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Synthesis and Properties of Two Energetic Salts from 3,3′-Dinitroamino-4,4′-azoxyfurazan

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Abstract: 3, 3′-Dinitroamino-4,4′-azoxyfurazan (NOF) was prepared via nitration of 3,3′-diamino-4,4′-azoxyfurazan (AOF) as raw material using pure nitric acid. New two kinds of energetic ion salts, carbohydrazide 3,3′-dinitroamino-4,4′-azoxyfurazan (NOF-CBH) and aminoguanidine 3,3′-dinitroamino-4,4′-azoxyfurazan (NOF-AG), were synthesized via metathesis reaction with nitrogen-rich cation (CBH and AG). Their structures were characterized via NMR, IR and elemental analysis. The thermal behaviors of the compounds were studies by TG-DTG. The geometric configuration of NOF and its anion (NOF^{2-}) were compared and studied by quantum chemistry calculations. The detonation performances of NOF-CBH and NOF-AG were predicted. Results show that the initial decomposition temperatures of NOF-CBH and NOF-AG are 144.9 ℃ and 151.6 ℃ respectively, which are higher than 90 ℃ of NOF. The standard molar enthalpy of formation and density are 515.86 kJ · mol^{-1} and 1.82 g · cm^{-3} for NOF-CBH and 815.96 kJ · mol^{-1} and 1.75 g · cm^{-3} for NOF-AG. Their values of calculated detonation velocities are greater than 8500 m · s^{-1}.

Key words: 3,3′-diamino-4,4′-azoxyfurazan(AOF); 3,3′-dinitroamino-4,4′-azoxyfurazan(NOF); energetic salts; thermal behavior; synthesis; quantum chemistry calculation.

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1 Introduction

Furazan is a kind of energetic structure unit with high density, high nitrogen content and oxygen balance[1]. Therefore, the combination of furazan with other energetic functional groups was favorable for maintaining a high level of energetic material in recent years[2-4]. 3, 3′-Dinitroamino-4, 4′-azoxyfurazan (NOF) was first obtained in 2014 through introducing nitramine ($—NH—NO_2$) and azoxy [—N═N(O)—] groups onto furazan backbones by Shreeve et al[5]. The crystal density, calculated detonation velocity, calculated detonation pressure and calculated specific impulse of NOF is 1.96 g · cm^{-3}, 9746 m · s^{-1}, 44.1 GPa and 283 s respectively, whose comprehensive energy performance is at the same proficiency level to CL-20. However the decomposition temperature of NOF is only about 90 ℃, which limits application in secondary explosive and propellant. It is well-known that the strong electron-withdrawing effect of nitro group in nitramine can deprotonate amine (—NH—) to form energetic salts when paired with bases[6-7]. And this is an effective method to improve the thermal stability of NOF.

In this study, NOF was prepared by through nitration 3,3′-diamino-4,4′-azoxyfurazan (AOF). And two new nitrogen-rich energetic salts, carbohydrazidium 3,3′-dinitroamino-4,4′-azoxyfurazan (NOF-CBH) and aminoguanidium 3,3′-dinitroamino-4,4′-azoxyfurazan (NOF-AG), were synthesized from NOF via metathesis reaction with carbohydrazide hydrochloride and aminoguanidine hydrochloride. These compounds were characterized using infrared and elemental analysis as well as multinuclear NMR spectroscopy. The thermal behaviors of compounds were studied by thermogravimetry derivative thermogravimetry (TG-DTG) method. The comparative study of molecular geometry and stability between NOF and its anion (NOF^{2-}) were conducted by quantum chemistry calculation. In addition, the energetic properties of NOF-CBH and NOF-AG were also estimated.

