Synthesis and Properties of 3,3'-Bis(trinitromethyl-*ONN*-azoxy)azoxyfurazan(BTNAF)

ZHANG Jia-rong[1,2], **BI Fu-qiang**[1,2], **WANG Bo-zhou**[1,2], **LIAN Peng**[1,2], **ZHAI Lian-jie**[1,2], **JIA Si-yuan**[1,2]

(1. *Xi'an Mordern Chemistry Research Institute, Xi'an 710065, China*; 2. *State Key Laboratory of Fluorine & Nitrogen Chemical, Xi'an 710065, China*)

Abstract：Using 3,3'-bis(nitromethyl-*ONN*-azoxy)azoxyfurazan(BNMAF) as starting material, an excellent energetic compound 3,3'-bis(trinitromethyl-*ONN*-azoxy)azoxyfurazan(BTNAF) was synthesized via two steps (nitration and second nitration) with a total yield of 68.7%. The thermal behavior of BTNAF was investigated by differential scanning calorimetry(DSC) for the first time (melting point：59−61 ℃, decomposition point：183.6 ℃, decomposition heat：1989 J · g^{-1}) The physicochemistry and detonation performances of 3,3'-bis(nitromethyl-*ONN*-azoxy)azoxyfurazan(BNMAF), 3,3'-bis(dinitromethyl-*ONN*-azoxy)azoxyfurazan(BDNAF) and BTNAF were fully analyzed and compared by Gaussian, which revealed that BDNAF (detonation velocity：9560 m · s^{-1}; detonation pressure：42.40 GPa) and BTNAF (detonation velocity：8944 m · s^{-3}; detonation pressure：38.48 GPa) were two promising energetic compounds with outstanding performances.

Key words：3,3'-bis(trinitromethyl-*ONN*-azoxy)azoxyfurazan(BTNAF)；synthesis；thermal behavior

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1 Introduction

Nowadays, the synthesis and development of nitrogen heterocycles with high density, high heat of formation, and good oxygen balance is becoming an increasingly important research area[1]. Furazan ring has at tracted scientist's attention in the synthesis of high energy density materials (HEDM), due to their N-rich structure and abundant C-N bonds[2−3]. Introducing energy-rich functional groups into furazan rings is an attractive and effectivemethod to obtain high-performance energetic materials[4−6]. Luk'yanov et al.[7−12] have designed and synthesized a series of novel energetic compounds by the combination of α-polynitromethyl-azoxy groups and furazan backbones. 2012, Luk'yanov.[13] synthesized 3,3'-bis(trinitromethyl-*ONN*-azoxy)azoxyfurazan (BTNAF), which is one of the most typical α-polynitromethyl-azoxy energetic compounds via oxidative-coupling, hydrolysis, reduction, nitration et al. procedures. According to our previous study about the physicochemistry and detonation performances of α-polynitromethyl-azoxy energetic compounds, BTNAF features high density of 2.01 g · cm^{-3}, high detonation velocity of 8944 m · s^{-1}, high detonation pressure of 38.48 GPa and high oxygen balance of 14.08%[14]. Although the literature synthesized BTNAF, but the yield of the two nitration reactions is only 21%, and the repeatability is not high.

Herein, BTNAF was synthesized via two steps following nitration and second nitration according to literature[13]. In order to obtain BTNAF successfully, we focused on the conditions of two nitration reactions and improve the yield of BTNAF. The thermal behavior of BTNAF was studied by DSC for the first time. Furthermore, the physicochemistry and detonation properties of 3,3'-bis(nitromethyl-*ONN*-azoxy)azoxyfurazan (BNMAF), 3,3'-bis(dinitromethyl-*ONN*-azoxy)azoxyfurazan (BDNAF) and BTNAF were investigated and compared at the B3LYP/6-31G** basis set level based on B3LYP method of density functional theory comprehensively.

