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A Melt-cast Explosive 3-Azido-1,3-dinitroazetidine (AzDNAZ) with Gem-azidonitro of Novel Energetic Group: Synthesis and Performance

JIA Si-yuan¹, ZHANG Hai-hao¹, ZHANG Jia-rong¹, LIU Qian¹, LUAN Jie-yu¹, BI Fu-qiang^{1,2}, WANG Bo-zhou^{1,2}

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

Abstract: Starting from (1-tert-butyl-3-nitroazetidin-3-yl)methanol, a melt-cast explosive of 3-azido-1,3-dinitroazetidine (AzDNAZ) with novel gem-azidonitro energetic group was obtained through an improved azidation-salinization-nitration strategy with a total yield of 58.8%. Structures of the intermediates and AzDNAZ were characterized by ¹H NMR, ¹³C NMR, IR and element analysis. One of the intermediates, 1-tert-butyl-3-azido-3-nitro-azetidinium nitrate (compound **2**), was obtained for the first time with the single crystal determined by X-ray single crystal diffraction, which reveals that it crystallizes in monoclinic, space group *P*2(1)/*n* with *a*=0.8281(314) nm, *b*=0.8607(2) nm, *c*=1.7195(2) nm, $\alpha=90^\circ$, $\beta=94.983(2)^\circ$, $\gamma=90^\circ$, *V*=1.2210(6) nm³, *Z*=4, *M_r*=262, *D_c*=1.427 g·cm⁻³, $\mu=0.174$ mm⁻¹, *F*(000)=552, *R*=0.0418 and $\omega R=0.1168$. Meanwhile, thermal behaviors of AzDNAZ were studied by subsequently differential scanning calorimetry (DSC) and thermal gravimetric analyzer (TG) methods. Based on the measured values of density and heat of formation, the detonation parameters were calculated by Gaussian 09 program and Kamlet-Jacobs equations. Results show that the melting point, decomposition point, density, heat of formation, detonation velocity and detonation pressure are 78.2 °C, 180.7 °C, 1.75 g·cm⁻³, 331.73 kJ·mol⁻¹, 8460 m·s⁻¹ and 31.83 GPa, respectively, indicating AzDNAZ can be applied as a promising melt-cast explosive or an energetic plasticizer with satisfactory performances.

Key words: gem-azidonitro energetic compound; 3-azido-1,3-dinitroazetidine; melt-cast explosive; oxidative azidation; synthesis; properties

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1 Introduction

Azetidine is an important energetic structural moiety with high density, large ring strain and good stability, which is a hotspot in the field of energetic materials^[1-5]. Based on azetidine skeleton, 1,3,3-trinitroazetidine (TNAZ)^[6-10], a famous energetic compound with four-membered heterocyclic ring and gem-dinitro energetic group was synthesized by

Archibald TG^[1]. TNAZ was once regarded as a candidate for melt-cast explosive with good energetic performances (density of 1.84 g·cm⁻³, melting point of 101 °C, decomposition temperature of 240 °C, detonation velocity of 8834 m·s⁻¹, impact sensitivity of 44% and friction sensitivity of 42%)^[11]. However, due to the high vapour pressure and the complicated synthetic process, it has been proved impossible to be applied in military equipments. Based on the gem-azidonitro energetic group, a similar melt-cast explosive 3-azido-1,3-dinitroazetidine (AzDNAZ) was prepared by Dmitry V. Katorov via oxidative azidation and nitrotration (N₂O₅/CH₃CN) with a total yield of 37.4%^[12]. Since both nitro and azide groups were introduced into the azetidine structure, the thermal behaviors and detonation properties of gem-azidonitro compounds attracted great interests^[13-16]. We believed that 3-azido-1,3-dinitroazetidine(AzDNAZ) is

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Biography: JIA Si-yuan(1981-), female, Pro. Research field: Synthesis and properties of energetic materials. e-mail: jiasiyuan125@163.com

Corresponding author: BI Fu-qiang (1982-), male, Pro. Research field: Synthesis and properties of energetic materials.

e-mail: bifuqiang@gmail.com

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possible to be a promising melt-cast explosive since it has melting point of 78–80 °C and decomposition temperature of 190 °C. Nevertheless, the physico-chemical properties and detonation performances for AzDNAZ, such as density, detonation velocity, impact sensitivity and friction sensitivity, were not fully reported in the Russian literature.

