Synthesis, crystal structure and properties of aminourea salt of 4,8-dihydrodifurazano[3,4-b,e]pyrazine

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Abstract. To reduce the acidity defect of 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP), a new energetic ionic compound aminourea salt of 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DSDFP) was designed and synthesized with a yield of 72.6%. The structure of target compound was characterized by means of NMR (1H and 13C), IR spectra, elemental analysis and single crystal X-ray diffraction. The thermal stability was tested by DSC and TG method and DSDFP shows good thermal stability with exothermic decomposition peaks in the range of 267.3 °C to 282.3 °C. The impact sensitivity was measured using BAM standard method and the detonation performance was computed by Kamlet-Jacobs equations. Results show that DSDFP exhibits excellent impact sensitivity of greater than 40 J and desirable detonation performance with detonation velocity of 7891 m/s and detonation pressure of 27.1 GPa. These results highlight its great promise of potential candidates for high-performance energetic salt.

1. Introduction

Energetic nitrogen-rich ionic salts, a newly developing branch of energetic materials, have received a surge of attention in the past few years. These high nitrogen energetic materials feature attractive characteristics including high density, insensitivity to external stimuli and environmentally benign decomposition products, which make them prospective and promising candidates for smokeless propellants, gas generators and novel low-sensitive high-energetic explosives[1-4]. The present research for energetic ionic salts concentrates on synthesizing energetic anions and surging for desirable cations. The furazan, triazole, tetrazole, tetrazene and pyrazine ring are effective fragments to construct energetic compounds owing to their inherent high nitrogen content and large positive heats of formation (HOFs) [5-9]. Among the NHEC community, furazanopyrazine derivatives stand out with excellent performance and good stability [10-12].

4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) is one kind of skeleton compound with two furazan rings fused by a pyrazine ring [13,14]. The presence of multiple C–N, N–O and C=N bonds contribute directly to its high enthalpy of formation. Evidently, DFP is a symmetric planar molecule with a high nitrogen content and a surprisingly high density of 2.01 g·cm−3 [15]. However, the acidity defect of DFP has hindered its further application. Fortunately, recent development in energetic ionic salts has significantly enhanced our confidence in solving the problem. Pyrazine ring in furazanopyrazine derivatives is known as a dibasic acid[16], indicating that both hydrogen atoms on the pyrazine ring
are acidic. Therefore, the combination of the furazan with pyrazine ring deprotonates viable anions. Meanwhile, aminourea cation with a high nitrogen content (56%) is often used to design and synthesize energetic ionic salt. In this paper, aminourea salt of 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DSDFP) was prepared via acid-base neutralization and metathesis reactions. The crystal structure, heat of formation (HOF), mechanical sensitivity and detonation performance of DSDFP were studied in detail. This work aims to provide some insights for the design and synthesis of energetic ionic salts.

2. Experimental

2.1. Materials

5,6-dihydroxyiminofurazano[3,4-b]pyrazine was prepared according to literature[17]. Other chemicals were analytical pure and used as received.

2.2. Synthesis

The synthetic pathway of DSDFP was shown as follows:

![Synthetic route of DSDFP](image)

**Figure 1.** Synthetic route of DSDFP.

2.2.1. 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP). To a solution of urea (5.9 g, 97.8 mmol) in water (45 mL) was added DOFP (6.0 g, 32.6 mmol) under stirring at below 25 °C. The mixture was then heated to 120 °C and refluxed for 24 h. Once the reaction was completed, the reaction mixture was cooled to room temperature, and the solid formed was filtered and washed with water and gave crude DFP. Recrystallization from water gave pure DFP. Yield: 75.3 %; mp 279.1 °C. 1H NMR (DMSO-d6, 500 MHz), δ: 8.71 (s, 2H, NH); 13C NMR (DMSO-d6, 125 MHz), δ: 149.16; IR (KBr) cm⁻¹: 3278 (N–H), 1588 (C=N), 1535, 1429, 1320, 1005 (furazan ring), 800; Anal. for C8H8N2O2 (mol. wt. 166.10): Calcd: C 28.92, N 50.60, H 1.21; Found: C 28.95, N 50.41, H 1.21.

