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# A Novel Unsymmetrical Furazan Ether 3-Azido-3'-nitrodifurazanyl Ether(ANFO): Synthesis and Quantum Chemistry Studies

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**Abstract:** Using 3-azido-4-aminofurazan (AAF) as starting material, 3-azido-3'-nitrodifurazanyl ether (ANFO) was designed and synthesized for the first time via Caro's acid oxidation, hydrolysis and intermolecular etherification sequence with a total yield of 32.7%, and the structures of ANFO and intermediates were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, MS and elementary analysis. The oxidation method for 3-azido-4-nitrofurazan (ANF) was improved from hydrogen peroxide (50%), sulfuric acid and sodium tungstate as new oxidation system with a yield of 75.1%. The optimal conditions of oxidation and etherification were discussed, and the best conditions were obtained as follows:  $n(\text{H}_2\text{O}_2):n(\text{H}_2\text{SO}_4)$  is 1:1.5 for oxidation system. The reaction temperature is at 30 °C for etherification system. The structure of ANFO was optimized by B3LYP/6-31G(d, p) method, the thermodynamic properties of ANFO at different temperatures were calculated on the basis of vibration analysis. The physico-chemical properties and detonation performances of ANFO were studied by DSC measurement and the density functional theory (DFT) method. The calculated density, melting point, detonation velocity, detonation pressure, impact sensitivity ( $H_{50}$ ) and heat of detonation are  $1.85\text{ g}\cdot\text{cm}^{-3}$ ,  $182.3\text{ }^\circ\text{C}(\text{dec.})$ ,  $8660\text{ m}\cdot\text{s}^{-1}$ ,  $33.81\text{ GPa}$ ,  $35.2\text{ cm}$  and  $6725\text{ kJ}\cdot\text{kg}^{-1}$ , respectively.

**Key words:** synthesis; 3-azido-3'-nitrodifurazanyl ether(ANFO); unsymmetrical furazan ether; performance

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## 1 Introduction

Furazan ether energetic compounds have become an important research direction in recent years as high energetic explosives and plasticizers due to their low melting point and good detonation performances<sup>[1-4]</sup>. Linear furazan ether and annular furazan ether are two typical furazan ether compounds. The former mainly includes 3, 3'-dinitrodifurazanyl ether (FOF-1)<sup>[5-6]</sup>, 3, 3'-dicyanodifurazanyl ether

(FOF-2)<sup>[7]</sup>, 3, 4-bis (3-nitro furazan-4-oxy) furazan (FOF-11)<sup>[8]</sup>, 3, 4-bis (3-cyanofurazan-4-oxy) furazan (FOF-12)<sup>[9-10]</sup>, and 3, 3'-bis (fluoro dinitromethyl) difurazanylether (FOF-13)<sup>[11]</sup>, while the latter mainly includes bifurazano [3, 4-b: 3', 4'-f] furoxano [3'', 4''-d] oxacyclo heptatriene (BFFO)<sup>[12]</sup>, and trifurazanooxacycloheptatriene (TFO)<sup>[13]</sup>. Most of these furazan ether compounds are symmetry structure due to the convenience in design and synthesis. From the synthetic point of view, the construction of unsymmetrical furazan ethers is much more difficult and there were few reports for the synthesis and properties of unsymmetrical furazan ether compounds. However, unsymmetrical furazan ethers usually exhibit good performances such as high density, good thermal stability and detonation performances<sup>[14]</sup>. In this paper, using 3-azido-4-aminofurazan (AAF) as starting material, a novel energetic compound 3-azido-3'-nitrodifurazanyl ether (ANFO) with a unsymmetrical structure was designed

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and synthesized for the first time. The structures of all intermediates and target compound were characterized by FTIR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS and elemental analyses. The key intermediate 3-azido-4-nitrofurazan (ANF) was synthesized by a new oxidation system, and the reaction conditions for the oxidation and etherification were optimized. The physicochemical properties and detonation performances of ANFO were studied by with density functional theory (DFT) method.