In this report, an improved synthetic strategy for AzDNAZ was designed and studied via oxidative azidation, nitric acid salinization and new nitrolysis system in order to simplify technology and increase the nitration yield. The single crystal of the intermediate 3-azido-1,3-dinitroazetidinium nitrate (compound 2) was firstly obtained and determined by X-ray single crystal diffraction. The physicochemical properties and detonation performances for AzDNAZ, such as density, detonation velocity and sensitivity, were studied in detail by the laboratory test or the theoretical calculation. Meanwhile, the thermal behaviors were also carried out through DSC-TG approaches in order to provide the basic parameters for its subsequent application research.

2 Experimental

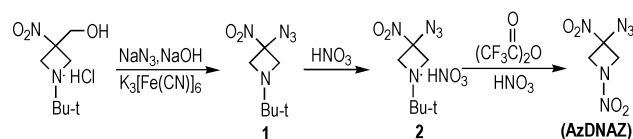
2.1 Materials and Instruments

(1-tert-butyl-3-nitroazetid-3-yl)methanol hydrochloride was prepared according to the published reference^[12]. Other chemicals were purchased from commercial sources.

¹³C NMR and ¹H NMR spectra were obtained in DMSO-*d*₆ with TMS as internal standard 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 was performed on a VARI-E1-3 elementary analysis instrument. Melting point was measured on a XT4A Melting-Point Apparatus with Microscope and uncorrected. Differential scanning calorimetry (DSC) was carried out on a Q200 apparatus (TA, USA) in the range of 10 °C and 400 °C at a heating rate of 10 °C·min⁻¹.

2.2 Synthesis

Starting from (1-tert-butyl-3-nitroazetid-3-yl)methanol hydrochloride, the title compound AzDNAZ was synthesized via oxidative azidation, nitric acid salinization and nitration sequence (Scheme 1).



Scheme 1 The synthesis of AzDNAZ

2.2.1 Synthesis of 3-Azido-1,3-dinitroazetidinium nitrate (2)

To a solution 5.0 g (22.3 mmol) (1-tert-butyl-3-nitroazetid-3-yl)methanol hydrochloride in 4 mL water, then the solution of NaOH 6.2 g (155.0 mmol) in 45 mL water was added at room temperature with stirring. After dissolution, a solution of NaN₃ 7.2 g (111.5 mmol) in 16 mL water was added dropwise. At 20–25 °C, the reaction mixture was added to a solution of K₃[Fe(CN)₆] 36.6 g (111.5 mmol) in 100 mL water. The mixture was maintained at 20–25 °C for 5 h. Then, the reaction mixture was extracted with dichloromethane (3×20 mL). HNO₃ was added dropwise to adjust the pH to 3–4. White precipitate was formed and filtered out. Drying the filter cake to give 3-azido-1,3-dinitroazetidinium nitrate (4.9 g, 84%). IR(KBr, ν/cm⁻¹): 3050 (CH₃), 2151 (—N₃), 1585 (ν^{as}NO₂), 1400 (—NO₂), 1325 (—NO₂), 1255, 1040, 825; ¹H NMR (D₂O, 500 MHz), δ: 5.26 (d, 2H J=13.6 Hz), 4.81 (d, 2H J=13.2 Hz), 1.641 (s 9H); ¹³C NMR (D₂O, 125 MHz), δ: 22.433, 57.512, 61.578, 90.270. Anal. calcd for C₇H₁₄N₆O₅: C 32.06, H 5.38, N 32.05; found: C 32.16, H 5.28, N 32.25.

