文章编号：1006-9941(2015)01-0018-05

Synthesis, Crystal Structure and Thermal Behavior of 3,4-Bis(3-nitrofurazan-4-oxy)furazan

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Abstract: 3,4-Bis(3-nitrofurazan-4-oxy)furazan (**1**) was synthesized from 3,4-diaminofurazan by Caro's acid oxidation, hydrolysis, neutralization and substituent reactions, and its structure was characterized by IR, NMR, elemental analysis, and X-ray single-crystal diffraction analysis. The crystal belongs to the monoclinic system, space group $P2_1/c$ with a=15.256(3)Å, b=11.579(3)Å, c=14.981(3) Å, β=117.624(4)°, M_r=328.14, V=2344.7(9) Å^3, Z=8, D_c=1.859 g·cm^{-3}, F(000)=1312, μ=0.177 mm^{-1}, S=1.012, the final R=0.0433 and wR=0.0987. X-ray single-crystal diffraction analysis indicate that compound **1** crystallizes in two crystallographic independent host molecules with different conformation and several intermolecular interactions among oxygen atoms and nitrogen atoms lead to a high density. The thermal behavior of compound **1** was studied by TG-DTG and DSC techniques. Results show that it melts at 72.9 ℃ and is highly exothermic from 245 ℃ to 346 ℃.

Key words: organic chemistry; furazanyl ether; crystal structure; conformation; thermal behavior
CLC number: TJ55; O62 **Document code**: A **DOI**: 10.11943/j.issn.1006-9941.2015.01.004

1 Introduction

In the field of high-energy materials, the synthesis and development of new energetic materials continues to focus on new heterocycles with high densities, high heats of formation, and good oxygen balance. Furazan ring has attracted considerable amount of attention as building block for the synthesis of a high-energy materials due to their high standard enthalpy of formation, high nitrogen content, high energy density, good thermal stability, and low melting point[1-4]. In addition to having furazan groups, furazanyl ether compounds have ether bonds. The introduction of ether bonds between furazan rings tends to lower melting point but contributes markedly to the overall energetic performance. In recent years, more furazanyl ether compounds, such as 3,3′-dicanyodifurazanyl ether, 3,3′-dinitrodifurazanyl ether, 3,3′-bis(fluorodinitromethyl) difurazanyl ether and bifurazano[3,4-b:3′,4′-*f*] furoxano [3″,4″-*d*] oxacyclohetpatriene, were developed[5-11]. 3,4-Bis(3-nitrofurazan-4-oxy)furazan was reported by Aleksei B. Sheremetev with the density of 1.91 g·cm^{-3} and melting point of 38-40 ℃[12], which suggest that it would be a potential candidate for high energy plasticizer.

In this paper, 3,4-bis(3-nitrofurazan-4-oxy)furazan was synthesized from 3,4-diaminofurazan by Caro's acid oxidation, hydrolysis, neutralization and substituent reactions, and its structure was characterized by the means of IR, NMR and elemental analysis. In order to confirm the molecular structure of the title compound, its single crystals were obtained firstly and then characterized by X-ray diffraction analysis.

Received Date: 2013-08-18; **Revised Date**: 2013-11-04
Project Supported: Natural Science Foundation of China (21243007) and National Defense Fundamental Scientific Research(B09201100051)

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2 Experimental

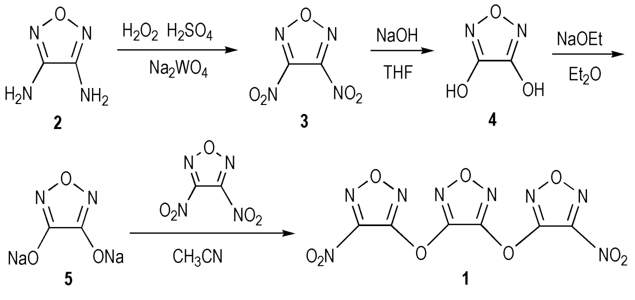
2.1 Materials and measurements

Melting point was measured on XT4A Melting-Point Apparatus with Microscope and uncorrected. ^{1}H NMR and ^{13}C NMR were obtained in DMSO-d_6 on Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on Nicolet NEXUS870 Infrared spectrometer in the range of 4000-400 cm^{-1}. Elemental analyses (C, H and N) were performed on VARI-El-3 elementary analysis instrument. Differential scanning calorimetry (DSC) were carried out in a platinum sample container using Q-200 at a rate of 10 ℃·min^{-1}. Thermogravimetric (TG) were carried out in a platinum sample container using Nicolet TA 2950.