## 2 Experimental

### 2.1 Materials and Measurements

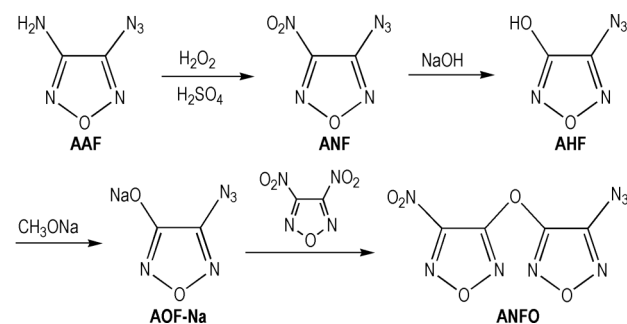
3, 4-Diaminofurazan was purchased from commercial sources and recrystallized from water. 3, 4-Dinitrofurazan<sup>[16]</sup> and 3-azido-4-aminofurazan<sup>[17]</sup> were prepared according to the references. Acetonitrile was chromatographical grade. Other chemicals were obtained from commercial sources and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were obtained in DMSO- $d_6$  on a Bruker AV500 NMR spectrometer. Infrared spectra were obtained from KBr pellets on a Nicolet NEXUS870 infrared spectrometer in the range of 4000–400  $\text{cm}^{-1}$ . Elemental analyses of C, H and N were performed on a VARI-EL-3 elementary analysis instrument. Differential scanning calorimetry (DSC) were carried out in a platinum sample container using a Q-2000 at a heating rate of 2.5  $^\circ\text{C}\cdot\text{min}^{-1}$ .

### 2.2 Synthesis and Characterization

Using 3-azido-4-aminofurazan (AAF) as the starting materials, our target compound ANFO was synthesized via Caro's acid oxidation, hydrolysis and intermolecular etherification, outlined in Scheme 1.

#### 2.2.1 Synthesis of 3-Azido-4-nitrofurazan (ANF)

At 0  $^\circ\text{C}$ , to a solution of sodium tungstate (1.65 g, 5.0 mmol) and 50% hydrogen peroxide (15 g, 220 mmol), 98% sulfuric acid (33 g, 330 mmol) was added dropwise under stirring. After the reaction of 30 min, 3-azido-4-aminofurazan (1 g, 8 mmol) was added in batches at 15  $^\circ\text{C}$ , and the reaction was carried out at 30  $^\circ\text{C}$  for 4 h. Then the mixture was



**Scheme 1** Synthetic route for the title compound ANFO

poured into ice-water, and extracted with  $\text{CH}_2\text{Cl}_2$  (4 $\times$ 50 mL). The combined organic phase was dried by anhydrous magnesium sulfate, filtered and dried by vacuum to give 0.93 g yellow liquid with a yield of 75.1% and a purity of 98.6% (HPLC). IR (KBr,  $\nu/\text{cm}^{-1}$ ): 2150, 1536, 1485, 1378, 1355, 1181, 1021;  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz)  $\delta$ : 155.495, 149.730; Anal. calcd for  $\text{C}_2\text{N}_6\text{O}_3$  (%): C 15.39, N 53.85; found C 15.74, N 53.44; GC-MS  $m/z$ (%): 156( $\text{M}^+$ ).

#### 2.2.2 Synthesis of 3-Azido-4-hydroxyfurazan (AHF)

To a solution of 3-azido-4-nitrofurazan (1.0 g, 6.5 mmol) in THF (40 mL), a solution of potassium hydroxide (5 g, 25 mmol) in water (15 mL) was added dropwise at room temperature under stirring. The reaction mixture was heated to 40  $^\circ\text{C}$  for 2 h. Then it was poured into water (60 mL), and acidified with 36% concentrated hydrochloric acid and extracted with  $\text{Et}_2\text{O}$  (4 $\times$ 50 mL). The combined organic phase was dried by magnesium sulfate, filtered and the solvent was removed, 0.74 g white solid was obtained with a yield of 91.5%. IR (KBr,  $\nu/\text{cm}^{-1}$ ): 3424, 2150, 1605, 1561, 1371, 1268, 1166, 1006, 864;  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz)  $\delta$ : 145.920, 158.441;  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz)  $\delta$ : 13.5203; Anal. Calcd. for  $\text{C}_2\text{HN}_5\text{O}_2$  (%): C 18.91, H 0.79, N 55.12; found C 18.74, H 0.73, N 54.98%.