2.2.2 Synthesis of 3-Azido-1,3-dinitroazetidinium nitrate (AzDNAZ)

3 mL 98% HNO₃ was dropped into 5 mL trifluoroacetic anhydride at -10–-5 °C, and 6.5 mL acetonitrile was added into the solution, then 1.0 g (5.3 mmol) 3-azido-1,3-dinitroazetidinium nitrate was added slowly. The mixture was kept at 0 °C for 2 h. and poured into ice. White solid was precipitated.

ed and filtered, dried to obtain 0.5 g 3-azido-1,3-dinitroazetidinium (AzDNAZ) with a yield of 70%, and 98% purity. IR(KBr, ν/cm^{-1}): 2135 (N_3), 1576 ($\text{N}-\text{NO}_2$), 1561, 1354 ($\text{C}-\text{NO}_2$), 1256 ($\text{N}-\text{NO}_2$); ^1H NMR (DMSO- d_6 , 500 MHz), δ : 4.856 (d, 2H $J=14$ Hz), 5.039 (d, 2H $J=14$ Hz); ^{13}C NMR (DMSO- d_6 , 125 MHz), δ : 90.220, 66.527. Anal. calcd for $\text{C}_3\text{H}_4\text{N}_6\text{O}_4$: C 19.16, H 2.14, N 44.68; found: C 19.26, H 2.08, N 44.58.

3 Results and discussion

3.1 X-ray Crystallography

The single crystal for 1-tert-butyl-3-azido-3-nitroazetidinium nitrate (compound **2**) was firstly cultivated by slow evaporation from the mixed solvent of water and ethanol ($V:V=1:1$) at room temperature in order to give satisfactory crystals for X-ray determination. The crystal data and structure refinement parameters for compound **2** are given in Table 1. The displacement ellipsoid plot with atomic numbering scheme and perspective view of the crystal in a unit cell are shown in Fig.1 and Fig.2.

It can be seen from Table 1 and Fig.2 that the crys-

Table 1 Crystal data and structure refinement parameters for compound **2**

formula	$\text{C}_7\text{H}_{14}\text{N}_6\text{O}_5$
formula mass	262
crystal system	monoclinic
space group	$P2(1)/n$
a/nm	0.8281(3)
b/nm	0.8607(2)
c/nm	1.7195(2)
V/nm^3	1.2210(6)
$\alpha/(\circ)$	90
$\beta/(\circ)$	94.983
$\gamma/(\circ)$	90
Z	4
$D_c/\text{g}\cdot\text{cm}^{-3}$	1.427
$F(000)$	552
crystal size / mm	0.20×0.20×0.15
goodness-of-fit on F^2	1.047
final R indexes [$I>2\sigma(I)$]	$R_1=0.0418$ $wR_2=0.1168$
final R indexes (all data)	$R_1=0.0560$ $wR_2=0.1271$
CCDC No.	1945690

