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A good balance between the energy density and sensitivity from assembly of bis(dinitromethyl) and bis(fluorodinitromethyl) with a single furazan ring

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ABSTRACT

In the field of energetic materials, the contradiction between energy density and sensitivity has long baffled the researchers in pursuing the high detonation-performance compounds with low sensitivity. The bis(dinitromethyl) and bis(fluorodinitromethyl) groups were introduced into a single 1,2,5-oxadiazole (furazan) ring for the first time to form a series of novel furazan-based energetic derivatives, which have been fully characterized by NMR, FTIR, elemental analysis and single crystal X-ray diffraction. The thermal decomposition behaviors were also investigated by multiple heating methods and TG-DSC. Interestingly, among these newly as-synthesized compounds, the dihydroxylammonium salt of bis(dinitromethyl)-furazan (**5**) possessed a high crystal density of 1.938 g cm^{-3} at room temperature and exhibited excellent detonation properties (v_D = 9679 m s^{-1}, P = 41.5 GPa), as well as moderate impact sensitivities (14 J), which achieved a high level of balance between high energetic density and low sensitivity to date for the furazan-based energetic salts. Furthermore, the neutral compound bis(fluorodinitromethyl)-furazan (**11**) showed a high positive oxygen balance of 10.19%, which also makes it a potential candidate for the high energetic oxidizer. Such fascinating properties demonstrate that the assembly of bis(dinitromethyl) groups with the single furazan ring is a favorable strategy for the design and synthesis of novel energetic materials with high energy and improved safety.

1. Introduction

Over the past several decades, researchers have never stopped exploring the novel energetic materials with more highly dense, thermally stable, environmentally friendly, nitrogen- and oxygen-rich, and insensitive properties. In particular, searching for high energetic and insensitive materials with the detonation performance comparable to HMX and the insensitivity of TATB continues to be a challenging and ongoing task for chemists and materials scientists [1,2]. Given the advantages of high densities, high positive heats of formation, ring strain, and good oxygen balance, nitrogen-rich heterocyclic rings including tetrazole [3,4], triazole [5], pyrazole [6], imidazole [7] and oxadiazole [8] provide fascinating backbones for the construction of novel energetic molecules. Further functionalization of these heterocyclic rings with explosive groups, such as nitro, nitramino, and dinitromethyl, very often satisfies different energetic materials applications in the field of explosives, propellants, and pyrotechnics.

In contrast to tetrazole, triazole, or pyrazole, oxadiazole has the unique characteristic of an intrinsic oxygen atom, which can increase the oxygen content, thus achieving oxygen balance more readily. It is well known that oxadiazole rings involve four tautomers: 1,2,5-oxadiazole (furazan), 1,2,4-oxadiazole, 1,3,4-oxadiazole, and 1,2,3-oxadiazole (unstable). Since molecular structure determines properties, insight into the oxadiazole structures helps to understand the key factors that determine their stability and detonation properties. Apart from the unstable Table 1,2,3-oxadiazole, the other three isomers can be disubstituted to form a series of novel energetic compounds (Scheme 1) [9]; such a combination can influence both the electron delocalization and the degree of conjugation, which further play an important role in improving the sensitivities.

In recent years, a large number of studies indicate that furazan rings have emerged as a class of promising synthetic building blocks, which can be converted into a diverse range of energetic compounds with high positive heats of formation, good detonation properties, and low sensitivities. Particularly, the introduction of the nitramino (-$NHNO_2$) [10], dinitromethyl (-$CH(NO_2)_2$) [8,11], and fluorodinitromethyl (-$CF(NO_2)_2$) [12] groups into furazan ring has been demonstrated to be an efficient way for the construction of high energy density materials because these functional groups not only can increase additional oxygen balance and density but

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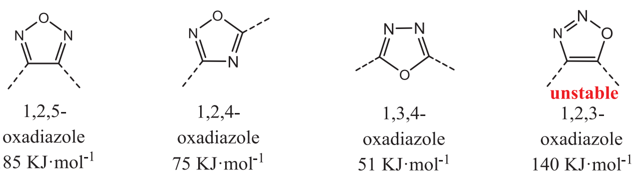