2 Experimental

2.1 Materials and Measurements

Melting pointwas measuredon a XT4A Melting-Point apparatus with microscope and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker 500 MHz spectrometer. Infrared spectra were obtained from Nicolet NEXUS870 Infrared spectrometer in the range of 4000 cm^{-1} to 400 cm^{-1}. Elemental analysis(C, H and N) were performed on a VARI-E1-3 elementary analysis instrument. Differential scanning calorimetry (DSC) studies were carried out on a Q200 apparatus (TA, USA) over the range from 10 ℃ to 350 ℃ at a heating rate of 10 ℃/min under dry oxygen-free nitrogen atmosphere with a flowing rate of 50 mL · min^{-1}.

3,3'-bis (nitromethyl-*ONN*-azoxy) azoxyfurazan (BNMAF) was prepared according to the literature[13]. Other chemicals were purchased from commercial suppliers and used without further purification.

2.2 Synthesis

Using 3,3′-bis(nitromethyl-*ONN*-azoxy) azoxyfurazan (BNMAF) as starting material, the title compound BTNAF was synthesized via the follow two-step reactions(Scheme 1).
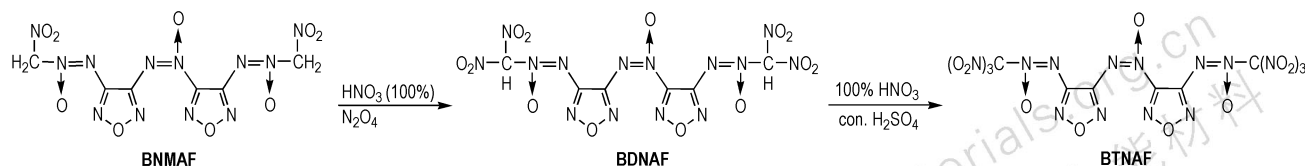
Scheme 1 The synthetic route of BTNAF

2.2.1 Synthesis of BDNAF

BNMAF(0.1 g, 0.26 mmol), 100% HNO_3(1.5 mL) and N_2O_4(0.6 mL) was heated to 50 ℃ in a sealed flask for 8h. Cooled down and poured the mixture into ice, and the white solid was formed and filtered(0.107 g, 87%). m. p. 149.1 ℃(dec.); ^1H NMR(Acetone-d_6, 500 MHz)δ: 9.366 (s, 2H, CH_2). ^{13}C NMR(Acetone-d_6, 125 MHz)δ: 114.454 (CH), 148.410, 148.860, 150.790, 151.101 (furazan cycles); IR (KBr, ν/cm^{-1}): 3003, 1607, 1589, 1522, 1487, 1310; Anal. calcd for $C_6H_2N_{14}O_{13}$: C 15.07, H 0.42, N 41.01; found C 15.10, H 0.41, N 41.14.

2.2.2 Synthesis of BTNAF

98% H_2SO_4(2 mL) was dropped to the ice cold solution of BDNAF(0.2 g, 0.42 mmol)) in 100% HNO_3(2 mL). The reaction mixture was heated at 72 ℃ for 18 h and poured into ice. The white solid was formed and filtered(0.16 g, 79%). m. p. 59 – 61 ℃; ^{13}C NMR (Acetone-d_6, 125 MHz) δ: 118.231 (C), 147.182, 149.089, 150.104, 153.911 (furazan cycles); IR (KBr, ν/cm^{-1}): 1643, 1612, 1530, 1494, 1265; Anal. calcd. for $C_6N_{16}O_{17}$: C 12.68, N 39.45; found C 12.62, N 39.52.