3,4-Diaminofurazan was purchased from commercial sources and recrystallized from water for further use. 3,4-Dinitrofurazan was prepared[13]. Acetonitrile was chromatographical pure. Other chemicals were analytically pure and obtained from commercial sources.

2.2 Synthesis and characterization

The title compound (**1**) was synthesized from Scheme 1.



Scheme 1 Synthesis of the title compound

Preparation of compound 4: To a solution of compound **3** (6.4 g, 40 mmol) in tetrahydro furan(THF) (40 mL) was added dropwise a solution of potassium hydroxide (16 g, 0.4 mol) in water (80 mL) at room temperature. The reaction mixture was heated to 40 ℃ for 1 h, diluted with water (60 mL), acidified with an appropriate concentrated hydrochloric acid and extracted with Et_2O (4×80 mL). The combined organic layer was dried over magnesium sulfate, filtered and the solvent was removed to give 3.77 g compound **4** (92.5%) and a purity of 99.3% (HPLC). m. p.: 152–153 ℃. IR (KBr, ν/cm^{-1}): 3559, 3388 (—OH), 1590, 1421, 1266 (furazan ring), 1020 (C—OH); ^1H NMR (DMSO-d_6, 500 MHz) δ: 12.386 (s, 2 H, OH); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 156.106 (C—OH); Anal. calcd for $C_2H_2N_2O_3$: C 23.54, H 1.98, N 27.45; found C 23.35, H 2.12, N 27.29.

Preparation of compound 5: Ethanol (8 mL) of sodium ethylate (1.43 g, 21 mmol) was added dropwise to solution compound **4** (1.02 g, 10 mmol) in 15 mL ether. The mixture was stirred at room temperature for 1 h. The precipitate was collected, washed with MeOH and Et2O to furnish of 1.38 g compound **5** (94.6%) and a purity of 98.8% (HPLC). IR (KBr, ν/cm^{-1}): 1597, 1584, 1350, 971 (furazan ring); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 165.596 (C—ONa); Anal. calcd for $C_2N_2O_3Na_2$: C 16.45, N 19.19; found C 16.63, N 19.08. (*CAUTIONS: This compound is high explosive and may be sensitive to shock or heating and must be handled with appropriate precautions*).

Preparation of compound 1: To a solution of **5** (1.48 g, 10 mmol) in absolute MeCN (20 mL) was added a solution of 3,4-dinitrofurazan (2.56 g, 16 mmol) in absolute MeCN at 30 ℃ under N_2. The reaction mixture was stirred at this temperature for 30 min, diluted with Et_2O (50 mL), washed with water and dried over magnesium sulfate, filtered and the solvent was evaporated. 1.65 g (yield 51.0%) Compound **1** was obtained with a purity of 99.8% (HPLC) by silica gel flash chromatograpy using pentroleum/ethyl acetate (V/V = 7/1) as eluent. m. p.: 72–73 ℃ (lit. 38–40 ℃)[12]. IR (KBr, ν/cm^{-1}): 1602, 1543, 1489, 1263, 1202 (furazan ring), 1034 (ether bond), 1584, 1365 (—NO_2); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 152.860 (O—C—C—O), 152.987 (C—NO_2), 154.833 (C—C—O); Anal. calcd for $C_6N_8O_9$: C 21.96, N 34.15; found C 21.64, N 33.45.

2.3 Crystal structure determination

The title compound was dispersed into solution of petroleum/diethyl ether (V/V=5/3) with a stirrer, and the mechanical impurities were eliminated by filtration. The saturated solution of title compound **1** was put in a conical flask for two weeks at room temperature to evaporate slowly the mixed solvent and obtain single crystal of title compound.