2 Experiment section

2.1 Synthetic route

2.2 Materials and Instrument

All chemical reagents and solvents were obtained from Sigma-Aldrich Inc. or Chengdu Kelong Reagent Company (analytical grade) and were used without further purification. 3,3′-Diamino-4, 4′-azoxyfurazan (AOF) was prepared according to the literature [8] procedure. Infrared spectra were obtained using a Nexus 87 Fourier transform infrared spectrometer (Nicolet USA). Organic elemental composition was analyzed on a Vario EL III elemental analyzer (Elementar Germany). Purity analysis with HPLC was carried out on a LC-20A system equipped with a C18 column (250 mm×4.6 mm, 5 mm, Agela) and a UV detector set at 254 nm (Shimadzu Japan). ^1H NMR (500.13 MHz) and ^{13}C NMR (125.76 MHz) spectra were recorded on a V500 spectrometer (Bruker, Germany). Chemical shifts were reported as a δ value in parts per million and tetramethylsilane was used as the internal standard. ^1H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6.

2.3 Synthesis

2.3.1 3,3′-Dinitroamino-4,4′-azoxyfurazan (NOF)

AOF (2 g, 9.5 mmol) was added slowly to 100% nitric acid (10 mL) and stirred to dissolving completely for 20 minutes at −5 ℃. The resulting mixture was held for an additional 4 h at 0 ℃ and then poured into ice water. The colorless precipitate was filtered, yielding 2.55 g. Its purity was 97.5%. ^1H NMR (DMSO-d_6) δ: 9.85 (s, 2H). ^{13}C NMR

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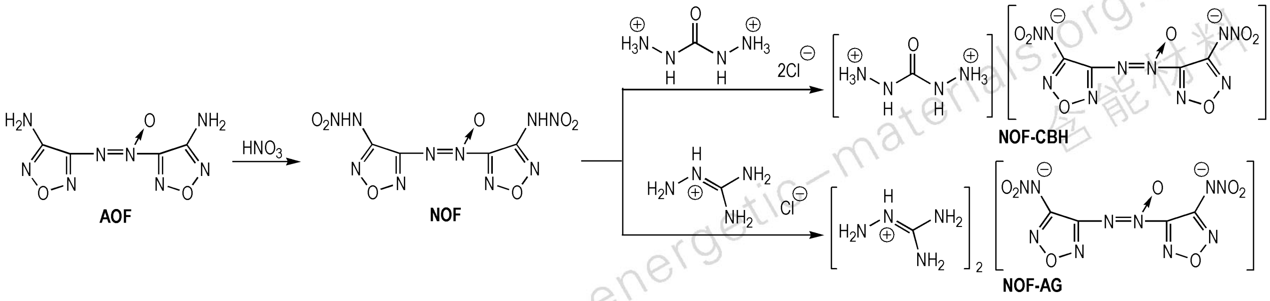
(DMSO-d_6)δ: 155.4, 153.3, 151.1, 148.4. IR (KBr, ν/cm^{-1}): 342 (w), 3393(w), 3279(m), 1620(s), 1562(s), 1499(vs), 1389 (m), 1315 (m), 1230 (m), 1007 (m), 950 (w). Anal. calcd for $C_4H_2N_{10}O_7$: C, 15.90; H, 0.67; N 46.36. found C,15.46; H, 0.70; N, 45.87.



Scheme 1 Synthetic route of NOF-CBH and NOF-AG

2.3.2 Carbohydrazide 3,3′-dinitroamino-4,4′-azoxyfurazan (NOF-CBH)

A solution of NOF (0.6 g,2 mmol) in ethanol (10 mL) was stirred at room temperature while a slight excess of carbohydrazide (0.81 g,5 mmol) was added. After 2 h the yellow precipitate was filtered and air-dried, yielding 0.71 g. Its purity was 98.9%. ^{1}H NMR (DMSO-d_6) δ: 9.73(s, 2H), δ: 3.60 (s, br, 6H). ^{13}C NMR (DMSO-d_6,) δ: 156.9, 155.1, 154.5, 153.9, 151.2. IR (KBr, ν/cm^{-1}): 3525(w), 3493(w), 3315(m), 2966(vw), 2713 (w), 1708 (s), 1663 (w), 1639 (vw), 1614(vw), 1580(w), 1561(w), 1531(w), 1517(w), 1489(m), 1473(m), 1421(s), 1399(s), 1324(vs), 1300(s), 1203 (m), 1053 (m), 1015 (m), 966 (w), 937(m), 896(w), 863(vs), 836(m), 799(vw), 772(vw), 740(vw), 723(m), 668 (w), 641(vw), 591(vw), 567(v), 468(vw), 405(vw). Anal. calcd for $C_5H_8N_{14}O_8 \cdot 5H_2O$: C, 12.45; H, 3.76; N 40.66. found C,12.56; H, 3.78; N, 40.42.

