文章编号：1006-9941(2016)09-0922-03

3,4-Bis(3-fluorodinitromethylfurazan-4-oxy)furazan：A New Thermally Stable Plasticizer with High Energy Density

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Abstract: A new fluorodinitromethyl-containing energetic plasticizer 3,4-bis(3-fluorodinitromethylfurazan-4-oxy)furazan was self-designed and synthesized. Its structure was characterized by FT-IR, ^{13}C NMR, ^{19}F NMR, elemental analysis, DSC and TG-DTG. Based on the calculated standard enthalpy of formation and the measured density, the detonation properties of 3,4-bis(3-fluorodinitromethylfurazan-4-oxy)furazan were estimated by Kamlet-Jacobs equations and compared with those of commonly used plasticizing agents, nitroglycerine(NG), bis(2-fluoro-2,2-diniroethyl)formal (FEFO), and 3,3′-dinitrodifurazanyl ether (FOF-1). Results show that 3,4-bis(3-fluorodinitromethylfurazan-4-oxy)furazan has good thermal stability (decomposition temperature of 197.8 ℃), high density(1.88 g·cm^{-3}), low melting point(50 ℃), which indicates that 3,4-bis(3-fluorodinitromethylfurazan-4-oxy)furazan is an energetic plasticizer with excellent comprehensive performance.

Key words: furazanyl ether; energetic plasticizer; detonation parameters

CLC number: TJ55; O62 **Document code**: A **DOI**: 10.11943/j.issn.1006-9941.2016.09.018

1 Introduction

The demand for high-performance explosives and propellants has led to intensive investigations relative to improving their energetic, mechanical, and storage properties and safe handling. One of the key steps is the development of new energetic ingredients, such as energetic plasticizers. Energetic plasticizers are important constituents of rocket and gun propellants, which aid in improving the mechanical properties of the propellant grain[1-5]. The basic objectives of developing energetic plasticizers are: (1) increase of the thermal stability, (2) increase in energy content, (3) adjustment of the oxygen balance in a formulation, (4) improvement of the plasticizer functions in formulations. Furazanyl ether compounds have attracted a considerable amount of attention as an energetic plasticizers due to their high energy density, good thermal stability and positive heat of formation[6-14]. When a bridged oxygen atom is introduced into furazans, it could be significantly increased both the flexibility and plasticizer of the molecule. A good example is the previously synthesized compound 3,3′-dinitrodifurazanyl ether (FOF-1), which shows a low melting point (T_m=63-64 ℃), high density (ρ=1.90 g·cm^{-3}) and good thermal stability (T_{dec}>200 ℃).

In order to raise the thermal stability and energy level of the energetic plasticizer, introducing furazanyl ether as backbone into fluorodinitromethyl group could be an effective method. Chemically, the substitution of one nitro group in the trinitromethyl moiety with a fluorine atom reduces the pseudohalide character[15]. In view of the observations above, a detailed study of the synthesis and characterization of 3,4-bis(3-fluorodinitromethylfurazan-4-oxy)furazan is presented in this work. In addition, thermal stability, sensitivity measurements and the detonation parameters were investigated.

2 Experimental

2.1 Instruments and Conditions

Elemental analyses of 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 a 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 50 mL·min^{-1}. The density was measured using a pycnometer method at room temperature. The impact sensitivity was determined with a ZBL-

Received Date: 2015-12-30; **Revised Date**: 2016-01-10

Project Supported: National Science Foundation of China (21373157)

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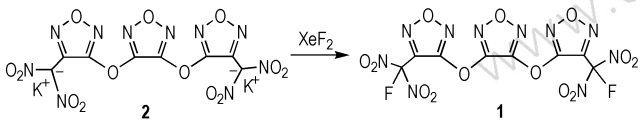
B impact sensitivity instrument. The heat of formation for 3, 4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan was theoretically computed using the Gaussian 09 (Revision A.02) program package[16]. To obtain very accurate energies, the enthalpies (H) were calculated by using the CBS-4M method[17-18].

Dipotassium of 3, 4-bis(3-dinitromethylfurazan-4-oxy) furazan (**2**) was prepared according to the published procedures[19]. Other chemicals were obtained from commercial sources and used without further purification.

