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A Novel Energetic Material Based on Nitro-*NNO*-azoxy: Synthesis and Characterization

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Abstract: A novel energetic compound, *N, N'*-dinitro-*N, N'*-bis [3-(nitro-*NNO*-azoxy) furazan-4-yl] methylenediamine, was synthesized using 3-amino-4-(*t*-Bu-*NNO*-azoxy) furazan as starting material. And its structure was characterized by nuclear magnetic resonance (¹H NMR and ¹³C NMR), infrared (IR) spectroscopy, elemental analysis and mass spectrometry, and its backbone was also confirmed by the X-ray structure study of the key intermediate. The detonation performance was calculated by VLW equation of state. Results show density is 1.94 g · cm⁻³, detonation velocity 9502.52 m · s⁻¹, detonation pressure 41.79 GPa and enthalpy of formation 1007.67 kJ · mol⁻¹, indicating it is a competitive energetic materials.

Key words: organic chemistry; energetic materials; nitro-*NNO*-azoxy; design; synthesis; performance**CLC number:** TJ55; O62**Document code:** A**DOI:** 10.11943/j.issn.1006-9941.2014.06.032

1 Introduction

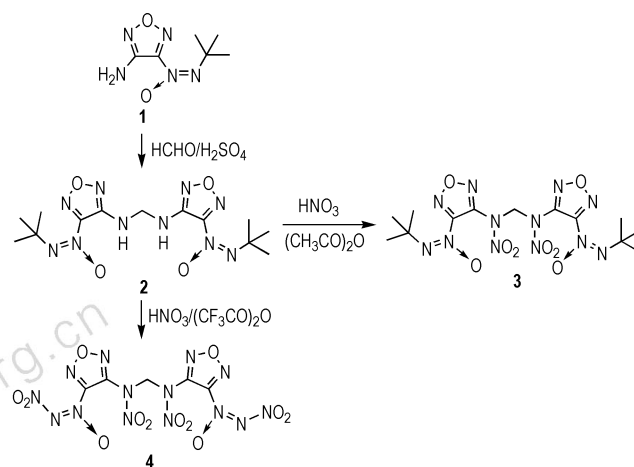
Five-membered nitrogen-containing heterocycles, with high thermal stability and positive heats of formation, have been recognized as the ideal precursors of high energy density materials (HEDM) [1-2]. Their high heats of formation is due to the large number of N—N and C—N bonds [3-4]. A number of five-membered heterocycle-based energetic compounds were reported as potential materials for military and space applications [5-7]. Of these, furazan ring served as an efficient build-block. The combination of furazan ring with energetic substituents, such as amino (—NH₂) [8], nitro (—NO₂) [9], azide (—N₃) [10] and nitramine (—NHNO₂) [11] have been widely investigated.

As an unconventional explosophoric group, nitro-*NNO*-azoxy was first reported by Churakov et al [12]. After that, bis-3, 3'-(nitro-*NNO*-azoxy)-difurazanyl ether [13] and bis-3, 3'-(nitro-*NNO*-azoxy)-4, 4'-azofurazan [14] was synthesized by Sheremetev and our group respectively, which are both of high crystal density and excellent detonation properties. In continuation of our study on the furazan-functionalized energetic material, a novel energetic compound, namely *N, N'*-dinitro-*N, N'*-bis [3-(nitro-*NNO*-azoxy) furazan-4-yl] methylenediamine (**4**), was designed and synthesized firstly from 3-amino-4-(*t*-Bu-*NNO*-azoxy) furazan (**1**) in this study. Its structure was confirmed by IR, NMR (¹H NMR and ¹³C NMR), elemental analysis and mass spectrometry. The nitration reaction of *N, N'*-bis [3-(*t*-Bu-*NNO*-azoxy) furazan-4-yl] methylenediamine (**2**) was also studied, and two nitration derivatives were obtained at different reaction conditions, which were not reported in the literature. Furthermore, the

detonation performance of **4** was also calculated.