2.2.2 Aminourea 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DSDFP). To a solution of DFP (0.415 g, 2.5 mmol) in methanol (7.5 mL) was added a solution of potassium hydroxide (0.292 g, 5.2 mmol) in water (5.0 mL) dropwise and stirred for 30 min. Then semicarbazide hydrochloride (0.558 g, 5.0 mmol) was added to the mixture solution and stirred for 2.5 h. After completion of the reaction, the mixture was filtered and washed with methanol and cold water and gave DSDFP. Yield: 72.6 %; mp 173.6 °C. 1H NMR(DMSO-d6, 500 MHz), δ: 5.80 (s, 2H, NH2), 7.12 (s, NH); 7.28 (s, NH); 8.18 (s, 3H, NH3⁺); 13C NMR(DMSO-d6, 125 MHz), δ: 147.03, 155.96, 161.61; IR(KBr, cm⁻¹), ν: 3366, 3338(–NH2), 3465(–NH), 1627(C=O), 1559(–N=N), 1428, 1375, 1176, 1008(furazan ring), 933, 819, 737; Anal. for C17H16N4O3 (mol. wt. 241.17): Calcd: C 24.90, N 52.27, H 2.93; Found: C 24.19, N 52.15, H 2.91.

2.3. Determination of performance

The thermal behavior of DSDFP was observed from a differential scanning calorimeter (TA 2950) at a flow rate of 50 mL/min. About 0.6 mg sample was sealed in aluminum pans for DSC. Infrared spectra was obtained from KBr pellets on a Nicolet NEXUS870 Infrared spectrometer in the range of 4000 ~ 400 cm⁻¹. Elemental analysis was performed on a Vario EL-III elementary analysis instrument. The
impact sensitivity was determined by BFH-10 falling Hammer apparatus, applying BAM standard method[18] using a 2 kg drop weight. The friction sensitivity was determined using FSKM-10 apparatus. The sample used for each test is about 20 mg.

2.4. Crystallographic measurements
The single crystal of DSDFP was obtained from water and X-ray diffraction data was collected with a Bruker SMART APEX CCD II detector (graphite-monochromated, Mo-Ka radiation). During the data collection the temperature was kept at 296 K. 14,718 diffraction data were collected and 5032 were unique with the \( R \text{(int)} = 0.0148 \) in the theta range of 1.68\(^\circ\) ~ 24.55\(^\circ\). The full-matrix least-squares refinement on \( F^2 \) included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The crystal structure was solved by direct method of SHELXS[19], structure solution program using direct method and refined with SHELXL[20].

3. Results and Discussion

3.1. Single crystal X-ray diffraction
The crystal structure of DSDFP was identified by single crystal X-ray diffraction and the crystallographic data of DSDFP are presented in Table 1. Selected bond lengths and bond angles of DSDFP have been listed in Table 2. It confirms that DSDFP crystal belongs to monoclinic system with \( P2_1/n \) group and the cell parameters \( a = 11.1096(16) \text{ Å} \), \( b = 4.8013(7) \text{ Å} \), \( c = 12.6016(17) \text{ Å} \) and \( \alpha = 90^\circ \), \( \beta = 108.509(2)^\circ \), \( \gamma = 90^\circ \). From Figure 2, it can be seen that the crystal asymmetric unit consists of one 4,8-dihydrodifurazano[3,4-\(b\),e]pyrazine and one aminourea molecule. The C–N, C=N and C–C bonds within the difurazano[3,4-\(b\),e]pyrazine ring are all in the range of formal C–N and C–C single and double bonds (C–N: 1.48 Å, 1.27 Å; C–C: 1.53 Å, 1.32 Å). The transfer of the proton from pyrazine ring to amine was confirmed by the crystal data. It could be seen from Figure 3 that the two furazan rings and pyrazine ring in the anion is a planar structure due to electron conjugation effect. The 3D network of the structure is formed further by the hydrogen bonding interactions between aminourea molecules and adjacent difurazano[3,4-\(b\),e]pyrazine layers, which are beneficial to the enhancement of thermal stability of DSDFP.

| Table 1. Crystallographic data of DSDFP. |
|---------------------------------------------------------------|
| **Empirical formula** | C\(_2\)H\(_6\)N\(_2\)O\(_3\) |
| **Formula weight** | 241.17 |
| **Crystal system, space group** | Monoclinic, \( P2_1/n \) |
| \( a(\text{Å}) \) | 11.1096(16) |
| \( b(\text{Å}) \) | 4.8013(7) |
| \( c(\text{Å}) \) | 12.6016(17) |
| \( \alpha(\degree) \) | 90 |
| \( \beta(\degree) \) | 108.509(2) |
| \( \gamma(\degree) \) | 90 |
| **Volume(Å\(^3\))** | 637.41(16) |
| **Density(g/cm\(^3\))** | 1.648 |
| **Z** | 2 |
| **\( F(000) \)** | 328 |
| **GOF** | 1.077 |
| **Final \( R \) indices\( (I>2\sigma(I)) \)** | \( R_1 = 0.0390 \), \( wR_2 = 0.1008 \) |
| **\( R \) indices(all data)** | \( R_1 = 0.0472 \), \( wR_2 = 0.1083 \) |
Table 2. Bond lengths and angles of DSDFP.

