O (3450-3600 cm⁻¹) and N₂O (2192-2330 cm⁻¹, 748 cm⁻¹), which was confirmed by the peak in the corresponding IR spectra.[50] In the second stage, the main gas products are HN₃ (3456 cm⁻¹), N₂O (2192-2330 cm⁻¹, 748 cm⁻¹). When the heating temperature increased to 594.6 K, infrared signals nearly disappeared, there by proving that **DUBTO** was completely decomposed.



Figure 6. FT-IR spectra of gas products of DUBTO during decomposition at individual temperatures.

2.4 Thermal decomposition Kinetics of DUBTO

The main exothermic process makes a dominant effect on the decomposition of energetic materials. To explore the decomposition mechanisms of **DUBTO** and obtain the corresponding kinetic parameters [the apparent activation energy (E) and the pre-exponential factor (A)], the Kissinger's method[51] and Ozawa–Doyle's method[52, 53] were employed, depending on the peak temperatures measured at four different heating rates of 5, 10, 15, 20 K/min (Figure 7). The Kissinger Equation (1) and Ozawa–Doyle Equation (2) are as follows, respectively:

$$ln(\beta/T_p^2) = ln(AR/E_a) - (E_a/RT_p)$$
⁽¹⁾

$$\lg \beta = C - 0.4567 E_a / RT \tag{2}$$

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); R is the gas constant (J/mol·K); β is the linear heating rate (K/min) and C is a constant.

The apparent activation energies E_k and E_o , pre-exponential factor A, linear correlation coefficients R_k and R_o for the complex were calculated by Kissinger's method and Ozawa–Doyle's method. The results are fairly similar and are shown in Table 4, which are all in the normal range of kinetic parameters for the thermal decomposition reaction of solid materials. From Table 4, it can be seen that the exothermic peak T_p shifts to higher temperatures as the heating rate increases and the linear correlation coefficients are very close to 1, demonstrating that the results are credible. Using the obtained E_a (the average of E_k and E_o) and lnA_k values, the Arrhenius equation can be expressed as $lnk = 46.85 - 218.485 \times 10^3/RT$ for the exothermic process, which can be applied to estimate the rate constants of the initial thermal decomposition processes of **DUBTO**.



Figure 7. DSC curves of the main exothermic decomposition of DUBTO at different heating rates

Table 4 Peak temperatures of the exothermic stage at different heating rates and the kinetic parameters

$\beta(K_{\min}) = T(K_{\min})$		Kissinger 法		Ozawa 法		
$p(\mathbf{Kinin})$	$I_{p}(\mathbf{K}/\mathbf{IIIII})$	$E_{\rm k}$ (kJ/mol)	<i>lnA</i> (s ⁻¹)	$r_{\rm k}$	$E_{\rm o}$ (kJ/mol)	ro
5	553.6					
10	561.2	210.42	16.95	0.005	217 54	0.006
15	565.2	219.45	40.85	0.995	217.34	0.990
20	569.8					

2.5 Energetic properties

The detonation parameters, detonation velocity (D) and detonation pressure (P) are important parameters of scaling the detonation characteristics of energetic materials. The empirical Kamlet-Jacobs equations[54] were employed to estimate the values of detonation velocity and detonation pressure for **DUBTO**, shown as Equation (3) and (4):

$$D = 1.01 (N\overline{M}^{1/2} Q^{1/2})^{1/2} (1+1.3\rho)$$
(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, ρ is the density (g·cm⁻³). The *Q* value should be calculated first to calculate the *D* and *P* values. *Q* is also determined by the ΔH_f of the detonation reactant and product.



Figure 8. Born-Haber circle of ionic salt

According to the Born–Haber[55] (m, n, o, and p stand for the factor of C, H_2 , N_2 , O_2) energy cycle (figure 8), the standard heat of formation of a salt can be simplified in equation (5):

$$\triangle H_f^{\heartsuit}(\text{ionic salt, 298k}) = \triangle H_f^{\heartsuit}(\text{anion salt, 298k}) + \triangle H_f^{\heartsuit}(\text{cation salt, 298k}) - \triangle H_L \tag{5}$$

Where ΔH_L is the lattice energy of salt and can be predicted by using the formula suggested by Jenkins et al.[56, 57] The calculated standard enthalpy of formation for the uronium and BTO²⁻ were 719.4[48] and 587.7 kJ/mol[42], respectively, as provided in the literature. With the calculated heats of formation and calculated density, detonation parameters were calculated by the Kamlet-Jacobs equation. The calculation of the parameters in the Kamlet–Jacobs equation is shown in Table 5.