A colorless single crystal of the title compound with dimensions of 0.36 mm×0.28 mm×0.20 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 =0.71073Å) using the φ-ω scan mode ($1.51° \leqslant \theta \leqslant 25.10°$) at 296(2) K. 11509 Reflections were collected, of which 4166 were independent (R_{int}=0.0464) and 2736 with $I>2\sigma(I)$ were considered to be 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[14–15]. All non-hydrogen atoms were refined anisotropically. The atomic scattering factors and anomalous dispersion corrections were taken from International Table for X-ray Crystallography[16]. Crystal data and structural refinement parameters for compound **1** 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 Crystallograpnic Data Centre with CCDC No. 942434.

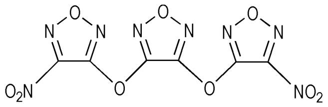
Table 1 Crystal data of the title compound

formula	$C_6N_8O_9$
formula weight/g·mol^{-1}	328.14
crystal system	monoclinic
space group	$P2_1/c$
a/Å	15.256(3)
b/Å	11.579(3)
c/Å	14.981(3)
crystal size/mm	0.36×0.28×0.20
volume/$Å^3$	2344.7(9)
Z	8
ρ_{calcd}/g·cm^{-3}	1.859
$F(000)$	1312
T/K	296(2)
λ/Å	0.71073
$2\theta_{max}$/(°)	50.20
reflections collected/unique	11509/4166
parameters	416
GOF on F_2	1.015
final R indexes ($I > 2\sigma(I)$)	0.0433
final R indexes (all data)	0.0755
largest diff. peak and hole/e·$Å^{-3}$	0.243 and −0.189

3 Results and Discussion

3.1 Improvement of synthesis of compound 5 and ^{13}C NMR analysis of title compound

Compound **5** is an important intermediate for compound **1**. It is a high explosive and may be sensitive to shock or heating. So NaOEt was selected as reaction reagent instead of sodium in order to make the operation in the preparation of compound 5 simpler and safer. In addition, THF was employed instead of MeCN as reaction medium in the acidification of compound **4** in order to reduce the toxicity of reaction system and avoid hydrolysis of MeCN. The elemental analysis, IR and ^{13}C NMR of the product are all in good agreement with the assumed structure. However, it was found that a few characteristic results of compound **1** performed in our laboratory were different from those reported by Sheremetev. For example, the melting point we determined was 72–73 ℃, which was 38–40 ℃ in the literature[12]. The ^{13}C NMR data of the title compound obtained in our study were 152.98 (C1), 154.83 (C2) and 152.86 (C3), which were different from the data of 153.6 (C1), 156.3 (C2) and 154.2 (C3)[12] (Scheme 2).



Scheme 2

3.2 Crystal structure

The single crystal X-ray diffraction analysis shows that the title compound crystallizes in monoclinc $P2_1/c$ space group and there are two crystallographic independent host molecules in the asymmetric unit, as shown in Figure 1. These two independent host molecules have different conformations (Ⅰ and Ⅱ), in which the bond angles and torsion angles show significant difference. The selected bond lengths, bond angles and dihedral angles are summarized in Table 2.