#### 2.2.3 Synthesis of Sodium 3-Azidofurazan-4-oxide (AOF-Na)

Methanol (8 mL) solution of sodium methylate (1.40 g, 7.77 mmol) was added dropwise to solution of 3-azido-4-hydroxyfurazan (1.0 g, 7.80 mmol) in 40 mL of ether. The mixture was stirred at room temperature for 1 h. The precipitate was collected,

and washed with MeOH and Et<sub>2</sub>O to get 1.07 g pale yellow solid with a yield of 91.3%. IR(KBr,  $\nu$ /cm<sup>-1</sup>): 2160, 1693, 1581, 1543, 1449, 1385, 1014, 863; Anal. Calcd. for C<sub>2</sub>N<sub>5</sub>NaO<sub>2</sub>(%): C 16.11, N 46.98%; found (%) C 16.44, N 46.63%. (CAUTIONS: This compound is high explosive and may be sensitive to shock or heating and must be handled with appropriate precautions).

#### 2.2.4 Synthesis of 3-Azido-3'-nitrodifurazanyl Ether (ANFO)

To a solution of 3-azido-4-hydroxyfurazan sodium salt(0.95 g, 6.4 mmol) in absolute MeCN (20 mL), a solution of 3, 4-dinitrofurazan (1.0 g, 6.3 mmol) in absolute MeCN was added at 30 °C under an atmosphere of N<sub>2</sub>. The reaction mixture was stirred at this temperature for 7 h, diluted with water (50 mL), extracted with CH<sub>2</sub>Cl<sub>2</sub> (4×50 mL). dried over anhydrous magnesium sulfate, filtered and the solvent was evaporated. 0.78 g yellow liquid was afford by silica gel flash chromatography using pentroleum/ethyl acetate (10:1) as eluent with a yield of 52.1%. IR (KBr,  $\nu$ /cm<sup>-1</sup>): 2146, 1594, 1532, 1487, 1357, 1292, 1197, 1034, 840; <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 146.729, 152.936, 154.980, 155.099; Anal. Calcd. for C<sub>4</sub>N<sub>8</sub>O<sub>5</sub> (%): C 20.01, N 46.67%; found C 20.42, N 46.19%; MS (EI) *m/z* (%): 240(M<sup>+</sup>).

#### 2.2.5 Quantum Chemistry Calculation

B3LYP method maintains the advantages of the ab initio method, and the structure and properties of the molecule calculated at the level of 6-31G(d, p) are close to the experimental values<sup>[18-20]</sup>. In the present work, B3LYP / 6-31G(d, p) method on Gaussian09<sup>[21-22]</sup> package was carried out to optimize the structure of ANFO, and the minimum value on the potential energy surface was obtained. The vibrational frequencies, IR spectra and thermodynamic prop-

erties in the range of 273 K to 1000 K were further obtained.

### 3 Results and Discussion

#### 3.1 Improved Synthetic Method for ANF

The synthesis of 3-azido-4-nitrofurazan (ANF) was reported for the first time in 1996<sup>[23]</sup>. The oxidation of amino group was carried out by N<sub>2</sub>O<sub>5</sub>/acetonitrile system, and ANF was extracted with dichloromethane with a yield of 63%. However, N<sub>2</sub>O<sub>5</sub> should be prepared from industrial nitric acid before each reaction because it is not stable in storage. Therefore the using of N<sub>2</sub>O<sub>5</sub> will increase the experimental steps and danger even it can be applied as efficient oxidant in the above method.

In 2014, Lin reported another oxidation process<sup>[24]</sup>. The 3-azido-4-aminofurazan was added into the oxidation system, which was composed of hydrogen peroxide(30%), sodium tungstate and methane-sulfonic acid. The product ANF was extracted by ethyl acetate, and further purified by silica gel chromatograph with a yield of only 25%.

In this paper, the synthetic process of ANF was improved by using a new oxidation system, which was composed of hydrogen peroxide(50%), sodium tungstate and sulfuric acid. The yield of ANF could reach up to 75.1% and the purity of the crude product is more than 98%.

Compared with the reported methods, our synthetic process of ANF is simple and convenient with higher yield. The crude product could be applied in the next step without further purification.

#### 3.2 The Optimization of Synthetic Condition for ANF

The effects of molar ratio of concentrated sulfuric acid and hydrogen peroxide on the yield of ANF was investigated at 30°C by reaction for 4 h, and the

**Table 1** Comparison of three methods for synthesis of ANF

oxidation method	oxidants	time / h	temperature / °C	purification method
Ref.[23]	N <sub>2</sub> O <sub>5</sub>	16	0	silica gel flash chromatography
Ref.[24]	30% H <sub>2</sub> O <sub>2</sub> /Na <sub>2</sub> WO <sub>4</sub> /CH <sub>3</sub> SO <sub>3</sub> H	2	20-22	silica gel flash chromatography
this paper	50% H <sub>2</sub> O <sub>2</sub> /Na <sub>2</sub> WO <sub>4</sub> /H <sub>2</sub> SO <sub>4</sub>	4	30	without purification

results are summarized in Table 2.