Table 5 Calculation of the parameters in the Kamlet–Jacobs equation

$M/(g \cdot mol^{-3})$	$\rho/(g \cdot cm^{-3})$	$N/(\text{mol}\cdot\text{g}^{-1})$	\overline{M} /(g·mol ⁻¹)	$\Delta H_f/(kJ \cdot mol^{-1})$
290.24	1.695	0.0379	22	689.57

The *Q* estimated through the ΔH_f was 1364.41 kJ·g⁻¹, and the theoretically computed detonation velocity (*D*) and detonation pressure (*P*) were 8267 m·s⁻¹ and 29.15 GPa, respectively. This exhibits superior detonation performance than that of TNT (6881 m s⁻¹, 19.50 GPa).[58]

Sensitivity should be extensively investigated because this parameter is closely linked with the safety of handling and applying explosives. In this work, the impact sensitivity of the compound was determined using the fall hammer test with approximately 30 mg samples (10 kg drop hammer). the impact sensitivity was determined using a BAM Fall hammer apparatus with a 10 kg drop weight. The sensitivity was > 40 J, classifying it as impact insensitive energetic materials. This result indicates that the energetic salt is more insensitive than RDX (7.4 J), HMX (7 J), TNT (15 J).[58]

3 Conclusions

A new energetic salt **DUBTO** was synthesized successfully and fully characterized through single-crystal X-ray diffraction, multinuclear NMR spectroscopy, IR spectroscopy and elemental analysis (EA). The thermal stability analysis indicated that a main exothermic process occurred in the temperature range from 523.8 K to 594.6 K as shown in the DSC curve corresponding to TG-DTG curves. The results of the non-isothermal kinetic analysis indicated that the Arrhenius equation of the main exothermic process can be expressed as follows: $lnk = 46.85 - 218.485 \times 10^3/RT$. Moreover, the detonation parameters of **DUBTO** were calculated by using Kamlet-Jacobs equations and the detonation velocity and detonation pressure were calculated as 8267 m·s⁻¹ and 29.15 GPa, respectively.

4 Experimental Section

4.1 General: 5,5'-bistetrazole-1,1'-diolate dihydrate was synthesized according to ref.[42]. All other materials were commercially available and used without further purification. Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet-5700 FTIR spectrometer by using pressed KBr pellets to evaluate the chemical bonding of the samples from 4000 cm⁻¹ to 400 cm⁻¹. ¹H NMR and ¹³C NMR spectra were obtained using a JEOL GSX 600 MHz nuclear magnetic resonance (NMR) spectrometer in a DMSO solution by using tetramethylsilane as an internal standard. DSC was performed by a Q200 DSC instrument (TA Instruments, United States) in flowing high-purity nitrogen at a heating rate of 5, 10, 15 and 20 K/min. TGA was performed with an SDT Q600 TGA instrument (TA Instruments, United States) at a heating rate of 10 K/min in flowing high-purity nitrogen.

4.2 X-ray Crystallography: The single crystal of **DUBTO** was cultured via a slow solvent evaporation method. A colorless prism crystal of dimensions 0.21 x 0.20 x 0.19 mm³ for **DUBTO** was used for single-crystal X-ray diffraction analysis. Data were collected using a three-circle Bruker platform diffractometer equipped with a graphite monochromator and Mo K α radiation (λ = 0.71073 Å). An Oxford Cobra low temperature device was used to maintain **DUBTO** at a constant 100 K during data collection. All calculations were performed using the Crystal Structure crystallographic software package except for refinement, which was performed using *SHELXL*2014. Hydrogen atoms were added theoretically and refined with riding model position parameters and fixed isotropic thermal parameters. The details of the data collection and refinement are presented in Table 1.

4.3 Synthesis of DUBTO: 1*H*,1'*H*-5,5'-bistetrazole-1,1'-diolate dihydrate (206 mg, 1 mmol) was suspended in a few milliliters of water, and urea (120 mg, 2 mmol) was added. The mixture was briefly heated to reflux and filtered. After cooling to room temperature, the resulting solution was evaporated slowly at room temperature for two weeks, and the **DUBTO** precipitated as colorless prism crystals were obtained, yield 194.3 mg (0.67 mmol, 67 %). IR (KBr) *v*/cm⁻¹: 3447 (vs), 2925 (w), 1665 (s), 1384 (w), 1321 (vw) 1178 (w), 1035 (w), 988 (w), 731 (w), 596 (w), 493 (w). ¹H NMR (600 MHz, [D₆]DMSO, 25 °C) δ /ppm: δ = 6.99. ¹³C NMR (150 MHz, [D₆]DMSO, 25 °C) δ /ppm: 160.55, 135.22. elemental analysis (%) calcd for C₄H₁₀N₁₂O₄ (290.24): C, 16.55; H, 3.45; N, 57.93; found: C, 17.31; H, 3.89; N, 57.13.

5 Acknowledgments

We are grateful for financial support from the National Natural Science Foundation of China (project no.51372211), Open Project of State Key Laboratory Cultivation Base for Nonmetal Composites and Functional (project no. 14zdfk05) and Southwest University of Science and Technology Outstanding Youth Fundation (project no. 13zx9107).

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