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A Novel Synthesis of 3,3′-Bis(fluorodinitromethyl) difurazanyl ether(FOF-13)

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Abstract: Using 3,3′-dicyanodifurazanyl ether (FOF-2) as starting materials, an excellent energetic plasticizer 3,3′-bis(fluorodinitromethyl) difurazanyl ether (FOF-13) was synthesized via a novel five-step synthetic method, and its structure was characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and elemental analysis. The main properties of FOF-13 are followed as: its density is 1.92 g·cm^{-3}, and melting point 43.5 ℃(DSC), impact sensitivity above 14 J, friction sensitivity 64%, and the mean detonation velocity is 8497 m·s (1.69 g·cm^{-1}). It shows that FOF-13 is a type of competitive energetic plasticizer.

Key words: organic chemistry; 3,3′-bis(fluorodinitromethyl) difurazanyl ether; synthesis; property

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1 Introduction

Furazanyl ether compounds have been becoming an important research direction in recent years as high energetic explosives and plasticizers due to their good performances [1-4]. FOF-13 is a new furazanyl ether energetic material firstly reported by Sheremetev[5] from 3,3′-dicyanodifurazanyl ether, and it exhibits a melting point of 48 ℃, a high density of 1.97 g·cm^{-3}, a decomposition temperature above 270 ℃ and a standard enthalpy of formation (ΔH_f) −146.3 kJ·mol^{-1}[1-3]. However, the synthesis conditions and other properties are few reported.

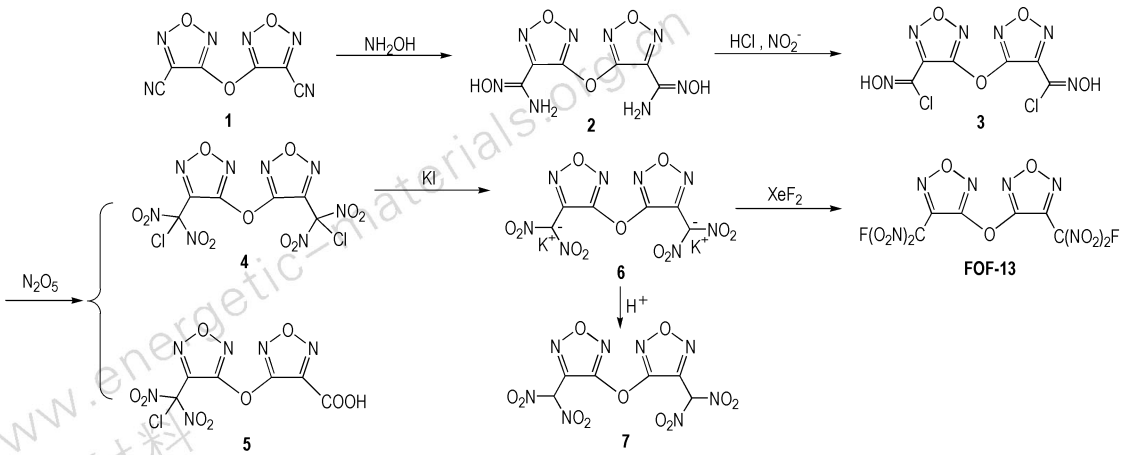
In order to investigate FOF-13 thoroughly, a novel five-step synthetic route was designed (Scheme 1) in the first time, and FOF-13 and its intermediates were characterized by IR, ^{13}C NMR, ^{19}F NMR and elemental analysis. At the same time, the main energetic properties of FOF-13 were also studied.

2 Experimental

2.1 Synthetic route

2.2 Instruments and conditions

^{1}H NMR, ^{13}C NMR and ^{19}F NMR were obtained on a Bruker AV500 NMR spectrometer. Elemental analyses (C, H and N) were performed on a VARI-El-3 elementary analysis instrument. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000 ~400 cm^{-1}. Differential scanning calorimetry (DSC) studies were carried out on a Q200 apparatus (TA, USA) with heating rates of 10 K·min^{-1}, using dry oxygen-free nitrogen as atmosphere with a flowing rate of 50 mL·min^{-1}. The TG-DTG experiment was performed with a SDT-Q600 apparatus (TA, USA) operating at a heating rate of 10 K·min^{-1} in a flow of dry oxygen-free nitrogen at 100 mL·min^{-1}.



Scheme 1 A novel synthetic route of FOF-13

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The impact and friction sensitivities of FOF-13 were determined with a ZBL-B impact sensitivity instrument and a MGY-2 friction sensitivity instrument (Nachen, China), respectively. The mass of fall hammer is 2 kg. The swing angle and gauge pressure is 60°. The sample used for each test is about 20 mg. The detonation velocity (D_{exp}) of FOF-13 was investigated with the GJB772A-1997 702.1. FOF-13 (18 g) was pressed into a cylinder (Φ=20 mm), and the loading density (ρ) was 1.69 g·cm^{-3}.

3,3′-Dicyanodifurazanyl ether (FOF-2) was prepared according to the published procedures [6]. Other chemicals were obtained from commercial sources and used without further purification.