**Table 2** Effect of molar ratio of concentrated sulfuric acid and hydrogen peroxide for ANF

H <sub>2</sub> SO <sub>4</sub> :H <sub>2</sub> O <sub>2</sub> (n:n)	yield / %	purity / %
1:1	71.2	98.1
1.5:1	75.1	98.5
2:1	70.6	98.2

It can be seen from Table 2 that the yield of ANFO was enhanced with increasing the amount of H<sub>2</sub>SO<sub>4</sub> under a certain quantity of hydrogen peroxide. When the molar ratio of H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub> was 1.5:1, the maximum yield can be obtained as 75.1%, while the yield of ANFO decreased by adding more excessive H<sub>2</sub>SO<sub>4</sub>. The reason may be ascribed to that oxidation was hampered because of the low reactivity of the amino group bound to the furazan ring which possesses a considerable electron-withdrawing effect, similar to that of the dinitrophenyl group. Usually, by enhancing the content of H<sub>2</sub>SO<sub>4</sub>, the oxidative ability of H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub> mixtures increases, which could convert amino compound AAF to nitro compound ANF easily. However, AAF was protonated just in very acid media, corresponding to a decrease in their capacity to be oxidized to ANF<sup>[25]</sup>. The decrease of product yield is probably attributed to the formation of —NH<sub>3</sub><sup>+</sup> in strong acid media.

### 3.3 Etherification Reaction Conditions of ANFO

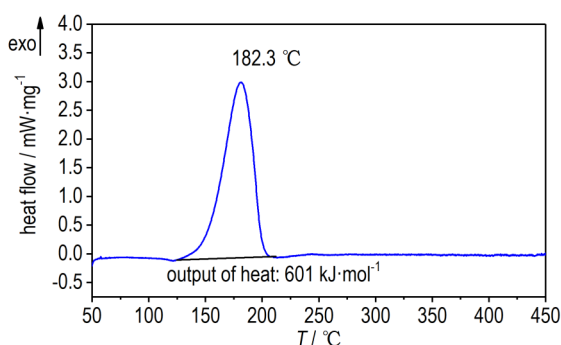
The effect of temperature on the yield of ANFO was studied and the result is listed in Table 3. It was found that the yield of ANFO was improved with the increasing of temperature. When the temperature was 30 °C, and the maximum yield can be reached up to 52.1% with the purity of 98.5%. Because bimolecular etherification reaction of 3, 4-dinitrofurazan run faster than the etherification reaction between 3, 4-dinitrofurazan and sodium 3-azido furazan-4-oxide at higher temperature<sup>[26]</sup>, continued attempts to obtain more ANFO samples by further increasing temperature were failed. In a word, the control of the appropriate temperature is essential for the synthesis of ANFO.

**Table 3** Influence of the reaction temperature on etherification reaction

temperature / °C	yield / %	purity / %
20	17.2	80.7
25	46.8	95.4
30	52.1	98.5
35	51.6	98.1
40	46.4	95.6
50	31.0	83.3

### 3.4 Thermal Behavior of ANFO

The thermal stability of ANFO was investigated using differential scanning calorimetry (DSC) under the conditions of heating rate of 2.5 °C·min<sup>-1</sup> and pressure of 1.0 MPa. In the DSC curve (Fig.1), thermal decomposition started at 122.0 °C and an exothermic peak temperature is at 182.3 °C. There is no endothermic peak in the DSC curve, which indicates that ANFO melts with concomitant decomposition under the heating condition. From the integral data in Fig.1, it can be seen that the output of heat of ANFO was 601 kJ·mol<sup>-1</sup>, which was almost same as the calculated standard molar enthalpy of formation of 630.0 kJ·mol<sup>-1</sup> (The calculated enthalpy of formation of ANFO can be seen from 3.11).

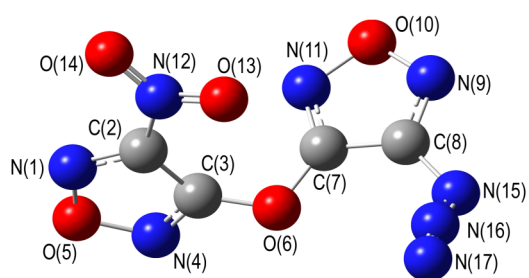


**Fig.1** DSC curve of ANFO at high pressure

### 3.5 Geometric Configuration

The optimized geometric configuration of ANFO was shown in Fig.2, The bond lengths, bond angles and dihedral angles were shown in Table 4. The geometries have been optimized based on the true local energy minima on the potential energy surface without imaginary frequencies.