2 Experimental

2.1 Synthetic route



Scheme 1

2.2 Materials and General Methods

¹H NMR and ¹³C NMR were carried out on the Bruker AV500 NMR spectrometer. Infrared spectra were tested with 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-EI-3 elemental analyzer. Mass spectra were obtained on GCMS-QP2010. 3-amino-4-(*t*-Bu-*NNO*-azoxy) furazan [14] and 100% nitric acid were prepared in our laboratory.

2.3 Synthesis of 2

37% formaldehyde (0.86 g, 10.6 mmol) was added to a suspension of **1** (3.93 g, 21.0 mmol) in 50% sulfuric acid

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(100 g), then the mixture was stirred at 30 °C overnight. The yellow precipitate was filtered, washed with water and dried to obtain 3.68 g of solid in a yield of 92.2%. ¹H NMR (DM-SO-*d*₆, 500 MHz): 1.43 (s, 18H), 4.87 (t, 2H), 7.14 (t, 2H); ¹³C NMR (DMSO-*d*₆, 125 MHz): 151.30, 150.14, 60.07, 53.32, 25.07; IR (KBr, ν/cm^{-1}): 3472, 3411, 3387, 2972, 1623, 1610, 1537, 1454, 1379, 1301, 1181, 1119, 910, 861 cm^{-1} ; Anal. Calcd. (%) for C₁₃H₂₂N₁₀O₄: C 40.83, H 5.80, N 36.63; Found (%): C 40.85, H 5.74, N 36.72.

2.4 Synthesis of 3

2 (0.38 g, 1 mmol) was added to a mixture of acetic anhydride (2.5 mL), CCl₄ (4 mL) and anhydrous nitric acid (1.0 mL, 23.5 mmol) at 10 °C, then the mixture was stirred at room temperature for 6 h. The reaction mixture was poured to ice-water (30 mL), then extracted five times with CH₂Cl₂ (15 mL). The extraction were washed with water and dried over magnesium sulfate, filtered and the solvent was removed to give 0.39 yellow solid in a yield of 82.6%. ¹H NMR (Acetone-*d*₆, 500 MHz): 1.43 (s, 18H), 6.64 (s, 2H); ¹³C NMR (Acetone-*d*₆, 125 MHz): 156.70, 147.36, 67.50, 61.78, 25.18; IR (KBr, ν/cm^{-1}): 2971, 1753, 1606, 1478, 1452, 1300, 1283, 1125, 904, 859 cm^{-1} ; Anal. Calcd. (%) for C₁₃H₂₀N₁₂O₈: C 33.05, H 4.27, N 35.58; Found (%): C 32.95, H 4.30, N 35.72.

2.5 Synthesis of 4

2 (0.38 g, 1 mmol) was added to a mixture of trifluoroacetic anhydride (13.5 mL) and anhydrous nitric acid (3.4 mL, 0.08 mol) at room temperature, then the mixture was stirred at 37 °C for 5 h. The reaction mixture was poured to ice-water (50 mL), then extracted five times with CH₂Cl₂ (15 mL). The extraction were washed with water and dried over magnesium sulfate, filtered and the solvent was removed to give yellow oil. The title compound (**4**) was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (*R*_f=0.4, 3 : 1, V/V) as an eluent, affording 0.3 g of yellow oil in a yield of 66.7%. ¹H NMR (Acetone-*d*₆, 500 MHz): 6.92 (s, 2H); ¹³C NMR (Acetone-*d*₆, 125 MHz): 153.67, 146.94, 66.73; IR (KBr, ν/cm^{-1}): 3041, 2906, 1784, 1636, 1610, 1556, 1495, 1369, 1283, 1220, 1172, 1082, 1023, 946, 835 cm^{-1} ; MS (ESI⁻) *m/z* (%): 512 (M+NO₃⁻); Anal. Calcd. (%) for C₅H₂N₁₄O₁₂: C 13.34, H 0.45, N 43.56; Found (%): 13.30, H 0.44, N 43.50.

