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Synthesis and Properties of 4,6-Dinitrobenzotriazol-3-dinitromethyl-1-oxide

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Abstract: Using 4,6-dinitrobenzotriazol-3-ium-1-oxide (DNBTO) as starting material, 4,6-dinitrobenzotriazol-3-dinitromethyl-1-oxide (TNBTO) was firstly designed and synthesized via the reactions of metathesis, substitution and nitration-hydrolysis. 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 Kamlet-Jacobs equations. Results show that the density of TNBTO is 1.81 g · cm⁻³, and the heat of formation is 143.7 kJ · mol⁻¹, the detonation velocity and detonation pressure are 8161.2 m · s⁻¹ and 30.2 GPa, respectively. However, thin layer chromatography shows that TNBTO easily decomposes at room temperature, indicating that its stability is relatively poor.

Key words: 4,6-dinitrobenzotriazol-3-dinitromethyl-1-oxide (TNBTO); synthesis; properties

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1 Introduction

N-oxides have been extensively studied in the field of energetic materials^[1-2]. Recently, the benzotriazol-3-ium-1-oxide compounds have attracted more attentions owing to their low sensitivities towards shock, friction, heat and electrostatic discharge^[3]. For example, 4,6-dinitrobenzotriazol-3-ium-oxide (DNBTO) was identified as a kind of potential explosive with the high-performance and insensitivity. It has some desirable traits, including a low impact sensitivity (20 J), and a low friction sensitivity (>360 N)^[4]. In order to search for the novel energetic derivatives with higher energy than DNBTO, a novel compound, 4,6-dinitrobenzotriazol-3-dinitromethyl-1-oxide (TNBTO) was designed and synthesized from DNBTO. Comparing with DNBTO, TNBTO exhibits higher density and detonation velocity because of the introduce of a dinitromethyl group^[5-9]. In view of the above observations, the detailed studies of the synthesis and characterization of TNBTO were carried out in this work. In addition, the detonation parameters and stability were investigated.

2 Experimental

2.1 Materials and Instruments

4,6-Dinitrobenzotriazol-3-ium-1-oxide (DNBTO) was

prepared and purified according to the reference^[10], and other reagents were purchased from the commercial sources. ¹H NMR and ¹³C NMR were obtained in DMSO-*d*₆ on a Bruker AV500 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.

2.2 Synthesis and Characterization

Using 4,6-dinitrobenzotriazol-3-ium-1-oxide (DNBTO) as starting materials, the title compound TNBTO was firstly synthesized via the reactions of metathesis, substitution and nitration-hydrolysis (Scheme 1).

2.2.1 Potassium 4,6-Dinitrobenzotriazol-3-ium-1-Oxide

DNBTO (1.0 g, 4.44 mmol) was dissolved in 80 mL ethanol, and then potassium hydroxide (0.25 g, 4.46 mmol) dissolved in a minimal amount of water was added dropwise at 40 °C. The solution was stirred at 40 °C for other 2 h. After evaporation of the solvent, the residue was washed with diethyl ether, and dried to give 1.0 g purple solid with a yield of 85.5%. IR (KBr, ν /cm⁻¹): 3106, 2398, 1765, 1643, 1559, 1508, 1438, 1384, 1341, 1189, 1157, 1055, 983, 933, 885, 826, 806. ¹H NMR (DMSO-*d*₆, 500 MHz), δ : 9.096 (1H, CH), 8.880 (1H, CH); ¹³C NMR (DMSO-*d*₆, 125 MHz), δ : 144.830, 137.430, 136.783, 130.260, 117.535, 115.295; Anal. Calcd. for C₆H₂N₅O₅K (%): C 27.38, H 0.77, N 26.61; Found: C 27.41, H 0.83, N 26.32.