It can be seen from Fig.2 and Table 4, the furazan ring attached to the nitro group is almost copla-



**Fig. 2** The geometric configuration of ANFO optimized at B3LYP/6-31G(d,p) level

nar with the nitro group (dihedral angle  $-178.414^\circ$ ). The furazan ring attached to the azido group is almost coplanar with the azido group (dihedral angle  $-178.975^\circ$ ), the dihedral angle between two furazan rings is about  $70^\circ$ . It is due to a conjugated system on each furazan ring, which counterpoises the C—C and C—N bond length (1.299 to 1.430 Å).

### 3.6 Atomic Charge

The charges of ANFO atoms are listed in Table 5. It can be seen from Table 5 and Fig.2 that the C(3) and C(7) atoms attached to the ether oxygen atom in the furazan ring have more positive charges due to the strong electronegativity of the O atom, The C(8) atom connected to the azido group on the furazan ring has a larger positive charge than the C(2) atom attached to the nitro group. It indicates that the electron withdrawing ability of the azido group is stronger than that of the nitro group.

### 3.7 Molecular Orbital

The molecular orbital theory presents that the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and their nearby molecular orbital have the greatest influ-

**Table 4** The geometric parameters of ANFO optimized at B3LYP/6-31G(d,p) level

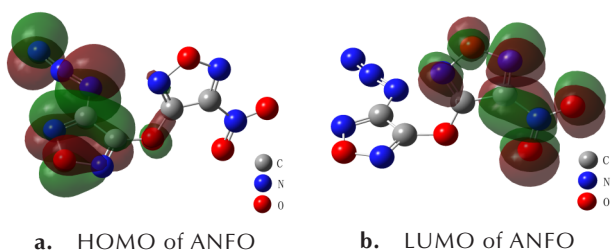
bond	length / Å	bond	angle / ( $^\circ$ )	bond	dihedral angle / ( $^\circ$ )
N(1)—C(2)	1.305	N(1)—C(2)—C(3)	109.123	N(1)—C(2)—C(3)—N(4)	-0.118
N(1)—O(5)	1.353	C(2)—C(3)—N(4)	108.687	O(5)—N(4)—C(3)—C(2)	0.248
C(2)—C(3)	1.429	C(3)—N(4)—O(5)	104.589	O(5)—N(1)—C(2)—C(3)	-0.074
C(3)—N(4)	1.306	N(1)—O(5)—N(4)	112.361	C(3)—N(4)—O(5)—N(1)	-0.310
N(4)—O(5)	1.385	C(2)—C(3)—O(6)	126.212	C(2)—C(3)—O(6)—C(7)	-173.818
C(3)—O(6)	1.343	C(3)—O(6)—C(7)	117.573	N(4)—C(3)—O(6)—C(7)	7.017
O(6)—C(7)	1.368	O(6)—C(7)—C(8)	128.381	C(3)—O(6)—C(7)—C(8)	70.022
C(7)—C(8)	1.430	C(7)—C(8)—N(9)	108.179	O(6)—C(7)—C(8)—N(9)	174.598
C(8)—N(9)	1.310	C(8)—N(9)—O(10)	104.976	C(7)—C(8)—N(9)—O(10)	-0.254
N(9)—O(10)	1.384	C(8)—C(7)—N(11)	109.913	C(8)—N(9)—O(10)—N(11)	0.2047
C(7)—N(11)	1.299	N(9)—O(10)—N(11)	112.067	N(9)—O(10)—N(11)—C(7)	-0.058
O(10)—N(11)	1.367	C(7)—N(11)—O(10)	104.862	O(6)—C(7)—N(11)—O(10)	-174.921
C(2)—N(12)	1.456	C(7)—C(8)—N(15)	124.258	C(7)—C(8)—N(15)—N(16)	-178.975
N(12)—O(13)	1.228	C(8)—N(15)—N(16)	116.722	C(8)—N(15)—N(16)—N(17)	-0.532
N(12)—O(14)	1.222	N(15)—N(16)—N(17)	171.338	N(1)—C(2)—N(12)—O(13)	-178.414
C(8)—N(15)	1.386	C(2)—N(12)—O(14)	117.446		
N(15)—N(16)	1.250				
N(16)—N(17)	1.133				