2.3.3 Aminoguanidine 3,3′-dinitroamino-4,4′-azoxyfurazan (NOF-AG)

NOF-AG was prepared according to the method of NOF-CBH. The yellow precipitate was filtered, yielding 0.84 g. Its purity was 99.0%. ^{1}H NMR (DMSO-d_6) δ: 8.58(s, 1H), 7.11(s, 2H), 4.99(s, 4H). ^{13}C NMR (DMSO-d_6) δ: 158.7, 155.1, 153.8, 153.1, 151.1. IR(KBr, ν/cm^{-1}): 3381(m), 3245(w), 3172 (m), 1687 (vs), 1665 (vs), 1560 (m), 1524(m), 1468(s), 1441(vw), 1410(m), 1387(s), 1294(vs), 1177(w), 1073(vw), 1044(m), 015(vw), 982(vw), 950(m), 908(vw), 883 (vw), 872 (vw), 827 (m), 773 (w), 745 (vw), 716(w), 675 (vw), 585 (m), 565 (m), 511(vw), 468(w), 404(vw). Anal (%) calcd for $C_6H_{14}N_{18}O_7 \cdot 2H_2O$: C, 14.82; H, 3.73; N 51.84. found C, 14.95; H, 3.63; N, 50.86.

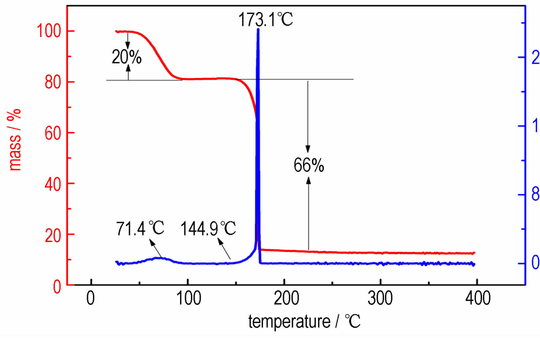
2.4 Thermal decomposition conditions

TG-DTG was conducted on a SDT-Q600 apparatus (TA, USA) under a nitrogen atmosphere at a flow rate of 100 mL · min^{-1}. The sample mass used in test was 0.5 mg and the heating rate was 5 ℃ · min^{-1}. The temperature range was from room temperature to 500 ℃.

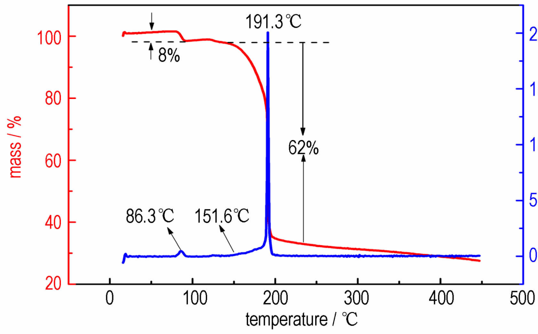
3 Results and discussions

3.1 Thermal Decomposition of NOF-CBH and NOF-AG

The thermal behavior of NOF-CBH and NOF-AG was studied by TG-DTG. As shown in Fig.1, the TG-DTG curves indicate that the thermal behaviors of NOF-CBH and NOF-AG are similar to each other and all can be divided into one endothermic dehydrating crystal water stage and one obvious exothermic decomposition stage at 50–200 ℃. The dehydration process of NOF-CBH occurs at 50–100 ℃ corresponding to a mass loss of about 20%, and the sharp maximum dehydration rate is at 71.4 ℃. The dehydration mass loss is consistent with theoretical value of elemental analysis corresponding to the