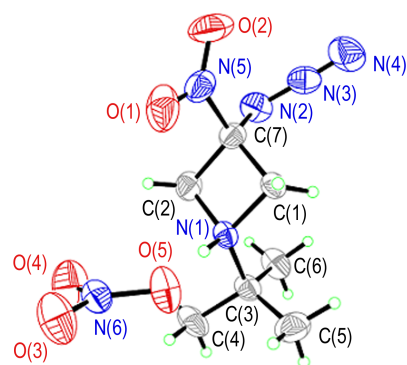


Fig.1 Crystal structure of compound **2**

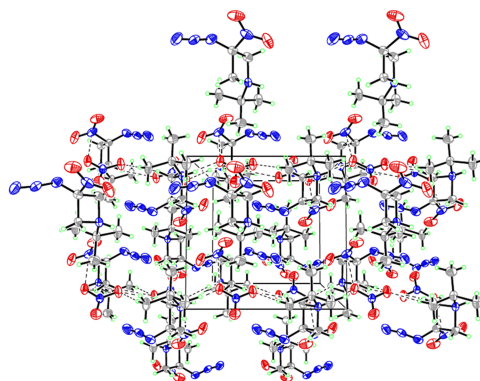


Fig.2 Molecular packing diagram of the unit cell for compound **2**

tal for compound **2** belongs to monoclinic with space group $P2(1)/n$ containing four molecular moieties in a unit cell with $a=0.8281(314)$ nm, $b=0.8607(2)$ nm, $c=1.7195(2)$ nm, $\alpha=90^\circ$, $\beta=94.983(2)^\circ$, $\gamma=90^\circ$, $V=1.2210(6)$ nm³, $Z=4$, $M_r=262$, $D_c=1.427$ g·cm⁻³, $\mu=0.174$ mm⁻¹, $F(000)=552$, $R=0.0418$ and $\omega R=0.1168$. Fig.1 and Fig.2 show that the four-membered ring azetidinium is basically co-planar. However, the substituent groups including nitro ($-\text{NO}_2$), azido ($-\text{N}_3$) and *t*-butyl ($-\text{C}(\text{CH}_3)_3$) are not co-planar. The angulations of nitro ($-\text{NO}_2$), azido ($-\text{N}_3$) and *t*-butyl ($-\text{C}(\text{CH}_3)_3$) are main reasons for the loose structure of compound **2** with a density of 1.427 g·cm⁻³.

3.2 Thermal Behavior for AzDNAZ

Based on differential scanning calorimeter (DSC) and thermal gravimetric analyzer (TG) measurements, the thermal behavior of AzDNAZ was determined at a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$ from 20 $^\circ\text{C}$ to 400 $^\circ\text{C}$. The results are shown in Fig.3.

From Fig.3, the thermal behavior of AzDNAZ

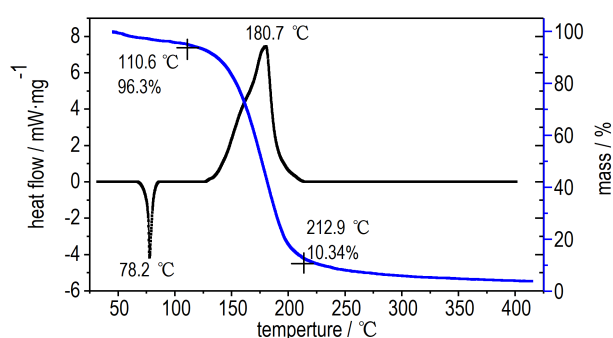


Fig.3 DSC-TG curves of AzDNAZ at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

undergoes two stages: first melting and then decomposing. The endothermic peak at $78.2\text{ }^{\circ}\text{C}$ and the exothermic peak at $180.7\text{ }^{\circ}\text{C}$ are corresponding to the melting point and the decomposition point of AzDNAZ, respectively. From the TG curve, a very small mass loss (nearly 7%) appears before $110.6\text{ }^{\circ}\text{C}$. A small amount of mass loss of AzDNAZ can be observed during melting process, which may due to the volatilization of the sample. As the temperature continue to rise, a dramatical mass loss of 83% is observed from $110.6\text{ }^{\circ}\text{C}$ to $212.9\text{ }^{\circ}\text{C}$. With the temperature increasing, AzDNAZ is further decomposed, and remains only 4% at $400\text{ }^{\circ}\text{C}$.

3.3 Physicochemical Properties

The detonation pressure and detonation velocity of AzDNAZ were obtained by Kamlet-Jacobs formulas with the help of calculated density and enthalpies of formation^[17-18], and compared with the well-known energetic compounds of TNAZ^[11] and RDX^[19] (Table 2). It was found that AzDNAZ possesses a

Table 2 Physicochemical and energetic properties of AzDNAZ compared with TNAZ and RDX

compound	AzDNAZ	TNAZ	RDX
formula	$\text{C}_3\text{H}_4\text{N}_6\text{O}_4$	$\text{C}_3\text{H}_4\text{N}_4\text{O}_6$	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$
M_r	188.10	192.01	222.15
$T_{m.p.}/^{\circ}\text{C}$	$78.2(\text{m.p.})$ $180.7(\text{dec.})$	101	$231.0(\text{dec.})$
$D_c/\text{g}\cdot\text{cm}^{-3}$	1.75	1.84	1.82
$\Delta H_f/\text{kJ}\cdot\text{mol}^{-1}$	331.73	-59.75	-21.61
$v_D/\text{m}\cdot\text{s}^{-1}$	8460	8691	8749
$p/\text{GPa}^{1)}$	31.83	36.46	34.9
IS/ $\text{J}^{2)}$	/	44% ^[11]	7
FS/ $\text{N}^{3)}$	>360	42% ^[11]	120