2.6 Determination of the Crystal Structure of 2

Block-like single crystals suitable for X-ray diffraction studies were obtained after 15 days by slow evaporation from a solution of compound **2** in CHCl₃ at room temperature. A yellow crystal of compound **2** with dimensions of 0.15 mm × 0.15 mm × 0.10 mm was chosen for X-ray diffraction analysis performed on Bruker SMART APE II CCD X-ray diffractometer with a MoK_α radiation ($\lambda=0.71073\text{\AA}$) by using a φ - ω scan mode at 296 (2) K. In the range of $2.10^\circ \leq \theta \leq 28.36^\circ$, a total of 5991 reflections were collected including 4424 unique ones (*R*_{int}=0.0186). The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined

with SHELXL package [15]. The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on *F*² for the non-hydrogen atoms.

The crystal belongs to the triclinic system, space group *P*-1 with *a* = 9.918(4) Å, *b* = 10.748(4) Å, *c* = 10.924(4) Å, $\alpha = 98.170(5)^\circ$, $\beta = 113.345(6)^\circ$, $\gamma = 108.484(6)^\circ$, *M*_r = 382.41, *V* = 964.8(6) Å³, *Z* = 2, *D*_c = 1.316 g · cm⁻³, *F*(000) = 404, $\mu = 0.101 \text{ mm}^{-1}$, *R* = 0.0476 and *wR* = 0.1053. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-961282).

3 Results and Discussion

3.1 Synthesis

1 was synthesized according to literature [14], and **2** was synthesized using **1** and formaldehyde by the aldehyde-amine condensation that widely used in constructing the backbone of HEDMs. The reaction progress was monitored by Thin-Layer Liquid Chromatography (TLC). With 10% aq. H₂SO₄ used, the reaction mixture contained the starting material **1**. While with 20% ~ 30% aq. H₂SO₄, the reaction mixture contained **1** and small amount of **2**. The optimal conditions for the preparation of **2** are stirring the starting components in 50% aq. H₂SO₄ at room temperature, and its yield is 92.2%.

Treating **2** with different nitrolysis agent may generate different products. When 100% HNO₃-Ac₂O mixture used, the dinitramine compound **3** was obtained in a yield of 82.6%. When a stronger nitrolysis agent 100% HNO₃(CF₃CO)₂O, TLC results show that **3** was appeared firstly and then transformed into **4**.

3 and **4** were well characterized by IR, ¹³C NMR, ¹H NMR, elemental analysis. In the IR spectra, **3** and **4** both have several main absorption bands which can attributed to the furazan ring and nitro group respectively. In the ¹³C NMR spectrum, the resonances of the furazan ring and methylene (—CH₂—) carbon was more downfield for **3** at 156.70, 147.36, 67.50, and 153.67, 146.94, 66.73 for **4** respectively. Furthermore, the M+NO₃⁻ peak of **4** at 512 *m/z* was detected and the formation of **4** was confirmed.

3.2 Crystal Structure

In order to elucidate the structure of backbone in the title compound, the single crystal of key intermediate **2** was obtained and studied. A perspective view of compound **2**, showing the atomic numbering scheme, is given in Fig. 1. In each molecule, the dihedral angle between furazan planes defined by O(1) \ N(1) \ C(1) \ C(2) \ N(2) and O(3) \ N(7) \ C(8) \ C(9) \ N(8), is about 78.31 (2)°. As shown in Fig. 2, intramolecular hydrogen bonds N—H...N and C—H...O forming S(6) motif produce six-membered ring and stabilize the molecular structure. Intermolecular hydrogen bonding C(13)—H(13)B...O(1) between alkyl carbon and furazan oxygen links neighboring molecule into dimer with a motif of *R*₂²(26). Furthermore, in Fig. 3, stronger $\pi \cdots \pi$ stacking interactions among adjacent furazan rings further stabilizes the crystal structure. With the help of above mentioned hydrogen bond and $\pi \cdots \pi$ stacking interactions, the title compound (**4**) was obtained with an infinite 2D sheet-like supermolecular structure. Hydrogen atoms in Fig. 2 and Fig. 3, except those in-

involved in hydrogen bonds, have been omitted for clarity.