a. NOF-CBH



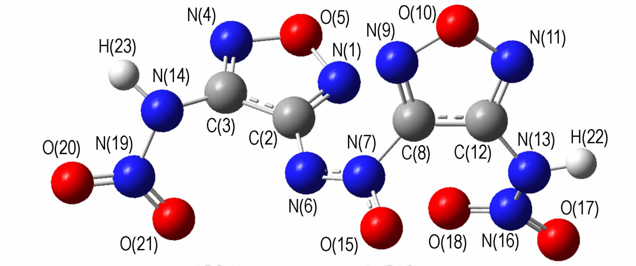
b. NOF-AG

Fig.1 TG-DTG curves of NOF-CBH and NOF-AG loss of 5 mol crystal water molecule. The exothermic decomposition of NOF-CBH starts at 144.9 ℃ with a mass loss of about 66%, and the tiptop temperature of decomposition is 173.1 ℃. The dehydration process range of NOF-AG is from 79 ℃ to 92 ℃, and the whole mass loss of dehydration process is only about 8%. The sharp maximum dehydration rate is at 86.3 ℃. The result agrees well with theoretical value of elemental analysis corresponding to the loss of 2 mol crystal water molecule. The exothermic decomposition of NOF-AG starts at 151.6 ℃ with a mass loss of about 62%, and the tiptop temperature of pyrolysis is 191.3 ℃. The decomposition temperature of NOF-CBH and NOF-AG are above 140 ℃, which can prove that their thermal stabilities are far better than 90 ℃ of NOF.

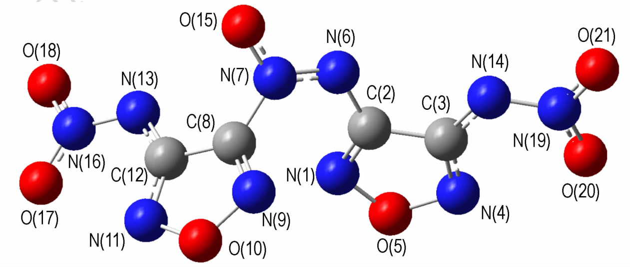
3.2 Optimized molecular geometry of NOF and NOF^{2-}

To gain a better understanding of structures for NOF and its anion (NOF^{2-}), the molecular geometry has been optimized using various ab initio methods including PM3 and B3LYP[9-10], and the most stable molecule conformations are shown in Fig. 2. The optimized structures show that molecule conformations of NOF and NOF^{2-} arevery semblable. The two furazan rings connecting with azoxy are not at the same plane, and the torsion angles (C(3)—C(2)—C(8)—C(12)) are 87.57° and 87.82° ,respectively. In molecule conformation of NOF, the torsion angles between furazan rings and nitramine are 113.12° and 135.71°, and the bond lengths of N—NO$_2$ are 1.43 Å and 1.41 Å. In contrast to molecule conformation of NOF, the furazan ring and nitramine of NOF^{2-} are nearly at the same plane, and the bond lengths of N—NO$_2$ are only 1.35 Å and 1.34 Å, much smaller than that of NOF. The results indicate preliminarily that the conjugate action between furazan ring and nitramine will be strengthened when the deprotonation of NOF is occurred to form NOF^{2-}. So the structure stability of NOF^{2-} is better than that of NOF.

It is significant and objective to further make comparison of the weakest bond order between NOF and NOF^{2-} for evaluating theoretically the stability. Through the bond order calculation, N—NO$_2$ was determined as the weakest bond[11], and the N—NO$_2$ length and order of NOF and NOF^{2-} were listed in Table 1. The two N—NO$_2$ order values of NOF^{2-}(N(13)—N(16) and N(14)—N(19)) are 1.1589 and 1.0910 respectively, which are all greater than those of NOF (0.9833 and 0.9887). The data show that the N—NO$_2$ of NOF^{2-} is stronger than that of NOF. Therefore the structure stability of NOF^{2-} is better than NOF.



a. NOF



b. NOF^{2-}

Fig. 2 The molecular geometry of NOF and its anion (NOF^{2-})

Table 1 The bond length and order of NOF and NOF^{2-}

	bond	length/Å	order
NOF	N(13)—N(16)	1.43	0.9833
	N(14)—N(19)	1.41	0.9887
NOF^{2-}	N(13)—N(16)	1.35	1.1589
	N(14)—N(19)	1.34	1.0910

