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Facile Synthesis and Crystal Structure of 3,4-Bis(1*H*-5-tetrazolyl) furoxan

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Abstract: 3,4-Bis(1*H*-5-tetrazolyl) furoxan was synthesized via cyclization reaction using 3,4-dicyanofuroxan and sodium azide as raw materials and water as solvent under the $ZnCl_2$ catalysis with a total yield of 91.0%. The structure was fully characterized by IR, NMR, elemental analysis, and X-ray single-crystal diffraction. Results show that the crystal belongs to the orthorhombic system, and space group is $P2_12_12_1$ with crystal parameters of $a=6.1172(14)\text{Å}$, $b=9.657(2)\text{Å}$, $c=14.220(3)\text{Å}$, $V=840.0(3)\text{Å}^3$, $Z=4$, $D_c=1.76\text{ g}\cdot\text{cm}^{-3}$, $F(000)=448$, $\mu=0.147\text{ mm}^{-1}$, $S=1.031$, the final $R=0.0800$ and $wR=0.2523$. The structure of 3,4-bis(1*H*-5-tetrazolyl) furoxan is almost in one plane, indicating that a strong conjugation effect exists in the molecules. At the same time, lots of weak bonds among nitrogen atoms in the molecules can improve the density of compounds and thermal stability.

Key words: synthesis; nitrogen-containing azoles; crystal structure; electrostatic potential

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1 Introduction

The rational design of new energetic materials with high performance properties has been becoming one of the most challenging tasks in the field of advanced materials [1-3]. At the early stages of energetic materials, scientists mainly focused on designing and synthesizing the polynitro compounds, such as 1,3,5,7-tetranitrotetraazacyclooctane (HMX), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20), and octanitrocubane (ONC). Although these materials exhibit excellent detonation properties, the synthesis is often expensive and includes multiple steps which make the industrial scale-up and practical use infeasible. Along with growing concerns about the environment and safety issues, considerable effort has been devoted to pursuing the integrated performance of HEDMs, for example, high density and energy, good thermal stability, low sensitivity, positive oxygen balance, environmentally benign decomposition products, and low cost [4-7]. However, in most cases, the requirements of insensitivity and high detonation velocity and pressure are often contradictory to each other, which makes the design and synthesis of new generation HEDMs an interesting and enormous challenge.

Five-membered nitrogen-containing azole compounds are traditional sources of energetic materials due to their high nitrogen content and the thermal stability which results from the aromatic ring system. Owing to the high positive heats of formation resulting from the large number of N—N and C—N bonds and the high level of environmental compatibility, triazole and tetrazole compounds have been studied over the last couple of years with growing interest [8-9]. Furthermore, a fur-

ther way of azole functionalization is the introduction of the heterocycles containing oxygen (e.g. oxadiazoles and nitro-substituted heterocycles). This type is strikingly represented by 3,4-bis(1*H*-5-tetrazolyl) furoxan, which was firstly reported by Huang et al [10]. It has a high decomposition temperature and high-nitrogen compound with better oxygen balance than those containing only C, H, and N, which suggest that it would be a potential candidate for green energetic materials.

In this paper, 3,4-bis(1*H*-5-tetrazolyl) furoxan was synthesized by a new method from 3,4-dicyanofuroxan with a higher yield (91%), and its structure was characterized by IR, NMR and elemental analysis. In order to confirm the molecular structure of the title compound, the crystal structure was characterized by X-ray diffraction analysis.

2 Experimental

2.1 Materials and Instruments

^1H NMR and ^{13}C NMR were obtained in $\text{DMSO}-d_6$ with a Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets with a Nicolet NEXUS870 Infrared spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$. Elemental analyses were performed with a VARI-EL-3 elementary analysis instrument. Differential scanning calorimetry (DSC) experiments were carried out in a platinum sample container using a Q-2000 at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$.

3,4-Dicyanofuroxan was prepared according to the literature procedure [13]. Other chemicals were obtained from commercial sources and used without further purification.

