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Synthesis and Properties of Diguanylurea 3,5-Bis(dinitromethyl)-1,2,4-triazolate

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Abstract: Using ethyl 2-(3-(dinitromethyl)-1*H*-1,2,4-triazol-5-yl)acetate as a starting material, diguanylurea 3,5-bis(dinitromethyl)-1,2,4-triazolate (DMDNMT) was firstly designed and synthesized via the reactions of nitration, hydrolysis and metathesis. The structures of all compounds were characterized by ¹H NMR, ¹³C NMR, IR and element analysis. Based on the theoretical values of densities and heat of formation, the detonation parameters were calculated using Gaussian 09 program and EXPLO5 6.04. Results show that the density of DMDNMT is 1.81 g·cm⁻³, the heat of formation is -446.1 kJ·mol⁻¹, the detonation velocity and detonation pressure are 8624.8 m·s⁻¹ and 29.2 GPa, respectively. DSC and TG-DTG measurements indicate that the decomposition temperature of DMDNMT is 177.3 °C, and its impact sensitivity determined by standard BAM method is 24 J.

Key words: diguanylurea 3,5-bis(dinitromethyl)-1,2,4-triazolate; synthesis; properties

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1 Introduction

Pursuing new insensitive high explosive is the main research hot-point in explosive field. To maximize the detonation performance while minimize the sensitivity, researchers have focused on azoles as the core of energetic compounds, such as triazoles, tetrazoles and furazans^[1-6]. In addition, one approach to synthesize new energetic compounds is the preparation of energetic salts, which mostly have a high density and high stability as a result of their high lattice energy^[7-8]. For example, diti-aminoguanidinium 3,5-bis(dinitromethyl)-1,2,4-triazolate was identified as a kind of potential explosive with high-performance and insensitivity. It has

some desirable traits, including a low impact sensitivity(22 J), a low friction sensitivity(>360 N), and a high detonation velocity (8557 m·s⁻¹)^[9]. In view of the above observations, based on 3,5-bis(dinitromethyl)-1,2,4-triazolate, a novel compound, diguanylurea 3,5-bis(dinitromethyl)-1,2,4-triazolate (DMDNMT) was firstly designed and synthesized. The detailed studies of the synthesis and characterization of DMDNMT were carried out in this work. In addition, the thermal stability and detonation parameters were investigated. The properties of DMDNMT were estimated by B3LYP^[10] method on 6-31G(d, p) basis set of Gaussian 09 procedure^[11] and EXPLO5 6.04^[12]. The main thermal property of DMDNMT was analyzed by DSC and TG-DTG.

2 Experimental

2.1 Materials and Instruments

Ethyl 2-(3-(dinitromethyl)-1*H*-1,2,4-triazol-5-yl)acetate was prepared and purified according to the reference [13], and other reagents were purchased from the commercial sources. ¹H NMR and ¹³C NMR were obtained in DMSO-*d*₆ on a Bruker AV500

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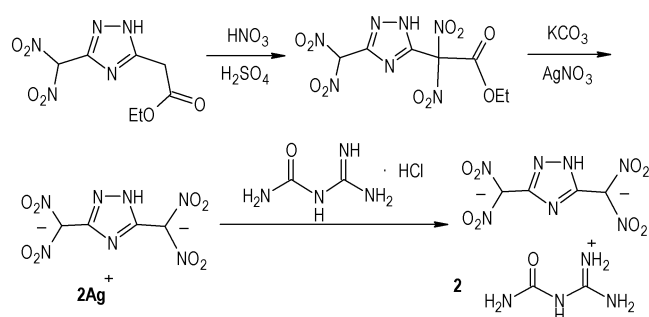
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NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000–400 cm^{-1} . Elemental analyses (C, H and N) were performed on a VARI-EL-3 elemental analyzer. Differential scanning calorimetry (DSC) studies were carried out on a Q200 apparatus (TA, USA) at a heating rate of 10 $\text{K} \cdot \text{min}^{-1}$ under dry oxygen-free nitrogen atmosphere with a flowing rate of 50 $\text{mL} \cdot \text{min}^{-1}$. The TG-DTG experiment was performed with a SDT-Q600 apparatus (TA, USA) operating at a heating rate of 10 $\text{K} \cdot \text{min}^{-1}$ in a flow of dry oxygen-free nitrogen at 100 $\text{mL} \cdot \text{min}^{-1}$.

2.2 Synthesis and Characterization

Using ethyl 2-(3-(dinitromethyl)-1*H*-1,2,4-triazol-5-yl)acetate as a starting material, the title compound DMDNMT was firstly synthesized via the reactions of nitration, hydrolysis and metathesis (Scheme 1).