2.2.2 4,6-Dinitrobenzotriazol-3-Acetone-1-Oxide

Potassium bromide (0.5 g, 4.2 mmol) and potassium 4,

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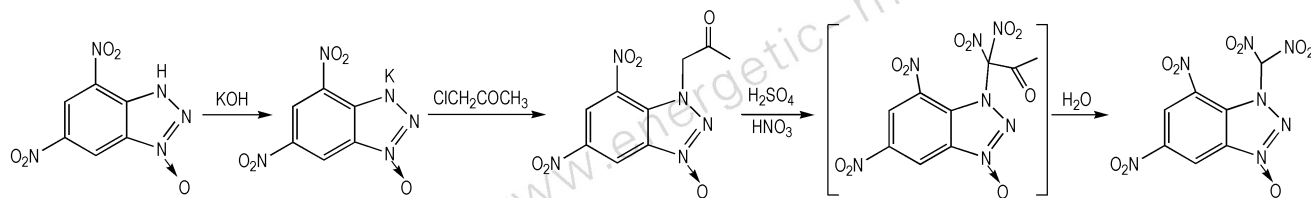
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6-dinitrobenzotriazol-3-ium-1-oxide (0.95 g, 3.6 mmol) were dissolved in 80 mL acetone at ambient temperature. To the reaction mixture, chloroacetone (0.38 g, 4 mmol) was added dropwise. The solution was stirred for 8 h at 58 °C. After evaporation of the solvent, the residue was washed with water and diethyl ether, and dried to give 0.41 g orange solid with a yield of 40.5% and a purity of 99.2% (HPLC). IR (KBr, ν/cm^{-1}): 3444, 3097, 2986, 2938, 2869, 1745, 1632, 1601,

4534, 1488, 1401, 1371, 1344, 1281, 1234, 1184, 1169, 1101, 1067, 1020, 998, 935, 911, 805; ^1H NMR (DMSO- d_6 , 500 MHz), δ : 9.370 (1H, CH), 8.938 (1H, CH), 5.603 (2H, CH_2), 2.147 (3H, CH_3); ^{13}C NMR (DMSO- d_6 , 125 MHz), δ : 202.223, 146.033, 137.988, 137.217, 117.602, 115.371, 84.192, 26.524; Anal. Calcd. for $\text{C}_9\text{H}_7\text{N}_5\text{O}_6$ (%): C 38.44, H 2.51, N 24.91; Found: C 38.40, H 2.75, N 24.82.



Scheme 1

2. 2. 3 4, 6-Dinitrobenzotriazol-3-Dinitromethyl-1-Oxide (TNBTO)

4,6-Dinitrobenzotriazol-3-acetone-1-oxide was dissolved in 5 mL 98% sulfuric acid. To the reaction mixture, 65% nitric acid (3.9 mL, 54 mmol) was added dropwise at -5 °C. The solution was stirred for 6 h at 40 °C. Then the reaction mixture was poured into ice water. The yellow precipitate was filtered to obtain 1.0 g solid with a yield of 52.6%. IR (KBr, ν/cm^{-1}): 3422, 3105, 2289, 1603, 1543, 1489, 1346, 1296, 1233, 1174, 1121, 1065, 1000, 934, 910, 847, 804, 776; ^1H NMR (DMSO- d_6 , 500 MHz), δ : 9.52–9.52 (1H, CH), 9.02–9.343 (1H, CH), 7.23–7.03 (H, $(\text{NO}_2)_2$); ^{13}C NMR (DMSO- d_6 , 125 MHz), δ : 146.61, 143.53, 133.31, 130.31, 123.16, 118.80, 76.95; Anal. Calcd. for $\text{C}_7\text{H}_3\text{N}_7\text{O}_9$ (%): C 25.54, H 0.92, N 29.79; Found: C 25.50, H 1.04, N 29.33.