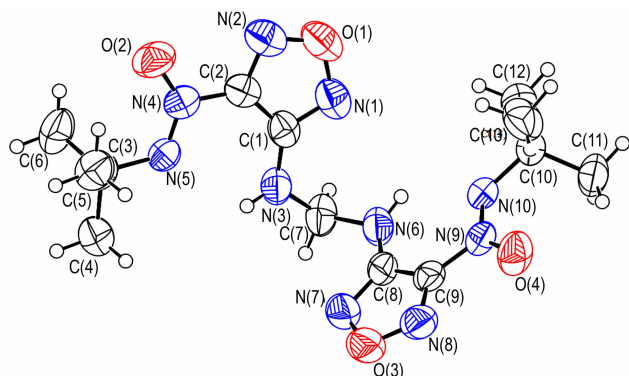


Fig. 1 ORTEP view of the crystal structure with thermal ellipsoids drawn at the 30% probability for title compound

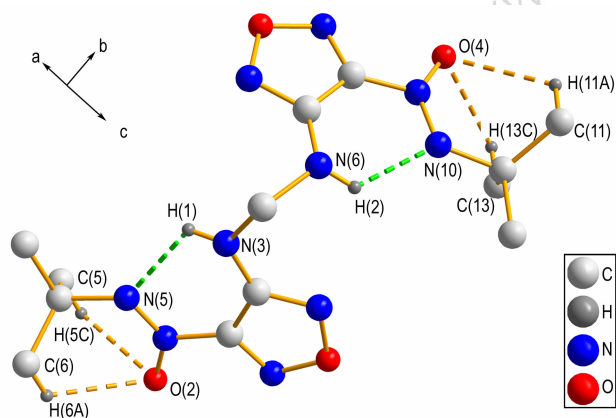


Fig. 2 Diagram of the intramolecular hydrogen bonds

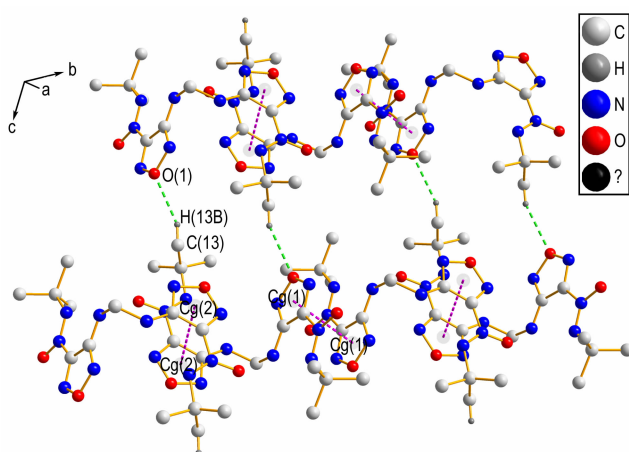


Fig. 3 Diagram of the intermolecular hydrogen bonds and $\pi \cdots \pi$ interactions

3.3 Calculated performance

The structure of **4** was optimized and its density and enthalpy of formation were calculated by Gaussian 09^[16]. The explosive parameters were obtained by VLW equation of state^[17] using density and enthalpy of formation as basic data. Results show that the density is $1.94 \text{ g} \cdot \text{cm}^{-3}$, enthalpy of formation $1007.67 \text{ kJ} \cdot \text{mol}^{-1}$, detonation velocity $9502.52 \text{ m} \cdot \text{s}^{-1}$ and C-J pressure 41.79 GPa . The calculated detonation parameters

are comparable to CL-20 ($9406 \text{ m} \cdot \text{s}^{-1}$, 44.6 GPa)^[18].