Scheme 1 Synthetic approach of DMDNMT

2.2.1 Ethyl 2-(5-(Dinitromethyl)-4*H*-1,2,4-triazol-3-yl)-2,2-dinitroacetate

5 mL 98% sulfuric acid was added dropwise to 6 mL 98% nitric acid and sulfuric acid at $-5\text{ }^{\circ}\text{C}$. To the reaction mixture, ethyl 2-(3-(dinitromethyl)-1*H*-1,2,4-triazol-5-yl)acetate (1.0 g, 3.86 mmol) was added slowly. After complete addition, the reaction mixture was stirred at room temperature for other 6 h. Then the reaction mixture was poured into ice water. The white precipitate was filtered to obtain 1.11 g solid with a yield of 82.4% and a purity of 98.5% (HPLC). IR (KBr, ν/cm^{-1}): 3345, 2997, 1759, 1619, 1596, 1524, 1379, 1353, 1306, 1282, 1260, 1190, 1117, 1070, 1029, 993, 973, 845, 801. ^1H NMR (DMSO- d_6 , 500 MHz) δ : 10.217–10.237(1H,

NH), 4.508–4.551 (2H, CH_2), 1.280–1.308 (3H, CH_3); ^{13}C NMR (DMSO- d_6 , 125 MHz) δ : 157.570, 153.268, 149.285, 66.234, 13.890; Anal. calcd for $\text{C}_7\text{H}_7\text{N}_7\text{O}_{10}$: C 24.08, H 2.02, N 28.08; found: C 24.25, H 1.96, N 27.81.

2.2.2 Diguanylurea 3,5-Bis(dinitromethyl)-1,2,4-triazolate (DMDNMT)

Ethyl 2-(5-(dinitromethyl)-4*H*-1,2,4-triazol-3-yl)-2,2-dinitroacetate (0.5 g, 1.43 mmol) was dissolved in 10 mL deionized water. To the reaction mixture, potassium carbonate (0.2 g, 1.43 mmol) was added. The solution was stirred for 30 min. Silver nitrate (2.9 g, 5.72 mmol) was added and the solution was stirred at ambient temperature for other 1 h, which started instantly to precipitate and was filtered. The wet powder was mixed with 10 mL water, and the mixture was transferred into a three-necked round-bottomed flask with a mechanical stirrer. Then guanylurea hydrochloride (0.3 g, 2.14 mmol) was added. The reaction mixture was stirred for 6 h at ambient temperature, and the mixture was filtered. The solution was evaporated to dryness to give 0.42 g with a yield of 61.1%. IR (KBr, ν/cm^{-1}): 3436, 3372, 3009, 1731, 1687, 1604, 1567, 1509, 1467, 1422, 1340, 1251, 1219, 1188, 1122, 999, 978, 930, 819; ^{13}C NMR (DMSO- d_6 , 125 MHz) δ : 156.108, 155.373, 151.465, 126.450; Anal. calcd for $\text{C}_8\text{H}_{15}\text{N}_{15}\text{O}_{10}$: C 19.96, H 3.14, N 43.65; found: C 19.75, H 3.44, N 43.20.

3 Physicochemical and Energetic Properties

All the quantum computations were performed using the Gaussian 09 (Revision A. 02) suite of programs^[11]. The optimized structure was characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The density of DMDNMT was computed based on Monte-Carlo method using the optimized structure at the B3LYP 6-3G (d, p) level of theory. The gas phase heat of formation was calculated by the atomization method using the Gaussian 09 program package at

the CBS-4M level of theory^[14]. Gas phase heat of formation was transformed to solid phase heat of formation by Trouton's rule^[15]. Based on the calculated density and heat of formation, the detonation velocity and detonation pressure for DMDNMT were calculated by EXPLO5 6.04. The thermal behaviors for DMDNMT were indicated by DSC and TG-DTG measurements. The properties of DMDNMT were obtained by calculation or test as follows: density is

$1.81 \text{ g}\cdot\text{cm}^{-3}$, detonation velocity is $8624.8 \text{ m}\cdot\text{s}^{-1}$, heat of formation is $-446.1 \text{ kJ}\cdot\text{kg}^{-1}$. DMDNMT exhibits a high density and detonation velocity. In order to evaluate the reliability and safety in the process of application, BAM standard method^[16] was used to determine the impact sensitivity (IS) for DMDNMT. It showed prospective low sensitivity (IS 24 J). The physicochemical and energetic properties of DMDNMT were listed in Table 1.