3 Physicochemical and Energetic Properties

All the quantum computations were performed using the Gaussian 09 (Revision A. 02) suite of programs^[11]. The optimized structures were characterized to be true local energy

minima on the potential-energy surface without imaginary frequencies. The densities of DNBTO and TNBTO were computed based on Monte-Carlo method using the optimized structure at the B3LYP/6-311+G(d, p) level of theory^[12-13]. The gas phase heats of formation were 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 DNBTO and TNBTO were calculated by Kamlet-Jacobs equations^[16]. The stability was analyzed by TLC. The properties of TNBTO were obtained by calculation or test as follows: density is $1.81 \text{ g} \cdot \text{cm}^{-3}$, detonation velocity is $8161.2 \text{ m} \cdot \text{s}^{-1}$, heat of formation is $143.7 \text{ kJ} \cdot \text{kg}^{-1}$. Due to the introduce of $\text{R}-\text{C}(\text{NO}_2)_2$ group, TNBTO exhibits a higher density and detonation velocity compared with DNBTO. However, the heat of formation of TNBTO was lower than that of DNBTO, and TNBTO showed a relatively poor stability because it easily decomposes at room temperature. The physicochemical and detonation properties of DNBTO and TNBTO were listed in Table 1.

Table 1 The performances of DNBTO and TNBTO

properties	DNBTO	TNBTO	condition
formula	$\text{C}_6\text{H}_3\text{N}_5\text{O}_5$	$\text{C}_7\text{H}_3\text{N}_7\text{O}_9$	
molar mass	225	321	calculated
nitrogen content/%	31.1	29.8	calculated
oxygen balance/%	-60.4	-31.6	calculated
appearance	orange solid	yellow solid	Eyeballing (tested)
decomposition temperature/°C	201.3 (DSC)	room temperature	TLC analysis (tested)
density/ $\text{g} \cdot \text{cm}^{-3}$	1.73	1.81	Gaussian09 program (calculated)
detonation velocity/ $\text{m} \cdot \text{s}^{-1}$	7371.1	8162.2	K-J formula (calculated)
detonation pressure/GPa	24.0	30.2	K-J formula (calculated)
heat of formation/ $\text{kJ} \cdot \text{mol}^{-1}$	1232.1	143.7	Gaussian09 program (calculated)

4 Conclusions

(1) TNBTO was firstly synthesized using 4,6-dinitrobenzotriazol-3-ium-1-oxide (DNBTO) as raw material via the reactions of metathesis, substitution and nitration-hydrolysis. Its structure was characterized by IR, NMR and element analysis.

(2) The main performance of TNBTO were obtained by theoretical calculation as follows: density is $1.81 \text{ g} \cdot \text{cm}^{-3}$, detonation velocity is $8161.2 \text{ m} \cdot \text{s}^{-1}$, heat of formation is $143.7 \text{ kJ} \cdot \text{kg}^{-1}$.

(3) TNBTO was easily decomposed at room temperature, and showed a relatively poor thermal stability.

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4,6-二硝基苯并连三唑-3-偕二硝甲基-1-氧化物合成与性能

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摘要: 以 4,6-二硝基苯并连三唑-1-氧化物 (DNBTO) 为原料, 通过复分解、取代、硝化-水解反应设计并合成了未见文献报道的新化合物 4,6-二硝基苯并连三唑-3-偕二硝甲基-1-氧化物 (TNBTO); 采用红外光谱、¹H NMR、¹³C NMR 及元素分析等表征了中间体及最终产物的结构; 理论计算了 TNBTO 的密度和生成焓, 利用 Kamlet-Jacobs 方程计算了 TNBTO 的爆轰性能, 其密度为 $1.81 \text{ g} \cdot \text{cm}^{-3}$, 爆速为 $8161.2 \text{ m} \cdot \text{s}^{-1}$, 爆压为 30.2 GPa; 利用薄层色谱法跟踪验证了 TNBTO 的热稳定性, 发现 TNBTO 常温下易分解。

关键词: 4,6-二硝基苯并连三唑-3-偕二硝甲基-1-氧化物 (TNBTO); 合成; 性能

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