2.3 Discussion

2.3.1 The Conditions of BDNAF Nitration Reaction

In our experiment, we found that the two nitration reactions are the most vital steps in the route provided by the literature[13]. During synthesis of BDNAF, we repeated the nitration reaction using 95% HNO_3 as nitrification reagent (as reported in ref. 13), it was found that the highest yield was only 30%. As an attempt to increase the yield, we conducted the nitration reaction with 98% HNO_3, 100% HNO_3, 98% HNO_3/98% H_2SO_4 and 100% HNO_3/98% H_2SO_4. However, the yields didn′t improve significantly. At last, We tried using N_2O_4/95% HNO_3[15] as nitrification reagent, but the highest yield was only 60%, and the reaction system spreads smoke. Then we conducted the nitration reaction in a high pressure reactor and an improved yield of 85% was achieved using N_2O_4/95% HNO_3 as the nitrification reagent. The reaction conditions and yields of BDNAF are summarized in Table 1.

Table 1 Yields of BDNAF under different reaction conditions

nitration system	yield/%
95% HNO_3	30
98% HNO_3	32
100% HNO_3	33
98% HNO_3/98% H_2SO_4	25
100% HNO_3/98% H_2SO_4	27
95% HNO_3/N_2O_4(atmospheric pressure conditions)	60
95% HNO_3/N_2O_4(in high pressure reactor)	85
100% HNO_3/N_2O_4(in high pressure reactor)	87

2.3.2 The Conditions of BTNAF Nitration Reaction

After obtaining BDNAF, we explored the nitration reaction conditions for BTNAF. Due to the increased proton activity in nitroso-methyl group, the nitration procedure was carried out with common nitroso-sulfuric acid. The highest yield of BTNAF(79%) was achieved using 98% H_2SO_4/100% HNO_3 as the nitrification reagent. The yields of BTNAF achieved using different nitration reagents are summarized in Table 2.

Table 2 The comparison of the nitration reagent of BTNAF

nitration system	yield/%
95% HNO_3/98% H_2SO_4	70
98% HNO_3/98% H_2SO_4	75
100% HNO_3/98% H_2SO_4	79

2.4 Physicochemistry Properties and Detonation Performances

Although our research group previously reported the theoretical properties of BTNAF[14], the effect of α-polynitromethyl-azoxygroups on the same furazan backbone is unclear. In order to clarify the effect of α-nitromethyl-azoxy, α-dinitromethyl-azoxy and α-trinitromethyl-azoxy on the properties of the compounds, we calculated the physicochemmistry properties and detonaion performances of BNMAF and BDNAF.

The densities of BNMAF and BDNAF were computed by Monte-Caolo method[16-17] using the optimized structure at the B3LYP/6-31G** basis set levelof theory. The enthalpy of sublimation of BNMAF and BDNAF was calculated from the equation proposed by Politzer et al[18], and the electrostatic potential of compound. The enthalpy of formation of solid was ob-

tained by the isodesmic reactions of BNMAF and BDNAF. With the help of the calculated enthalpies of formation and densities, the detonation velocities and detonation pressures for BNMAF and BDNAF were calculated by Kamlet-Jacobs formulae[19].

The physicochemistry properties and detonation performances of BNMAF, BDNAF and BTNAF[14] are listed in Table 3. The densities and oxygen balances of BNMAF, BDNAF and BTNAF increased with the introduction of nitro, also, BDNAF and BTNAF were typical high-density energetic compounds with the densities of 1.95 g·cm⁻³ and 2.01 g·cm⁻³, respectively. BDNAF is a potential high energetic compound with the oxygen balance of 0%, the detonation velocity of 9562 m·s⁻¹ and detonation pressure of 42.40 GPa. Although, the detonation velocity and pressure of BTNAF was slightly decreased, it is a promising high energetic oxidizing agent with excellent energetic performances.