3.3 The detonation performances of NOF-CBH and NOF-AG

The detonation performances of NOF-CBH and NOF-AG were calculated by Monte-Carlo method[12], Atomization scheme[13] and Kamlet-Jacobs formula[14] based on the optimized molecular geometry, and listed in Table 2. Standard molar enthalpies of formation of NOF-CBH and NOF-AG are 515.86 kJ · mol^{-1} and 815.96 kJ · mol^{-1} respectively, revealing highly positive heat of formation. The calculated densities of NOF-CBH and NOF-AG are 1.82 g · cm^{-3} and 1.75 g · cm^{-3}, respectively. The detonation velocities of NOF-CBH and NOF-AG are all over 8500 m · s^{-1}, revealing that NOF-CBH and NOF-AG have the detonation performance level approaching that of RDX.

Table 2 Calculated performances of NOF-CBH and NOF-AG in comparison to RDX

compound	$\rho^{1)}$/g · cm^{-3}	$\Delta_f H^o(s, M)^{2)}$/kJ · mol^{-1}	$T_d{}^{3)}$/℃	$N^{4)}$/%	$\Omega^{5)}$/%	$D^{6)}$/m · s^{-1}	$p^{7)}$/GPa
NOF-CBH	1.82	515.86	144.9	50	-24.5	8648	33.7
NOF-AG	1.75	815.96	151.6	56	-42.7	8513	32.5
RDX[15]	1.80	85.00	230.0	38	-21.6	8748	34.9

Note: 1) density; 2) standard molar enthalpy of formation; 3) decomposition temperature; 4) nitrogen content; 5) oxygen balance; 6) detonation velocity; 7) detonation pressure.

4 Conclusions

Two new nitrogen-rich energetic salts, NOF-CBH and NOF-AG are synthesized. Their initial decomposition temperatures are 144.9 ℃ and 151.6 ℃ respectively, which are far higher than 90 ℃ of NOF. The structure stability of NOF^{2-} is better than NOF. The standard molar enthalpy of formation, density

and detonation velocity are 515.86 kJ · mol^{-1}, 1.82 g · cm^{-3} and 8648 m · s^{-1} for NOF-CBH and 815.96 kJ · mol^{-1}, 1.75 g · cm^{-3} and 8513 m · s^{-1} for NOF-AG, revealing that they have highly positive heat of formation and the detonation performance level approaching that of RDX.

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3,3′-二硝胺基-4,4′-氧化偶氮呋咱基含能离子盐的合成及性能

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摘 要: 以3,3′-二胺基-4,4′-氧化偶氮呋咱(AOF)为原料,经纯硝酸硝化得到3,3′-二硝胺基-4,4′-氧化偶氮呋咱(NOF)。通过复分解反应与多氮阳离子(碳酰肼(CBH)、氨基胍(AG))结合得到了两种新的含能离子盐—3,3′-二硝胺基-4,4′-氧化偶氮呋咱碳酰肼盐(NOF-CBH)和3,3′-二硝胺基-4,4′-氧化偶氮呋咱氨基胍盐(NOF-AG)。通过^{1}H NMR、^{13}C NMR、IR及元素分析表征了化合物的结构。用TG-DTG研究了化合物的热行为。采用量子化学方法对比研究了NOF及其阴离子NOF^{2-}的几何构型。预估了化合物的爆轰性能。结果表明,NOF-CBH和NOF-AG的初始分解温度分别为144.9,151.6 ℃,高于NOF的90 ℃。NOF-CBH和NOF-AG的标准摩尔生成焓分别为515.86 kJ · mol^{-1}和815.96 kJ · mol^{-1},密度分别为1.82 g · cm^{-3}和1.75 g · cm^{-3},理论爆速均大于8500 m · s^{-1}。

关键词: 3,3′-二胺基-4,4′-氧化偶氮呋咱(AOF); 3,3′-二硝胺基-4,4′-氧化偶氮呋咱(NOF); 含能离子盐; 热行为; 合成; 量子化学
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