2.3 Synthesis

2.3.1 Synthesis of 3,3′-bis(amidoximino) difurazanyl ether (2)

To a mixture of water (50 mL), isopropanol (25 mL), 3,3′-dicyanodifurazanyl ether (**1**) (4.16 g, 20.0 mmol) and hydroxylamine hydrochloride (2.85 g, 41 mmol), sodium carbonate anhydrous was added in batches, and then the reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered, washed with ice water, and dried in vacuo to obtain a white solid 5.02 g with a yield of 91.2%. m.p. 203 ~ 204 ℃. ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 10.67 (s, 2H, OH), 6.28 (s, 4H, NH_2). ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.31 (C—O), 142.23 (C—C=N), 141.33 (C—NH_2). IR (KBr, ν/ cm^{-1}): 3495, 3454, 3349, 3172, 2919, 1680, 1656, 1525, 1101, 1021, 969. Calc. for $C_6H_6N_8O_5$: C 26.67, N 41.18, H 2.24; Found: C 26.62, N 41.07, H 2.18.

2.3.2 Synthesis of 3,3′-bis(chloroximido) difurazanyl ether (3)

Appropriate above compound **2** (5.40 g, 20.0 mmol) was dissolved in 55 mL of concentrated hydrochloric acid and 30 mL of water at room temperature. Saturated sodium nitrite (2.38 g, 41.0 mmol) in water was added dropwise to a stirred solution of amide oxime. After stirring for 2 h at 273 K, the reaction mixture was heated to 293 K for 1.5 h until N_2 evolution stopped. The resulting white precipitate was filtered, washed with water, recrystallized from MeOH/H_2O (1∶1) and dried in vacuo to yield white solid 5.40 g with a yield of 87.5%. m.p. 60 ~ 61 ℃. ^{1}H NMR (DMSO-d_6, 500 MHz): δ=13.71 (s, 2H, OH). ^{13}C NMR (DMSO-d_6, 125 MHz): δ =158.99 (C—O), 143.03 (C—C=N), 123.40 (C—Cl). IR (KBr, ν/cm^{-1}): 3533, 3167, 3020, 1570, 1518, 1126, 1024, 942, 657. Calc. for $C_6H_2N_6O_5Cl_2$: C 23.32, N 27.20, H 0.65; Found: C 23.30, N 27.15, H 0.68.

2.3.3 Synthesis of 3,3′-bis(chlorodinitromethyl) difurazanyl ether (4) and 3-chlorodinitro- methyl-3′-carboxyl difurazanyl ether (5)

To a suspension of the above compound **3** (0.55 g, 1.8 mmol) in 50 mL of $CHCl_3$ at 293 K was added N_2O_5 (2.2 g, 20 mmol). The mixture was heated to 318 K and kept at this temperature for 40 min. The solvent was evaporated and the residue was subjected to column chromatography on silica gel to isolate colorless crystals **4** (0.23 g, 30.0 %) and **5** (0.25 g, 41.6 %). Compound **4**: m.p. 68-69 ℃. ^{13}C NMR (DMSO-d_6, 125 MHz): δ=157.67 (C—O), 140.37 (C—C=N), 112.75 ($CCl(NO_2)_2$). IR (KBr, ν/ cm^{-1}): 1613, 1582, 1515, 1291, 1049, 971. Calc. for $C_6N_8O_{11}Cl_2$: C 16.72, N 26.00%; Found: C 16.82, N 25.94%. Compound **5**: m.p. 127-128 ℃. ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 13.84 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.74, 139.82, 133.01, 124.66, 113.58, 106.14. IR (KBr, ν/cm^{-1}): 3140, 2916, 2675, 1752, 1620, 1605, 1580, 1510, 1269, 1131, 1030, 982. Calc. for $C_6HN_6O_9Cl$: C 21.41, H 0.30, N 24.97; Found: C 21.38, H 0.41, N 24.86.

2.3.4 Synthesis of potassium salt of 3,3′-bis(dinitromethyl) difurazanyl ether (6)

Compound **4** (1.0 g, 2.3 mmol) was dissolved in MeOH (8 mL) and treated with solution of KI (1.5 g, 9.0 mmol) in MeOH (15 mL) at room temperature. The resulting mixture was stirred at room temperature for 1 h and triturated with Et_2O (20 mL). Precipitate was collected, washed with ice-cold water, MeOH, and Et_2O to furnish a yellow solid (0.81 g, 85.7%). m.p. 98 ℃ (loss of H_2O), 245 ℃ (dec., DSC measurement, 10 K·min^{-1}). ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 160.77 (C—O), 142.31 (C—C=N), 118.67 (C—$(NO_2)_2$). IR (KBr, ν/cm^{-1}): 1589, 1526, 1479, 1239, 1070, 997. Calc. for $C_6N_8O_{11}K_2$: C 16.44, N 25.57; Found: C 16.15, N 25.36.