Table 1 The physicochemical and energetic properties of DMDNMT

properties	DMDNMT	condition
formula	$\text{C}_8\text{H}_{15}\text{N}_{15}\text{O}_{10}$	
molar mass	481	calculated
nitrogen content / %	43.65	calculated
oxygen balance / %	-44.9	calculated
appearance	orange solid	eyeballing (tested)
decomposition temperature/°C	177.3 (DSC)	DSC (tested)
density / $\text{g}\cdot\text{cm}^{-3}$	1.81	Gaussian 09 program (calculated)
detonation velocity / $\text{m}\cdot\text{s}^{-1}$	8624.8	EXPLO5 6.04 (calculated)
detonation pressure / GPa	29.2	EXPLO5 6.04 (calculated)
heat of formation / $\text{kJ}\cdot\text{mol}^{-1}$	-446.1	Gaussian 09 program (calculated)
impact sensitivities / J	24	BMW (tested)

4 Thermal Stability

As show in Fig.1, the DSC curve of DMDNMT exhibits two thermal decomposition peaks at $177.3 \text{ }^\circ\text{C}$ and $221.2 \text{ }^\circ\text{C}$, respectively. The TG-DTG curves (Fig.2) show that there are two stages in the decomposition process of HDNMT with a mass loss of 82.8% before $192.4 \text{ }^\circ\text{C}$ at first stage, and a total mass loss of 87.4% before $250.9 \text{ }^\circ\text{C}$, finally, 7.2% residue at $381.6 \text{ }^\circ\text{C}$.

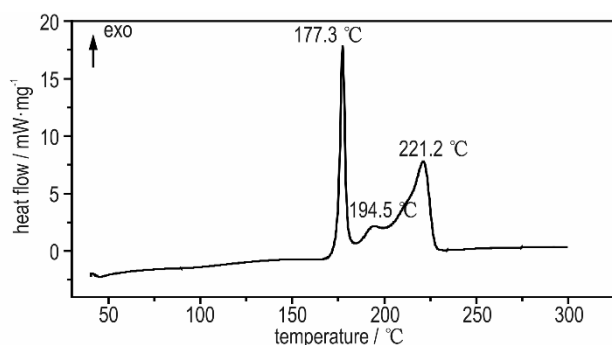


Fig.1 DSC curve of DMDNMT

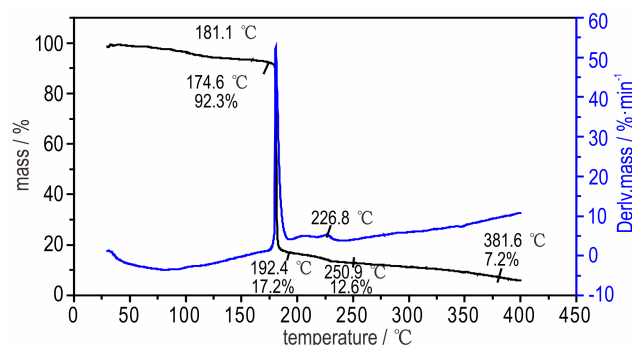


Fig.2 TG-DTG curves of DMDNMT

5 Conclusions

(1) DMDNMT was firstly synthesized using ethyl 2-(3-(dinitromethyl)-1*H*-1,2,4-triazol-5-yl) acetate as a raw material via the reactions of nitration, hydrolysis and metathesis. The structure of DMDNMT was characterized by IR, NMR and element analysis.

(2) The main performance of DMDNMT was calculated by theoretical method. The obtained density

is $1.81 \text{ g}\cdot\text{cm}^{-3}$, heat of formation is $-446.1 \text{ kJ}\cdot\text{kg}^{-1}$, detonation velocity is $8624.8 \text{ m}\cdot\text{s}^{-1}$, and detonation pressure is 29.2 GPa.

(3) The thermal stability of DMDNMT was analyzed by DSC and TG-DTG. The results show that the decomposition temperature of DMDNMT is $177.3 \text{ }^\circ\text{C}$. The impact sensitivities of DMDNMT was tested by BAM standard method, and it shows a low sensitivity (IS 24 J).

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3,5-双(二硝甲基)-1,2,4-三唑的双胍基脲盐的合成与性能

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摘要: 以3-偕二硝甲基-5-乙酸乙酯基-5,5-二硝基-1H-1,2,4-三唑为原料,通过硝化、水解和离子交换反应设计并合成了未见文献报道的新化合物3,5-双(二硝甲基)-1,2,4-三唑的双胍基脲盐(DMDNMT);采用红外光谱、¹H NMR、¹³C NMR及元素分析等对中间体及最终产物进行了结构表征;对DMDNMT的密度和生成焓进行了理论计算,并利用EXPLO5 6.04软件对DMDNMT的爆轰性能进行了计算,其密度为 $1.81 \text{ g}\cdot\text{cm}^{-3}$,爆速为 $8624.8 \text{ m}\cdot\text{s}^{-1}$,爆压为29.2 GPa;利用DSC和TG-DTG验证了DMDNMT的热稳定性,DMDNMT的分解点为 $177.3 \text{ }^\circ\text{C}$ 。

关键词: 3,5-双(二硝甲基)-1,2,4-三唑的双胍基脲盐(DMDNMT);合成;性能

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