2.2 Synthesis and Characterization

The title compound was synthesized from Scheme 1.

To a solution of 3,4-dicyanofuroxan (1.36 g, 10 mmol) and NaN_3 (1.95 g, 30 mmol) in water (30 mL) ZnCl_2 (1.36 g, 10 mmol) was added at room temperature. The reaction mixture was heated to refluxing temperature and stirred for 5 h, cooled to room temperature, and acidified with an appropriate concentrated hydrochloric to pH 1–2. Then, the

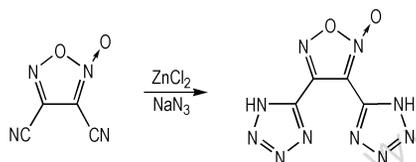
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precipitated product was filtered, washed with water, dried under vacuum and finally to yield a white solid (2.02 g) with a purity of 98.6% (HPLC). DSC (10 °C · min⁻¹): 229–230 °C. ¹H NMR (DMSO-*d*₆, 500 MHz), δ: 8.28 (s, 2H, NH); ¹³C NMR (CDCl₃, 125 MHz), δ: 149.01, 146.18 (C—C=N), 146.05, 106.76; IR (KBr, ν/cm⁻¹): 3139, 2990, 2905, 2752, 2667, 2514, 1622, 1581, 1458, 1419, 1387, 1281, 1234, 1204, 1182, 1130, 1094, 1071, 1026, 1015, 1004, 960, 935, 824, 782, 736, 704, 544; Anal. calcd For C₄H₂N₁₀O₂: C 21.63, H 0.91, N 63.06; Found C 21.56, H 1.08, N 62.79.



Scheme 1 Synthetic route of the title compound

2.3 Determination of the Single Crystal Structure

The title compound was dispersed into hot water (60 °C) with a stirrer, and the mechanical impurities were eliminated by filtration. The saturated solution of the title compound was put in a conical flask for two weeks at room temperature to evaporate slowly the solution and obtain single crystals of title compound.

A colorless single crystal of the title compound with dimensions of 0.35 mm×0.30 mm×0.23 mm was selected for X-ray diffraction analysis, and the data collection was performed on a Bruker SMART Apex-II CCD X-ray diffractometer equipped with a graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) using the φ-ω scan mode (2.55° ≤ θ ≤ 25.09°) at 296(2) K. A total of 4143 reflections were collected, of which 1498 were independent (*R*_{int} = 0.0431) and 1378 with *I* > 2σ(*I*) were considered to observed and used for the refinement.

The structure was solved by direct methods and refined by full-matrix least squares techniques on *F*² using SHELXS-97 and SHELXL-97 programs [11–12]. All non-hydrogen atoms were refined anisotropically. Crystal data and structural refinement parameters for the title compound are listed in Table 1.

Further information on the crystal-structure determinations can be obtained free of charge at www.ccdc.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre with CCDC No. 1402690.

3 Results and Discussion

3.1 Synthesis

3,4-Bis(1*H*-5-tetrazolyl) furoxan was synthesized from 3,4-dicyanofuroxan, which was in turn prepared according to a literature procedure [13]. 3,4-Dicyanofuroxan was treated with sodium azide and ZnCl₂ in water according to the method reported by Demko and Sharpless [14]. 3,4-Bis(1*H*-5-tetrazolyl) furoxan was successfully obtained in high yield (91.0%), which is catalyzed by Zn²⁺ in water. However, 3,4-bis(1*H*-5-tetrazolyl) furoxan was catalyzed by NH₄Cl in *N,N*-dimethylformamide (DMF) in the literature, and the re-

action mixture has to be diluted with water, extracted with ethyl acetate, washed with brine, and evaporated process [10]. Those procedures are not good for environment protection and reducing the cost. Furthermore, the yield of the target compound was increased significantly compared to the literature's method.