In the crystal, the bond lengths and bond angles in the furazan rings are generally normal and each ring is almost planar[17-18]. The average bond length of C—N of nitro group and furazan ring is 1.441 Å, which is good agreement with the corresponding values in related nitrofurazan derivatives[8]. Because of the *p*-*π* conjugative effect with O atom of ether bond between furazan rings, the bond distances of C(2)—O(4) [1.347(3) Å], C(3)—O(4) [1.358(3) Å], C(4)—O(6) [1.353(3) Å], C(5)—O(6) [1.354(3) Å], C(2A)—O(4A) [1.349(3) Å], C(3A)—O(4A) [1.344(3) Å], C(4A)—O(6A) [1.368(3) Å] and C(5A)—O(6A) [1.347(3) Å] are shorter than those of the normal C—O single bond (1.41 Å)[19]. The bond angles C(2)—O(4)—C(3) [120.2(2)°], C(4)—O(6)—C(5) [118.3(2)°], C(2A)—O(4A)—C(3A) [121.2(2)°], C(4A)—O(6A)—C(5A) [116.26(19)°] indicate an sp^2 hybridization nature of O atom. However, the whole molecular structure is not planar. Both nitro groups are twisted slightly relative to their adjacent furazan rings. The torsion angles of O(1)—N(1)—C(1)—N(2), O(9)—N(8)—C(6)—N(7), O(1A)—N(1A)—C(1A)—N(2A), O(8A)—N(8A)—C(6A)—N(7A) in conformation Ⅰ and Ⅱ are 10.6(4)°, −17.7(4)°, −159.1(3)°, −13.4(4)°, respectively. Both furazan rings are also twisted relative to the central furazan ring. The dihedral angles between the central furazan ring (C(3)—N(4)—O(5)—N(5)—C(4)) and terminal furzan rings (C(1)—N(2)—O(3)—N(3)—C(2) and C(5)—N(6)—O(7)—N(7)—C(6)) in conformation Ⅰ are 15.95° and 66.23°, respectively. In conformation Ⅱ, the corresponding dihedral angles are 7.81° and 69.38°, respectively. Obviously, the terminal furazan ring (C(1A)—N(2A)—O(3A)—N(2A)—C(1A)) and the central furazan ring (C(3A)—N(4A)—O(5A)—N(5A)—C(4A)) in conformation Ⅱ exhibit better conjugation than that in conformation Ⅰ, which causes a bigger dihedral angle between the other terminal furazan ring (C(5A)—N(6A)—O(7A)—N(7A)—C(6A)) and the central furazan ring (C(3A)—N(4A)—O(5A)—N(5A)—C(4A)) in conformation Ⅱ than that in conformation Ⅰ.

In the crystal structure of compound **1**, there are several weak intermolecular contacts. In conformation Ⅰ: the short contacts of $O(6)\cdots O(8^{i})$ (2.890 Å, symmetric code i: −x, 2−y, −z) link two molecules into dimer, as shown in Figure 2. In conformation Ⅱ: the short contacts of $O(3A)\cdots N(6A^{ii})$ (3.021 Å) and $N(3A)\cdots C(5A^{ii})$ (3.164 Å, symmetric code ii: x, 0.5−y, 0.5−z) connect the molecules into one-dimensional chain, as depicted in Figure 3. A three-dimensional supramolecular structure is formed through the short contacts between the dimers and the one-dimensional chains ($O(1)\cdots N(1A^{iii})$, 2.895 Å, $O(2)\cdots O(5A^{iv})$, 2.887 Å, symmetric code iii: 1−x, 0.5+y, 0.5−z; iv: x, 1+y, z). These intermolecular short contacts as well as absence of hydrogen atoms in the molecules lead to a sufficiently dense structure (ρ_{calcd} = 1.859 g·cm^{-3}, which is higher than that of TNT[20]).