Note: 1)Detonation pressure. 2)Impact sensitivity. 3)Friction sensitivity.

density of $1.75\text{ g}\cdot\text{cm}^{-3}$, detonation velocity of $8460\text{ m}\cdot\text{s}^{-1}$ and detonation pressure of 31.83 GPa. All of these properties are comparable to those of TNAZ^[11] and RDX^[19], which indicates that AzDNAZ is a promising melt-cast energetic compound with low melting temperature and high decomposition point.

4 Conclusions

(1) Starting from (1-tert-butyl-3-nitroazetid-3-yl)methanol, 3-azido-1,3-dinitroazetid-3-yl)methanol, 3-azido-1,3-dinitroazetid-3-yl)methanol, 3-azido-1,3-dinitroazetid-3-yl)methanol (AzDNAZ) was synthesized via oxidative azidation, nitric acid salinization and nitration with a total yield of 58.8%. The structures of the intermediates and AzDNAZ were characterized by ^1H NMR, ^{13}C NMR, IR and element analysis. The single crystal of intermediate compound **2** was firstly determined and the results show that **2** was crystallized in monoclinic with a space group of $P2(1)/n$, and the density of $1.427\text{ g}\cdot\text{cm}^{-3}$.

(2) Results show that the density, melting point, heat of formation, detonation velocity and detonation pressure were $1.75\text{ g}\cdot\text{cm}^{-3}$, $78.2\text{ }^{\circ}\text{C}$, $331.73\text{ kJ}\cdot\text{mol}^{-1}$, $8460\text{ m}\cdot\text{s}^{-1}$ and 31.83 GPa, respectively, indicating AzDNAZ is possible to be applied as a promising melt-cast explosive or an energetic plasticizer with satisfactory performances.

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新型含能基团偕叠氮硝基熔铸炸药载体 AzDNAZ 的合成及性能

贾思媛¹, 张海昊¹, 张家荣¹, 刘 愆¹, 栾杰玉¹, 毕福强^{1,2}, 王伯周^{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1-叔丁基-3-硝基-3-羟甲基氮杂环丁烷盐酸盐为原料, 经氧化-叠氮化、成盐、硝化等反应合成了具有偕叠氮硝基的熔铸炸药3-叠氮基-1,3-二硝基氮杂环丁烷(AzDNAZ), 总收率达到58.8%, 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; 培养了新的中间体1-叔丁基-3-叠氮基-3-硝基氮杂环丁烷硝酸盐的单晶, X射线单晶衍射分析表明: 1-叔丁基-3-叠氮基-3-硝基氮杂环丁烷硝酸盐晶体结构属单斜晶系, 空间群为P2(1)/n, a=0.8281(314) nm, b=0.8607(2) nm, c=1.7195(2) nm, $\alpha=90^\circ$, $\beta=95(2)^\circ$, $\gamma=90^\circ$, V=1.2210(6) nm³, Z=4, M_r=262, D_c=1.427 g·cm⁻³, $\mu=0.174$ mm⁻¹, F(000)=552, R=0.0418, wR₂=0.1168。利用DSC-TG方法分析了热性能, 结果表明: AzDNAZ的熔点为78.2 °C, 分解点为180.7 °C。采用Gaussian 09程序和Kamlet-Jacobs方程预估了AzDNAZ的性能, 结果表明: AzDNAZ的密度为1.75 g·cm⁻³, 生成焓为331.73 kJ·mol⁻¹, 爆速8460 m·s⁻¹爆压31.83 GPa。表明AzDNAZ可以作为熔铸炸药和含能增塑剂的候选含能材料。

关键词: 偕叠氮硝基含能化合物; 3-叠氮基-1,3-二硝基氮杂环丁烷; 熔铸炸药; 氧化-叠氮化; 合成; 性能

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