Table 1 Crystal data and structure refinement details

Formula	C ₄ H ₂ N ₁₀ O ₂
Formula weight/g · mol ⁻¹	222.16
<i>T</i> /K	296(2)
crystal system	Orthorhombic
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	6.1172(14)
<i>b</i> /Å	9.657(2)
<i>c</i> /Å	14.220(3)
α/(°)	90.0
β/(°)	90.0
γ/(°)	90.0
crystal size/mm	0.35×0.30×0.23
volume/Å ³	840.0(3)
<i>Z</i>	4
<i>D</i> _c /g · cm ⁻³	1.76
<i>F</i> (000)	448
λ/Å	0.71073
2θ _{max} /(°)	50.18
Index ranges	-6 ≤ <i>h</i> ≤ 7 -11 ≤ <i>k</i> ≤ 9 -16 ≤ <i>l</i> ≤ 16
reflections collected/unique parameters	4134/1498 145
<i>GOF</i> on <i>F</i> ²	1.031
final <i>R</i> indexes(<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0800, <i>wR</i> ₂ = 0.2523
final <i>R</i> indexes (all data)	<i>R</i> ₁ = 0.0884, <i>wR</i> ₂ = 0.2626
largest diff peak and hole/e · Å ⁻³	0.477 and -0.431

The infrared vibrational spectra of 3,4-bis(1*H*-5-tetrazolyl) furoxan show the presence of the N—H (3139 cm⁻¹) group. Other vibrations also suggest the presence of the tetrazole ring and furoxan rings. In the ¹H NMR spectra 3,4-bis(1*H*-5-tetrazolyl) furoxan shows resonance at 7.63, which is in the expected N—H range. The ¹³C NMR spectrum of 3,4-bis(1*H*-5-tetrazolyl) furoxan shows two signals with chemical shifts of 112.6 and 123.1, which correspond to the tetrazole ring carbon atoms and the exocyclic carbon atoms of the nitrile groups. However, since the chemical shifts of both are very similar, an assignment has not been made.

3.2 Crystal Structure

Crystals of 3,4-bis(1*H*-5-tetrazolyl) furoxan suitable for X-ray analysis were obtained from water. Its structure is shown in Fig. 1 and the selected bond lengths, bond angles and dihedral angles are summarized in Tables 2 and 3. Single-crystal X-ray diffraction analyses reveal that 3,4-bis(1*H*-5-tetrazolyl) furoxan is orthorhombic, space group *P*2₁2₁2₁ with a calculated density of 1.76 g · cm⁻³. It was found that the whole molecular structure tends to be coplanar. Both tetrazole rings are slightly twisted relative to the central furoxan ring, with dihe-

dral angles between them of 9.52° and 11.59° , respectively. The oxygen atom outside of the furoxan ring is approximately coplanar with the ring, and the dihedral angle is 178.3° ($O(1)-N(5)-C(2)-C(3)$). The N—O bond length ($O(1)-N(5)$: 1.214 \AA) outside of the furoxan ring is much shorter than the N—O distances in the furoxan ring ($O(2)-N(5)$: 1.462 \AA , $O(2)-N(6)$: 1.371 \AA). Meanwhile, the $O(2)-N(5)$ bond length is the largest, such that cleavage of this bond may trigger decomposition of compound 3. The N—N bond lengths in the tetrazole ring of the title compound vary from $1.305(42)$ to $1.371(78) \text{ \AA}$ and lie between those of N—N single bonds (1.454 \AA) and N=N double bonds (1.245 \AA), which is good agreement with the corresponding values in related tetrazole derivatives^[15–17].

The final three dimensional networks (as shown in Fig. 2) are formed by extensive weak intermolecular contacts. One molecule was connected with four adjacent molecules through four contacts of $N\cdots N$ (2.75 – 2.92 \AA). These intermolecular short contacts between the molecules not only stabilize the structure, but also lead to a sufficiently dense structure ($D_c = 1.76 \text{ g} \cdot \text{cm}^{-3}$).