| Bond length(Å) | Bond angle(°) |
|----------------|---------------|
| O(3)–C(5)     | 1.251(18)     | N(5)–O(2)–N(6) | 110.75(12) |
| O(2)–N(6)     | 1.406(18)     | C(5)–N(8)–N(9) | 120.70(14) |
| O(2)–N(5)     | 1.401(18)     | C(4)–N(4)–C(3) | 115.25(13) |
| N(8)–N(9)     | 1.407(18)     | C(3)–N(6)–O(2) | 104.67(12) |
| N(8)–C(5)     | 1.338(19)     | C(4)–N(5)–O(2) | 104.80(13) |
| N(4)–C(3)     | 1.369(2)      | O(3)–C(5)–N(8) | 118.69(15) |
| N(4)–C(4)     | 1.365(2)      | O(3)–C(5)–N(7) | 123.02(14) |
| N(7)–C(5)     | 1.326(2)      | N(7)–C(5)–N(8) | 118.30(14) |
| O(3)–C(5)     | 1.495(2)      | N(6)–N(1)–C(5) | 114.89(14) |
| N(6)–O(2)     | 1.406(18)     | N(4)–C(3)–C(4) | 122.52(15) |
| N(6)–C(3)     | 1.290(2)      | N(6)–C(3)–N(4) | 127.61(14) |
| N(5)–C(4)     | 1.289(2)      | N(6)–N(1)–C(5) | 127.30(2)  |
| C(3)–C(4)     | 1.433(2)      | N(6)–C(3)–C(4) | 109.86(15) |
| N(8)–H(8)     | 0.860         | N(4)–C(4)–C(3) | 122.23(14) |
| N(9)–H(9A)    | 0.869         | N(5)–C(4)–N(4) | 127.82(14) |

Figure 2. The structure of DSDFP with thermal ellipsoids at 30% probability.

Figure 3. The packing structure of DSDFP.

3.2. Thermal behavior

The thermal behavior of DSDFP is determined by differential scanning calorimetry (DSC) and thermogravimetry (TG) measurements at a heating rate of 10 °C/min and its DSC and TG curves are presented in Figure 4 and Figure 5. With multiple functional groups in the structure, the
decomposition process of DSDFP is complex. It can be seen from Figure 4 that the first endothermic peak appears at 79.8 °C, which could be assigned to the decomposition of water in the molecule. The melting point of DSDFP is 173.6 °C. One can observe that there are two exothermic peaks at 267.3 °C and 282.3 °C, respectively. From Figure 5, it could be seen that there are four main continuous decomposition steps. The first mass loss process ended at 79.3 °C with residue mass of 95.11%, corresponding to the decomposition of water molecule. The second mass loss process ended at 212.5 °C with residue mass of 87.08%, which may be caused by melting sublimation loss. The next two mass loss process ended at 334.6 °C with residue mass of 38.78%. The heterocycle delocalized conjugate system contributes to the improvement of the thermal stability of DSDFP.

![Figure 4. DSC curve of DSDFP.](image1)

![Figure 5. TG curve of DSDFP.](image2)

3.3. Mechanical sensitivity
The impact and friction sensitivity of DSDFP were tested according to BAM standard method. The impact sensitivity of DSDFP is more than 40 J and the friction sensitivity is more than 360 N, indicating that DSDFP is a quite insensitive energetic compound, which may be attributed to the extensive hydrogen bonding interactions between cation and anion after salt formation.

3.4. Detonation performance
The heat of formation (HOF) of DSDFP was predicted on the basis of Born-Haber energy cycle and atomization reactions. The detonation properties including the detonation velocity (D) and pressure (P) were predicted by the empirical Kamlet-Jacobs equations based on the density and calculated HOF. It is found that the HOF of DSDFP is 648.94 kJ/mol, owing to its high nitrogen content and multiple N=N, C=N and N=N bonds in the molecule. DSDFP exhibits better detonation performance than that of TNT with detonation velocity of 7891 m/s and detonation pressure of 27.1 GPa.

4. Conclusion
(1) The aminourea salt of 4,8-dihydrodifurazano[3,4-b,e]pyrazine was synthesized and characterized by NMR, IR and elemental analysis.
(2) The single crystal X-ray diffraction analysis confirms that DSDFP crystal belongs to monoclinic system with P21/n group. The extensive intramolecular and intermolecular hydrogen bonding interactions between cation and anion play a vital role in molecular density, thermal stability and sensitivity.
(3) DSDFP shows good thermal stability with thermal decomposition temperature between 260 ~ 285 °C, low sensitivity (40 J) and excellent detonation performance.
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