Scheme 1. Four different regioisomeric forms of oxadiazole with calculated gas-phase heats of formation.

also can further form the energetic salts to decrease the sensitivity. Up to now, several typical examples such as dihydroxylammonium 3,3′-bis(dinitromethyl) difurazanyl ether [13], dihydroxylammonium 3,4-dinitramino-furazante [14], dihydroxylammonium 3,3′-dinitramino-4,4′-bifurazante [15], 3,3′-bis(fluorodinitromethyl) difurazanyl ether [16] and 3,3′-bis(fluorodinitromethyl)-4,4′-azofurazan [17], have been reported and shown in Scheme 2. Although a series of novel oxadiazole-based energetic materials have been developed and characterized, these oxadiazole-based energetic materials can hardly reach an optimal balance between high energy and low sensitivity.

So far, although furazan ring is often taken as the first choice of the oxadiazole family in the design of energetic materials, the introduction of two vicinal bulky groups into a single furazan ring has not been reported. Therefore, encouraged by the study results of dipotassium 3-nitramino-4-dinitromethyl-furazante [18] and dihydroxylammonium 2,5-bis(dinitromethyl)-1,3,4-oxadiazolate [19], we synthesized dinitromethyl derivatives based on single furazan ring, which would have high positive oxygen balances and contain only very small amounts of carbon and hydrogen (Scheme 2). The high nitrogen and oxygen contents of these compounds should lead to high crystal densities. In this work, a series of energetic salts based on a furazan ring containing double dinitromethyl or fluorodinitromethyl group were designed and synthesized. All of the new compounds were experimentally characterized and theoretically studied. Their thermal stabilities and sensitivities towards impact and friction, as well as detonation properties, suggest that these new moieties may have potential applications as oxidizers or high-performance energetic materials.

2. Experimental

2.1. Materials

2.1.1. 3,4-Diethylcarboxylate-furazan (A)

A solution of 31.6 g (0.1 mol) of 3,4-dicarboxyl-furazan in 200 ml of alcohol saturated with hydrogen chloride gas was refluxed for 4 h, after which the alcohol was removed by evaporation, and the residue was dissolved in ether. The ether solution was washed with a solution of sodium carbonate and dried over anhydrous sodium sulfate. The ether was removed by evaporation to give intermediate **A** (35.5 g, 83% yield) as a colorless liquid [20]. IR (KBr, cm^{-1}): 2989, 2943, 2909, 2877, 1753, 1620, 1552, 1484, 1448, 1390, 1372, 1313, 1229, 1173, 1098, 1023, 906, 856, 827, 777, 622. ^{1}H NMR (DMSO-d_6, δ, ppm): 1.31–1.37 (t, CH_3), 4.45–4.49 (q, CH_2). ^{13}C NMR (DMSO-d_6, δ, ppm): 14.0, 63.8, 147.7, 156.9. Anal. Calcd (%) for $C_8H_{10}N_2O_5$: C 44.86, H 4.71, N 13.08. Found: C 44.92, H 4.63, N 12.97.

2.1.2. 3,4-Dicarboxamide-furazan (B)