Table 3 The physicochemistry properties and detonation performances of BNMAF, BDNAF and BTNAF

compounds	density /g·cm⁻³	oxygen balance/%	detonation velocity/m·s⁻¹	detonation pressure/GPa
BNMAF	1.84	−20.60	8778	35.31
BDNAF	1.95	0	9562	42.40
BTNAF[14]	2.01	14.08	8944	38.48

2.5 Thermal Behavior of BTNAF

The thermal behavior of BTNAF was determined from 0 ℃ to 350 ℃ under dry oxygen-free nitrogen atmosphere. The DSC curve of BTNAF obtained was depicted in Fig.1. The endothermal peakat 60.4 ℃ is the phase change from solid to liquid andthe exothermic peak at 183.6 ℃ is caused by the decomposition reaction. By integrating the DSC curve, the heat released during the decomposition procedure is determined as 1989 J·g⁻¹. These resultsindicate that BTNAF possesses high energy and satisfactory thermal stability.
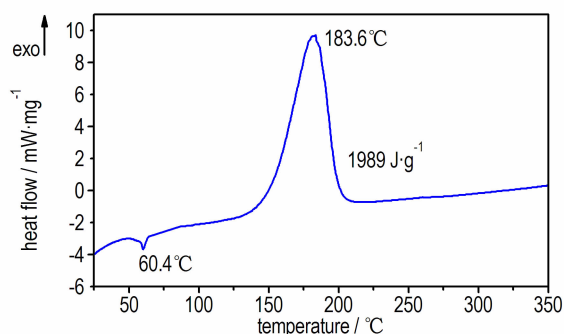
Fig.1 DSC curve of BTNAF at a heating rate of 10 ℃·min⁻¹

3 Conclusions

(1) Using BNMAF as starting material, an energetic compound BTNAF was synthesized via two nitration steps with a total yield of 68.7%. The DSC revealed that the melting point of BTNAF was 59 – 61 ℃, the decomposition point was 183.6 ℃ and the exothermic quantity was 1989 J·g⁻¹.

(2) Using 100% HNO_3/N_2O_4 as nitrification reagent, the yield of BDNAF was significantly improved from 30% to 87% in a high pressure reactor. Based on the increase of proton activity in nitroso-methyl group, BTNAF was obtained by 100% HNO_3/98% H_2SO_4 as nitrification reagent with a yield of 79%.

(3) The theoretical calculation data of BNMAF, BDNAF and BTNAF indicated that densities and oxygen balances of BNMAF, BDNAF and BTNAF was increased with the introduction of nitro. The detonation velocity and pressure of BDNAF was increased to 9560 m·s⁻¹ and 42.40 GPa. Although, the detonation velocity and pressure of BTNAF was slightly decreased compared with BDNAF, it was a promising high energetic oxidizing agent with excellent energetic performances.

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3,3′-双［三硝甲基-*ONN*-氧化偶氮基］氧化偶氮呋咱的合成与性能

张家荣[1,2]，毕福强[1,2]，王伯周[1,2]，廉鹏[1,2]，翟连杰[1,2]，贾思媛[1,2]
(1. 西安近代化学研究所，陕西 西安 710065；2. 氟氮化工资源高效开发与利用国家重点实验室，陕西 西安 710065)

摘　要：以 3,3′-双［单硝甲基-O*NN*-氧化偶氮基］氧化偶氮呋咱为原料，经过硝化，二次硝化两步反应合成了 3,3′-双［三硝甲基-O*NN*-氧化偶氮基］氧化偶氮呋咱(BTNAF)，总收率为 68.7%；首次利用示差扫描量热法(DSC)研究了 BTNAF 的热行为，其熔点为 59～61 ℃，分解温度为 183.6 ℃，放热量为 1989 J·g^{-1}；通过高斯计算，对比了 BNMAF，BDNAF 和 BTNAF 的物化性能和爆轰性能，结果表明，BDNAF (爆速9560 m·s^{-1}，爆压 42.40 GPa)和 BTNAF(爆速 8944 m·s^{-3}，爆压 38.48 GPa)是潜在的性能突出的含能化合物。
关键词：3,3′-双［三硝甲基-O*NN*-氧化偶氮基］氧化偶氮呋咱(BTNAF)；合成；热行为
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