Table 2 Selected bond lengths and bond angles/torsion angles of compound **5**

bond	length/Å	bond	length/Å	bond	length/Å
N(1)—O(1)	1.209(3)	C(2)—C(1)	1.406(4)	O(4)—C(2)	1.347(3)
N(1A)—O(1A)	1.206(3)	C(2A)—C(1A)	1.402(4)	O(4A)—C(2A)	1.349(3)
N(1)—O(2)	1.196(3)	C(2)—N(3)	1.296(3)	O(4)—C(3)	1.358(3)
N(1A)—O(2A)	1.207(3)	C(2A)—N(3A)	1.291(3)	O(4A)—C(3A)	1.344(3)
N(1)—C(1)	1.441(4)	O(3)—N(2)	1.363(3)	O(6)—C(4)	1.353(3)
N(1A)—C(1A)	1.437(4)	O(3A)—N(2A)	1.357(3)	O(6A)—C(4A)	1.368(3)
C(1)—N(2)	1.287(3)	O(3)—N(3)	1.387(3)	O(6)—C(5)	1.354(3)
C(1A)—N(2A)	1.284(3)	O(3A)—N(3A)	1.388(3)	O(6A)—C(5A)	1.347(3)
bond	angle/(°)	bond	angle/(°)	bond	angle/(°)
O(1)—N(1)—O(2)	125.7(3)	O(3)—N(2)—C(1)	104.9(2)	O(1)—N(1)—C(1)—N(2)	10.6(4)
O(1A)—N(1A)—O(2A)	125.9(3)	O(3A)—N(2A)—C(1A)	104.8(2)	O(1A)—N(1A)—C(1A)—N(2A)	−159.1(3)
O(1)—N(1)—C(1)	118.1(3)	C(2)—O(4)—C(3)	120.2(2)	N(2)—C(1)—C(2)—N(3)	180.0(2)
O(1A)—N(1A)—C(1A)	115.9(3)	C(2A)—O(4A)—C(3A)	121.2(2)	N(2A)—C(1A)—C(2A)—N(3A)	−0.5(3)
O(2)—N(1)—C(1)	116.2(3)	C(4)—O(6)—C(5)	118.3(2)	N(3)—C(2)—O(4)—C(3)	6.5(4)
O(2A)—N(1A)—C(1A)	118.2(3)	C(4A)—O(6A)—C(5A)	116.26(19)	N(3A)—C(2A)—O(4A)—C(3A)	0.5(4)
N(2)—C(1)—C(2)	110.0(3)	O(8)—N(8)—C(6)	116.0(2)	N(6)—C(5)—O(6)—C(4)	34.7(4)
N(2A)—C(1A)—C(2A)	109.8(3)	O(8A)—N(8A)—C(6A)	118.3(3)	N(6A)—C(5A)—O(6A)—C(4A)	−3.7(4)
N(2)—O(3)—N(3)	111.6(2)	O(9)—N(8)—C(6)	118.5(2)	O(8)—N(8)—C(6)—C(5)	−17.3(4)
N(2A)—O(3A)—N(3A)	111.9(2)	O(9A)—N(8A)—C(6A)	115.4(3)	O(8A)—N(8A)—C(6A)—C(5A)	164.9(3)

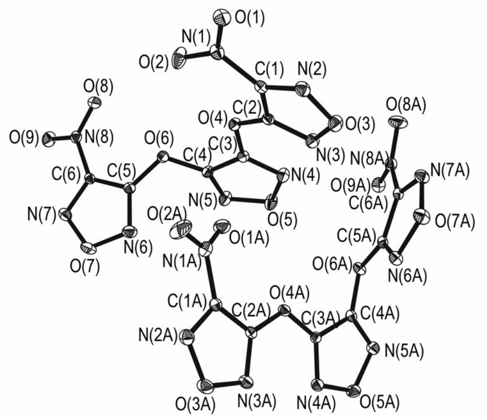


Fig. 1 Molecular structure of the title compound

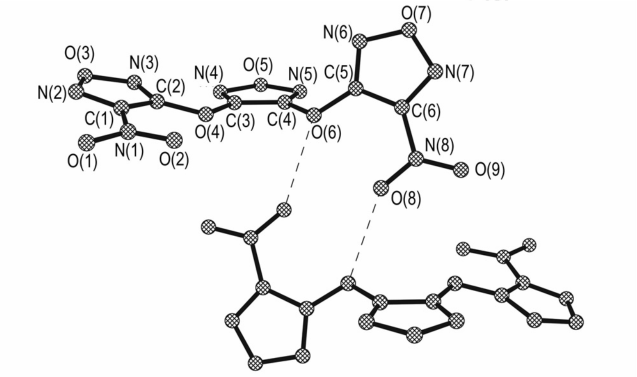


Fig. 2 Dimer structure linked by short contacts between the molecules with conformation Ⅰ

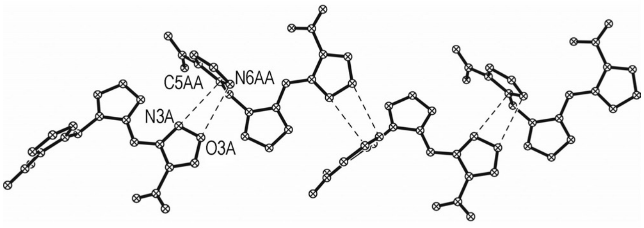


Fig. 3 One-dimensional chain connected by short contacts between the molecules with conformation Ⅱ