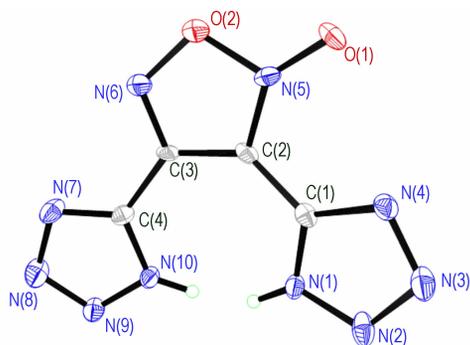


Fig. 1 Molecular structure of the title compound

Table 2 Selected bond lengths and bond angles of the title compound

bond	lengths/ \AA	bond	angle/ $(^\circ)$
N(1)—C(1)	1.326(7)	C(1)—N(1)—N(2)	109.6(5)
N(1)—N(2)	1.340(7)	N(3)—N(2)—N(1)	105.7(5)
N(2)—N(3)	1.309(7)	N(2)—N(3)—N(4)	109.8(5)
N(3)—N(4)	1.371(7)	C(1)—N(4)—N(3)	106.2(5)
N(4)—C(1)	1.304(7)	O(1)—N(5)—C(2)	135.4(6)
N(5)—O(1)	1.215(6)	O(1)—N(5)—O(2)	117.4(4)
N(5)—C(2)	1.330(7)	C(2)—N(5)—O(2)	107.2(5)
N(5)—O(2)	1.462(7)	C(3)—N(6)—O(2)	107.5(5)
N(6)—C(3)	1.292(7)	N(8)—N(7)—C(4)	105.8(5)
N(6)—O(2)	1.371(6)	N(7)—N(8)—N(9)	107.1(5)
N(7)—N(8)	1.306(7)	N(8)—N(9)—N(10)	112.8(5)
N(7)—C(4)	1.337(8)	C(4)—N(10)—N(9)	101.7(5)
N(8)—N(9)	1.307(7)	N(6)—O(2)—N(5)	107.3(4)
N(9)—N(10)	1.333(7)	N(1)—C(1)—C(2)	126.5(5)
N(10)—C(4)	1.316(7)	C(3)—C(2)—C(1)	134.6(5)
C(1)—C(2)	1.454(9)	N(6)—C(3)—C(2)	112.4(5)
C(2)—C(3)	1.430(8)	C(2)—C(3)—C(4)	128.1(5)
C(3)—C(4)	1.466(7)	N(10)—C(4)—C(3)	122.9(5)

Table 3 Selected torsion angles of the title compound

bond	angle/ $(^\circ)$
C(1)—N(1)—N(2)—N(3)	0.1(6)
N(3)—N(4)—C(1)—C(2)	-179.5(5)
N(1)—N(2)—N(3)—N(4)	0.2(7)
N(2)—N(1)—C(1)—N(4)	-0.4(6)
N(2)—N(3)—N(4)—C(1)	-0.4(7)
N(2)—N(1)—C(1)—C(2)	179.6(5)
C(4)—N(7)—N(8)—N(9)	-0.9(7)
O(1)—N(5)—C(2)—C(3)	178.3(6)
N(7)—N(8)—N(9)—N(10)	0.5(7)
O(2)—N(5)—C(2)—C(3)	-0.1(5)
N(8)—N(9)—N(10)—C(4)	-1.2(6)
N(1)—C(1)—C(2)—N(5)	-172.1(5)
C(3)—N(6)—O(2)—N(5)	-177.9(5)
N(1)—C(1)—C(2)—C(3)	12.2(10)
C(2)—N(5)—O(2)—N(6)	0.8(6)
O(2)—N(6)—C(3)—C(2)	1.2(6)
N(3)—N(4)—C(1)—N(1)	0.5(6)
O(2)—N(6)—C(3)—C(4)	180.0(5)