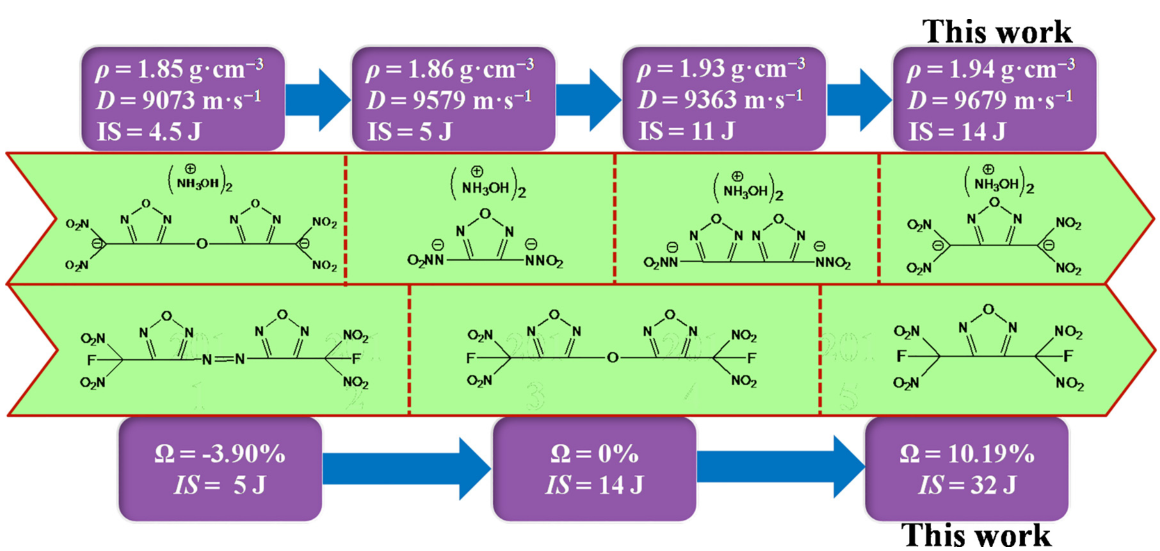
To the solution of intermediate **A** (21.4 g, 0.1 mol) in ethanol (50 mL) was added the 25% ammonia water (20.5 g, 0.3 mol) dropwise with vigorous stirring at room temperature. And then, after continuous stirring for 4 h at room temperature, the reaction mixture was filtrated off and washed with water and ethanol successively to afford (13.9 g, 89% yield) the intermediate **B** as a white solid. T_d: 261°C. IR (KBr, cm^{-1}): 3444, 3222, 3132, 1706, 1686, 1604, 1531, 1468, 1411, 1316, 1141, 1121, 1019, 918 808, 763, 716, 685, 610, 594, 526, 482. ^{1}H NMR (DMSO-d_6, δ, ppm): 8.26, 8.70. ^{13}C NMR (DMSO-d_6, δ, ppm): 150.1, 158.2. Anal. Calcd (%) for $C_4H_4N_4O_3$: C 30.78, H 2.58, N 35.89. Found: C 30.82, H 2.64, N 35.82.

2.1.3. 3, 4-Dicarbonitrile-furazan (C)

To a magnetically stirred mixture of the intermediate **B** (15.6 g, 0.1 mol) in dry CH_2Cl_2 (100 mL) was added dry triethylamine (32.2 mL, 0.4 mol) at room temperature. After the resulting mixture was cooled to 0°C in an ice-water bath, $(CF_3CO)_2O$ (52.8 mL, 0. 38 mol) was added dropwise at 0 ~ 5°C. Then, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 4 h. After addition of water (20 mL), the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3*20 mL). The combined organic extracts were washed with water, then with 10% HCl and again with water and dried over $MgSO_4$. The solvent was evaporated under reduced pressure to give intermediate **C** (10.9 g, 91% yield) as colorless crystals. T_m: 39°C. IR (KBr, cm^{-1}): 2266 (-CN), 1744, 1625, 1466, 1367, 1285, 1236, 1196, 1029, 907, 619. ^{13}C NMR (DMSO-d_6, δ, ppm): 136.2, 106.6. Anal. Calcd (%) for C_4N_4O: C 40.01, N 46.66. Found: C 39.97, N 46.73.

2.1.4. Bisaminohydroximoyl-furazan (D) and bischlorohydroximoyl-furazan (E)

Intermediate D (yield of 81%) and E (yield of 96%) were prepared



Scheme 2. Comparison of physical and detonation properties for the furazan derivatives with dinitromethyl or fluorodinitromethyl group.