2.2 Synthesis



Scheme 1

3,4-Bis(3-fluorodinitromethylfurazan-4-oxy) furazan(**1**): To a suspension of dipotassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan (0.35g, 0.67mmol) in an hydrous acetonitrile (15 mL) was added XeF_2(0.46 g, 2.7 mmol) with stirring and reaction mixture was stirred for 20 h at 30 ℃. The acetonitrile was evaporated, and the residue was treated with water. The white crystals was collected by filtration to afford **1** (0.18 g, 56.2%) as a colorless crystals. mp 50 ℃; ^{13}C NMR (DMSO-d_6, 125 MHz) δ 159.85, 153.33, 138.03, 114.21; ^{19}F NMR (DMSO-d_6, 470.5MHz) δ: −106.84; IR (KBr, ν/cm^{-1}) 1608, 1576, 1545, 1507, 1350, 1309, 1250, 1194, 1033, 982; Anal. Calcd. for $C_8N_{10}O_{13}F_2$(%): C 19.93, N 29.05; Found C 20.08, N 29.13.

3 Physicochemical and Energetic Properties

The physicochemical and energetic properties of 3,4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan were determined or calculated, and listed in Table 1. It was found that 3,4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan possesses a good thermal stability with decomposition temperature of 197.8 ℃, moderate impact sensitivity of 11 J. The density of 3,4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan is 1.88 g·cm^{-3}. The oxygen balance is calculated to be −6.6%, and this value is lower than that of NG (3.5%), but higher than that of FEFO (−10%).

Based on the calculated heats of formation and the experimentally measured densities, the detonation pressures and detonation velocities were calculated based on Kamlet-Jacobs equations and shown in Table 1. Compound **1** has a detonation velocity of 8644.5 m·s^{-1} and a detonation pressure of 34.0 GPa, which are significantly better than those of nitroglycerine (NG) (25.7 GPa, 7813 m·s^{-1})[20] and bis(2-fluoro-2,2-diniroethyl) formal (FEFO) (25 GPa, 7500 m·s^{-1})[21], and comparable with detonation velocity of 3,3′-dinitrodifurazanyl ether (FOF-1) (8930 m·s^{-1})[22], revealing a higher energy level as a new high-performance energetic plasticizer.

Table 1 The physicochemical properties and detonation parameters of 3,4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan compared with the well-known plasticizers NG, FEFO and FOF-1

compound	**1**	NG	FEFO	FOF-1
formula	$C_8F_2N_{10}O_{13}$	$C_3H_5N_3O_9$	$C_5H_6F_2N_4O_{10}$	$C_4N_6O_7$
molar mass	482.1	227.1	320.1	244
nitrogen content/%	28.1	18.5	17.5	34.4
density/g·cm^{-3}	1.88	1.59	1.60	1.90
melting point/℃	50	13	14.5	63
oxygen balance/%	−6.6	3.5	−10	−6.5
impact sensitivity/J	11	0.2	13.5	−
enthalpy of formation /kJ·mol^{-1}	−128.5	−371	849.8	350.5
detonation velocity /m·s^{-1}	8644.5	7813	7500	8930
detonation pressure /GPa	34.0	25.7	25	−

4 Conclusions

In this study we reported the synthesis and structural property, spectroscopic characterization and detonation performances of 3, 4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan (**1**). Compound **1** exhibits good physicochemical and detonation properties, such as high density(1.88 g·cm^{-3}), good thermal stability (T_{dec}=197.8 ℃), moderate impact sensitivity(11 J), acceptable oxygen balance(−6.6%), and high detonation pressure(34.0 GPa) and detonation velocity(8644.5 m·s^{-1}). In many aspects, such as thermal stability, density, sensitivity, and detonation parameters, it is far superior to NG. This promising result makes the 3, 4-bis(3-fluorodinitromethylfurazan-4-oxy) furazan interesting for future application as a potential high-energy dense plasticizer.

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3,4-二(3-氟偕二硝基-4-氧)呋咱：一种新型热稳定高能量密度增塑剂

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摘 要： 自行设计并合成了一种含有氟偕二硝基的新型高能增塑剂3,4-二(3-氟偕二硝基-4-氧)呋咱。通过FT-IR、^{13}C NMR、^{19}F NMR、元素分析、DSC等分析手段进行了结构表征。基于计算的标准生成焓以及实测的密度，采用Kamlet-Jacobs方程计算了3,4-二(3-氟偕二硝基-4-氧)呋咱的爆轰性能，并与常用增塑剂：硝化甘油(NG)和二(氟偕二硝基)甲醛(FEFO)和3,3′-二硝基双呋咱醚(FOF-1)的爆轰性能进行了对比。结果表明，3,4-二(氟偕二硝基-4-氧)呋咱具有热稳性好(分解温度197.8 ℃)、密度大(1.88 g·cm^{-3})、熔点低(50 ℃)和能量水平高等特点，是一种综合性能优异的含能增塑剂。

关键词： 呋咱醚；含能增塑剂；爆轰性能

中图分类号： TJ55；O62 **文献标志码：** A **DOI：** 10.11943/j.issn.1006-9941.2016.09.018