4 Conclusions

In conclusion, a novel furazan compound (**4**) was synthesized and characterized. The crystal structure of **2** was studied for confirming the backbone of title compound (**4**) and it forms an infinite 2D sheet-like supermolecular structure. Furthermore, the calculations indicate the detonation properties of **4** are comparable to CL-20. Results show that the density $1.94 \text{ g} \cdot \text{cm}^{-3}$, enthalpy of formation $1007.67 \text{ kJ} \cdot \text{mol}^{-1}$, detonation velocity $9502.52 \text{ m} \cdot \text{s}^{-1}$ and C-J pressure 41.79 GPa .

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一种含硝基-*NNO*-氧化偶氮基新型含能材料的合成与表征

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摘要: 以 3-氨基-4-(特丁基-*NNO*-氧化偶氮)基咪唑为原料, 经过缩合和硝化两步反应合成了未见文献报道的化合物亚甲基-双-[3-(硝基-*NNO*-氧化偶氮)基-4-硝氨基-咪唑], 并采用核磁共振、红外(IR)、元素分析和质谱确定了其结构。通过对其关键中间晶体结构的研究确认了目标化合物的骨架结构。此外, 通过量子化学计算方法预估了目标化合物的爆轰性能, 密度为 $1.94 \text{ g} \cdot \text{cm}^{-3}$, 爆速 $9502.52 \text{ m} \cdot \text{s}^{-1}$, 爆压 41.79 GPa , 生成焓 $1007.67 \text{ kJ} \cdot \text{mol}^{-1}$ 。

关键词: 有机化学; 含能材料; 硝基-*NNO*-氧化偶氮; 设计; 合成; 性能

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《含能材料》第七届编委会在成都召开

2014年11月20日《含能材料》编辑部在成都双流组织召开《含能材料》第七届编委会。北京理工大学、南京理工大学、天津大学、中北大学、西南科技大学、第二炮兵工程大学、石家庄军械工程学院、中国兵器204研究所、山西北方兴安化学工业有限公司及中国工程物理研究院流体物理研究所、化工材料研究所、总体工程研究所等单位的近30位编委参加了会议。

会议由李明副主编主持, 田勇主编代表期刊主办单位及编辑部对远道而来的编委表示欢迎与感谢并对新一届编辑委员会的调整与组成进行了说明, 聂福德执行主编强调了新一届编委的职责并向与会者介绍了编辑部的努力方向和今后四年的初步工作计划, 编辑部向新一届编辑委员会汇报了编辑部在上一届(第六届)编委会领导下近四年的工作情况, 对期刊近年影响因子的提升、网络化与电子化进展及多种形式丰富刊载内容和提高可读性等情况进行了介绍。会议还宣布了评选出的20篇优秀论文(2008~2011年发表的)。

本刊特聘顾问冯长根教授参加了本次编委会, 他在讲话中指出《含能材料》经历了艰难的办刊之路, 经过20余年的努力, 终于使期刊走上良性发展道路, 但期刊只是一个交流平台, 这个平台的核心还是创新的科研成果和优秀的学术论文, 希望历史能翻开新的一页, 老编委与新编委共同努力提高《含能材料》的学术水平和出版质量。

与会编委认真听取了编辑部的工作汇报, 充分肯定了编辑部在上一届编委会领导下所取得的成绩, 以编委、审稿专家、作者及读者身份分别从不同角度围绕期刊如何在新形势下, 加快网络化、国际化发展, 缩短论文发表时滞, 办出特色这一主题展开了热烈讨论。大家一致认为, 论文的学术水平和编校质量是期刊的立足之本, 办刊观念必须紧跟期刊界形势的发展, 一方面要向国际化发展, 一方面要真正注重内涵, 不能放松三审三校, 同时更要注重论文的学术水平, 办出特色栏目, 在本行业内做强。

最后, 由田勇主编进行了总结, 他再次向到会的编委表示感谢, 并表示会后将对各位专家提出的宝贵意见进行认真研究, 梳理出可操作的建议尽快实施, 进一步改进编辑部的工作, 努力提升《含能材料》学术水平和出版质量, 为业内科技人员搭建良好的交流平台。