3.3 Thermal behavior

The DSC and TG-DTG curves measured with a linear heating rate of 10 K · min^{-1} under nitrogen atmosphere are shown in Figures 4 and 5, respectively. In Fig. 4, curve 1 was measured at general pressure and curve 2 in a sealed condition at a pressure of 3.0 MPa, respectively. In the curve 1, there are two main endothermic processes from 50 ℃ to 240 ℃. The first endothermic process is an intense melting process that starts at 67.0℃, the peak temperature is 72.9 ℃ and this is the melting point of compound **1**. The second endothermic process is a very tardy volatile process that starts at 156.4 ℃ and ends at 238.5 ℃, which indicates that compound **1** is rather volatile in melten state. In Fig. 4, the curve 2 shows that the endothermic process is a little different from curve 1 owing to increase of the pressure. The successive exothermic decomposition step begins at 245.1 ℃ with the exothermic decomposition peak temperature at 305.9 ℃. TG-DTG curves also show that compound **1** has volatilized before decomposition in accordance with the tardy endothermic processes in the curve 1. Thermal studies reveal that compound **1** has a very high thermal stability.

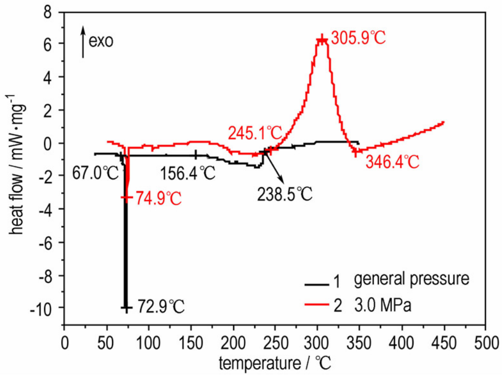


Fig. 4 DSC curves of compound **1**

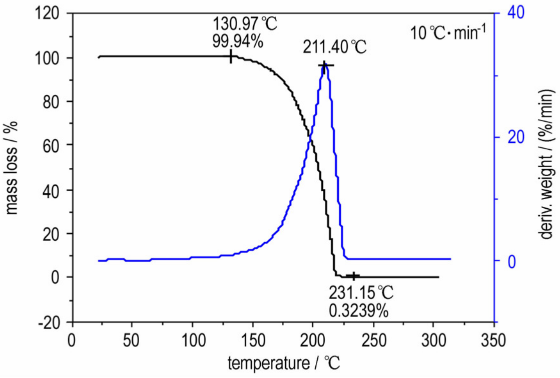


Fig. 5 TG-DTG curves of compound **1**

4 Conclusion

The title compound was synthesized using THF instead of CH_3CN and NaOEt instead of sodium. X-ray single-crystal diffraction analysis indicated that there are two host molecules of different conformation. It is also found that several different weak intermolecular contacts lead to a high density and stable structure. The title compound has low melting point (72.9 ℃), and high computing density (1.859 g · cm^{-3}, cacluated). It could be used as a high energy plasticizer in the future.

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3,4-双(3-硝基呋咱-4-氧基)呋咱合成、晶体结构及热性能

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摘　要:以二氨基呋咱为原料,经氧化、水解、中和和取代反应合成了 3,4-双(3-硝基呋咱-4-氧基)呋咱,并采用红外光谱、核磁共振、元素分析、X 射线单晶衍射等进行了结构表征。晶体属于单斜晶系,空间群为 $P2_1/c$,a=15.256(3) Å, b=11.579(3) Å, c=14.981(3) Å, β=117.624(4)°, M_r=328.14, V=2344.7(9) Å^3, Z=8, D_c=1.859 g·cm^{-3}, F(000)=1312, μ=0.177 mm^{-1}, S=1.012, R_1=0.0433, wR_2=0.0987。晶体结构分析结果表明,在不对称单元中存在两种构象不同的分子,分子中含有大量的弱键,能够提高化合物的密度和热稳定性。采用差示扫描量热法和热重分析研究了 3,4-双(3-硝基呋咱-4-氧基)呋咱的热分解过程,在 10 ℃·min^{-1} 的升温条件下,其熔点为 72.9 ℃,在 245 ~346 ℃ 之间存在明显放热过程。

关键词:有机化学;呋咱醚;晶体结构;构象;热行为
中图分类号:TJ55;O62　　**文献标识码:**A　　**DOI:**10.11943/j.issn.1006-9941.2015.01.004