2.3.5 Synthesis of 3,3′-bis(dinitromethyl) difurazanyl ether (7)

Compound **6** (0.65 g, 1.5 mmol) was suspended in water (3 mL), and then acidified with 50% sulfuric acid (1 mL) at room temperature. The mixture was extracted with diethyl ether (3×10 mL), dried over $MgSO_4$, and the solvent was evaporated to obtain compound **7** (0.44 g, 81.5 %). m.p. 68-69 ℃. ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 10.49 (s, 2H, CH). ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 161.22 (C—O), 142.77 (C—C=N), 119.10 ($CH(NO_2)_2$). IR (KBr, ν/cm^{-1}): 3004, 2983, 1623, 1585, 1524, 1481, 1366, 1322, 1239, 1148, 1037, 999. MS (ESI) m/z: 360.98 [M−H]$^-$. Calc. for $C_6H_2N_8O_{11}$: C 19.90, H 0.56, N 30.94; Found: C 19.74, H 0.73, N 30.78.

2.3.6 Synthesis of 3,3′−bis(fluorodinitromethyl) difurazanyl ether (FOF-13)

To a suspension of compound **6** (0.6 g, 1.37 mmol) in anhydrous acetonitrile at 20 ℃, XeF_2 (0.92 g, 5.50 mmol) was added. After the mixture was stirred for 48 h at 20 ℃, the acetonitrile was evaporated, and the residue was treated with some water to afford many colorless crystals (0.23 g, 42.6%). m.p. 43.5 ℃ (DSC measurement, 10 K·min^{-1});

13C NMR (DMSO-d_6, 125 MHz): δ=158.41 (s, C—O), 137.00 (d, J13C-19F=25, C—C=N), 113.88 (d, J13C-F19=294.0 Hz, $CF(NO_2)_2$). 19F NMR (DMSO-d_6, 470.5 MHz): δ=-106.29. IR (KBr, ν/cm^{-1}): 1616, 1576, 1515, 1310, 1196, 1138, 1048, 981. Calc. for $C_6N_8O_{11}F_2$: C 18.10, N 28.15%; Found: C 18.26, N 27.92%.

3 Physical chemistry properties and detonation performances for FOF-13

Some main energetic properties of FOF-13 were determined or calculated, and listed in Table 1. The results show that the mean detonation velocity is 8497 m·s^{-1} with the standard deviation of 160. Moreover, we also speculated the detonation velocity (D_{calc}=9300 m·s^{-1}) based on the maximum density obtained from the crystal structure.

Table 1 Physical chemistry and detonation properties of FOF-13

compound	FOF-13	RDX	FEFO
formula	$C_6F_2N_8O_{11}$	$C_3H_6N_6O_6$	$C_5H_6F_2N_4O_{10}$
molar mass	398.1	222.1	320.1
nitrogen content/%	28.1	37.8	17.5
density/g·cm^{-3}	1.92[1)]	1.800[7]	1.601[9]
melting point/ ℃	43.5[2)]	203	14.5
oxygen balance/%	0[3)]	-21.61	-10
impact sensitivity/J	14[4)]	7.4[7]	13.5[9]
friction sensitivity/%	64[5)]	—	—
detonation velocity /m·s^{-1}	8497[ρ=1.69 g·cm^{-3}][6)]	8800[8]	7500[10]

Note: 1) crystal density (CCDC: 942431). 2) melting point (DSC). 3) oxygen balance (%) for CaHbOcNdXe: 1600[(c+e/2-2a-b/2)/Mw] (X=F, Cl). 4) measured with a ZBL-B impact sensitivity instrument. 5) measured with a MGY-2 friction sensitivity instrument. 6) measured with the GJB772A-97 702.1.

4 Conclusions

An excellent energetic plasticizer FOF-13 was synthesized via a novel five-step reaction process, and its structure was fully characterized. FOF-13 exhibits low melting point (43.5 ℃). Its impact sensitivity (15 J) and friction sensitivity (64%) are superior to RDX. The detonation velocity for FOF-13 (D_{exp}=8497 m·s^{-1}, ρ=1.69 g·cm^{-3}) were measured to show a high energy, making it suitable as a promising high energy plasticizer for solid propellant.

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3,3′-二(氟偕二硝基)二呋咱基醚(FOF-13)新法合成

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摘 要: 自行设计了3,3′-二(氟偕二硝基)二呋咱基醚(FOF-13)新的合成路线,采用3,3′-二氰基二呋咱醚(FOF-2)为原料,经氰基加成、重氮化、硝化、还原、氟化5步反应合成了FOF-13,总收率为8.5%,并通过IR、^{13}C NMR、^{19}F NMR、元素分析等分析手段进行了结构表征。开展了FOF-13物化与爆轰性能研究,实验结果为:结晶密度1.92 g·cm^{-3},熔点43.5℃(DSC),撞击感度大于14 J,摩擦感度为64%,爆速为8497(ρ=1.69 g·cm^{-3}),表明FOF-13为一种性能优异的增塑剂。

关键词: 有机化学; 3,3′-二(氟偕二硝基)二呋咱基醚(FOF-13); 新法合成;性能

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