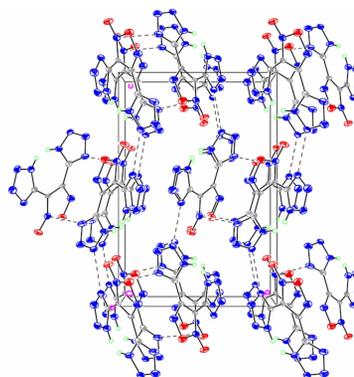


Fig. 2 Molecular packing diagram of the unit cell of the title compound

3.3 Electrostatic Potential (ESP)

To obtain a better understanding of structure for target compound, electrostatic potential (ESP) calculations was carried out based upon the B3LYP/6-31+g(d, p) method with optimized structure. Fig. 3 shows the ESP for the 0.001 electron/bohr³ isosurface of the electron density evaluated at the B3LYP level of theory. It has recently been found, and is extensively used, that the computed ESP is generally related to the impact sensitivity of the bulk energetic materials^[18–20]. In contrast to non-energetic organic molecules for which the positive potential is larger but weaker in strength, in energetic compounds usually more extensive regions with larger and stronger positive potentials are observed which can be related to increased impact sensitivities. In Fig. 3, it can be clearly seen that the positive ESP region of BBF is larger and also a higher charge separation. This is in good accord with the experimental result of relatively high impact sensitivity of BBF^[8].

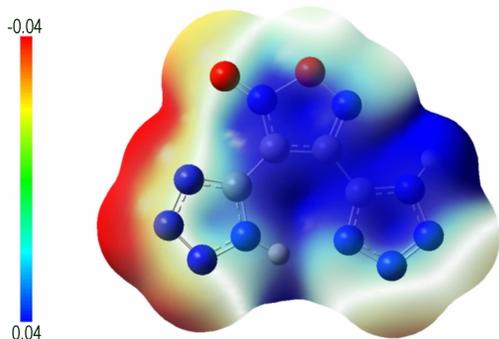


Fig. 3 Calculated [B3LYP/6-31+G(d,p)] electrostatic potential of the title compound. The 3D isosurface of electron density is shown between -0.04 hartree (electron-rich regions) and $+0.04$ hartree (electron-poor regions)

4 Conclusions

3,4-Bis(1H-5-tetrazolyl) furoxan was prepared using 3,4-dicyanofuroxan and sodium azide, and the reaction is catalyzed by Zn^{2+} . This method has many advantages, such as high yield, simple post-processing steps. The crystal structure was determined using single crystal X-ray diffraction. The title compound is almost planar with dihedral angles of 9.52° and 11.59° , respectively. There are extensive weak intermolecular contacts leading to a high density and good thermal stability. These properties make it suitable as a promising green energetic material for solid propellant.

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3,4-双(四唑-5-基)氧化呋咱的简易合成及晶体结构

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摘要: 以 3,4-二氰基氧化呋咱和叠氮化钠为原料, 以水做溶剂, 在 $ZnCl_2$ 催化作用下, 经环化反应合成了 3,4-双(四唑-5-基)氧化呋咱, 总收率达 91%。采用红外光谱、核磁共振、元素分析、X 射线单晶衍射进行了结构表征。结果表明, 晶体属于正交晶系, 空间群为 $P2_12_1$, 晶体学参数: $a=6.1172(14)$ Å, $b=9.657(2)$ Å, $c=14.220(3)$ Å, $V=840.0(3)$ Å³, $Z=4$, $D_c=1.76$ g·cm⁻³, $F(000)=448$, $\mu=0.147$ mm⁻¹, $S=1.031$, $R_1=0.008$, $wR_2=0.2523$ 。3,4-双(四唑-5-基)氧化呋咱分子基本在一个平面, 表明分子中存在强烈的共轭效应。同时, 分子中氮原子之间存在大量的弱键, 能够提高化合物的密度和热稳定性。

关键词: 合成; 富氮唑类化合物; 晶体结构; 静电势

中图分类号: TJ55; O62

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