Synthesis, Crystal structure and Properties of Aminourea Salt of 4,8-Dihydrodifurazano[3,4-b,e]pyrazine

B H Duan, N Liu, B Z Wang and X M Lu

Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

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. Among the NHEC community, furazanopyrazine derivatives stand out with excellent performance and good stability.

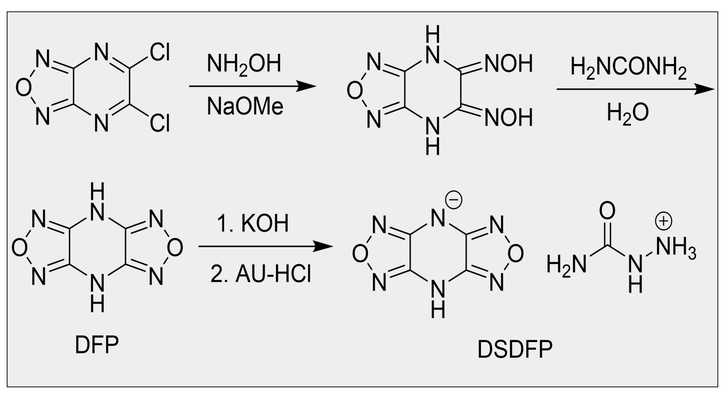
4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP) is a symmetric planar molecule with a high nitrogen content and a surprisingly high density of 2.01 $g \cdot cm^{-3}$. However, the acidity defect of DFP has hindered its further application.

Aim

Pyrazine ring in furazanopyrazine derivatives is known as a dibasic acid, 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. This work aims to provide some insights for the design and synthesis of energetic ionic salts.

Method

- Synthesis of 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DFP)
- Synthesis of aminourea 4,8-dihydrodifurazano[3,4-b,e]pyrazine (DSDFP)
- Determination of performance
  DSC, TG, IR, Elemental Analysis, Impact sensitivity, Friction sensitivity
- Crystallographic measurements



Synthetic route of DSDFP

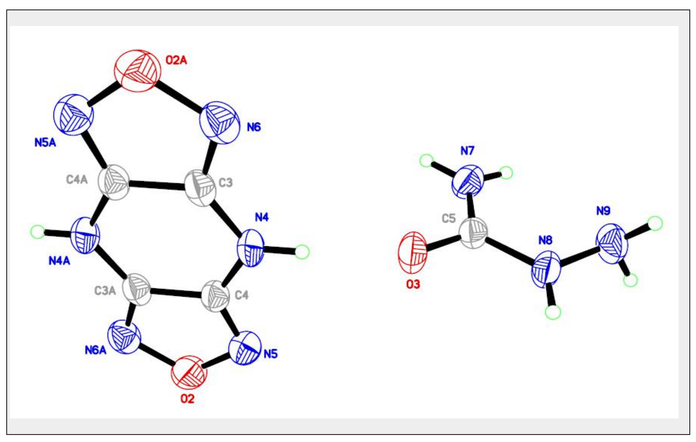
Results

Single crystal X-ray diffraction

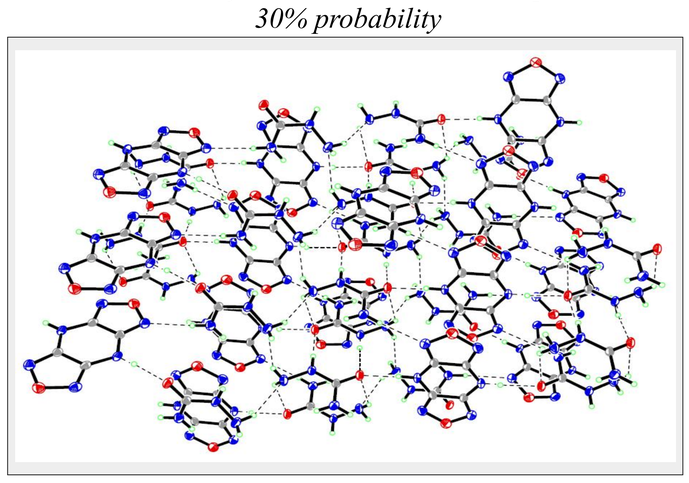
DSDFP crystal belongs to monoclinic system with P21/n group and the cell parameters a = 11.1096(16) Å, b = 4.8013(7) Å, c = 12.6016(17) Å and α = 90°, β = 108.509(2)°, γ = 90°. The crystal asymmetric unit consists of one 4,8-dihydrodifurazano[3,4-b,e]pyrazine and one aminourea molecule.

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 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.



The structure of DSDFP with thermal ellipsoids at 30% probability



The packing structure of DSDFP

Mechanical sensitivity

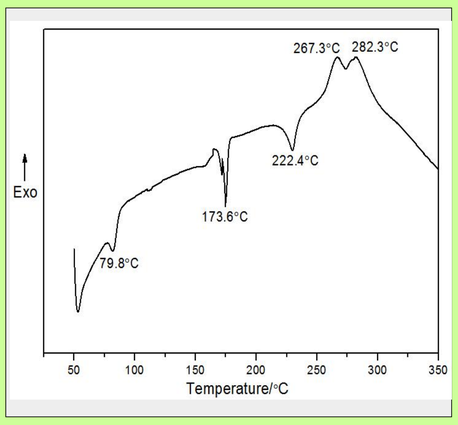
The impact sensitivity of DSDFP is more than 40 J and the friction sensitivity is more than 360 N, indicating that DSDFP is a quite insensitive energetic compound.

Detonation performance

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.

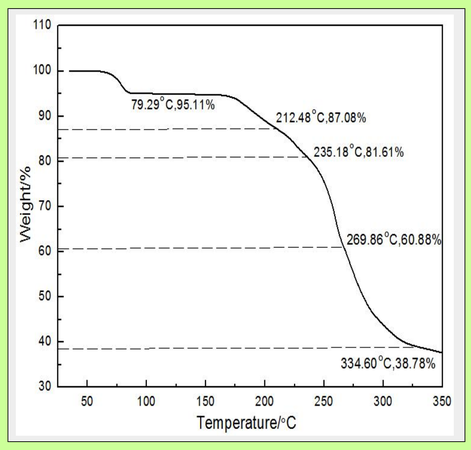
Thermal behavior

With multiple functional groups in the structure, the decomposition process of DSDFP is complex. The first endothermic peak appears at 79.8 ºC, which could be assigned to the decomposition of water in the molecule. The melting point of DSDFP is 173.6 ºC. One can observe that there are two exothermic peaks at 267.3 ºC and 282.3 ºC, respectively.



DSC curve of DSDFP

There are four main continuous decomposition steps. The first mass loss process ended at 79.3 ºC with residue mass of 95.11%, corresponding to the decomposition of water molecule. The second mass loss process ended at 212.5 ºC with residue mass of 87.08%, which may be caused by melting sublimation loss. The next two mass loss process ended at 334.6 ºC with residue mass of 38.78%. The heterocycle delocalized conjugate system contributes to the improvement of the thermal stability of DSDFP.



TG curve of DSDFP

Conclusion

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

References

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