**Table 5** The atomic charges of ANFO

atom	charge	atom	charge	atom	charge	atom	charge
N(1)	-0.125	C(2)	0.470	C(3)	0.569	N(4)	-0.173
O(5)	-0.181	O(6)	-0.516	C(7)	0.487	C(8)	0.549
N(9)	-0.212	O(10)	-0.194	N(11)	-0.138	N(12)	0.370
O(13)	-0.363	O(14)	-0.350	N(15)	-0.469	N(16)	0.450
N(17)	-0.175						



ence on the activity of the compound. Therefore, studying the properties of the frontier orbital can provide important information for determining the active site on the molecule and exploring its mechanism. HOMO acts as an important role to provide electrons, LUMO has an important role in receiving electrons. The HOMO (Fig.3a) and the LUMO (Fig.3b) of ANFO are  $-8.0355$  eV and  $-3.6365$  eV respectively, and the frontier orbital energy difference  $\Delta E$  is  $4.3990$  eV. It can be seen that C(3) and C(8) occupy the smallest proportion in the LUMO though they have the maximum positive charges. So, it is not easy to play the role of electron acceptor. The O atom on the ether group has the maximum negative charge, and occupies slight proportion in the HOMO. Therefore, it is not easy to play the role of electron donor. The above results show that the stability of ANFO is good.



**Fig.3** HOMO and LUMO of ANFO at B3LYP/6-31G(d,p) level

### 3.8 Bond Order

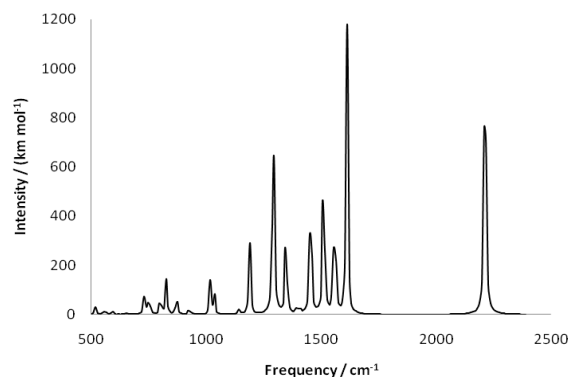
The bond order plays a very important role in judging the strength of the bond in the molecule. The bond order of ANFO obtained by natural bond orbital (NBO) analysis are shown in Table 6. It can be seen that in the ANFO structure, the C—N bond order attached to furazan ring and nitro group is the smallest. It indicates that the bond is easy to break. Moreover, the C—O bond order attached to the ether bond and furazan ring is also smaller.

**Table 6** The bond order of ANFO at B3LYP/6-31G(d,p) level

bond	order	bond	order
N(1)—C(2)	1.5999	C(2)—C(3)	1.1605
N(4)—O(5)	1.0685	N(1)—O(5)	1.1570
O(6)—C(7)	0.9336	C(7)—C(8)	1.1450
N(9)—O(10)	1.0796	C(7)—N(11)	1.6300

### 3.9 Vibration Spectroscopy

The vibration frequency and intensity of ANFO (the correction factor is 0.96) was shown in Fig.4. It can be seen from Fig.4 and Table 7 that the calculated absorption peaks was almost same as the experimental values.



**Fig.4** The calculated IR spectrum of ANFO

**Table 7** Comparison of calculated absorption peaks and experimental values of ANFO

attribution	calculated values	experimental values
N—N bond of the azido group	2213	2146
the nitro group	1511, 1347	1532, 1357
C—N bond of furazan ring	1612, 1453	1594, 1487
C—O bond.	1292	1292

### 3.10 Thermodynamic Properties

The relationship curves between the standard thermodynamic functions and temperature of ANFO in the temperature range of 273 K to 1000 K were shown in Fig.5.

It can be seen from Fig.5 that, all the thermodynamic functions in the range of 273–1000 K are increased with temperature. It is because high temperature can increase the vibration. The thermodynamic properties of ANFO at different temperatures were calculated, and the relationship between the thermo-energy ( $E_{i,m}^\theta$ ), heat capacity ( $c_{p,m}^\theta$ ), entropy ( $S_{p,m}^\theta$ ) and temperature ( $T$ ) in the range of 273 K to 1000 K was as follows:

$$E_{i,m}^\theta = 0.00003T^2 + 0.031T + 47.82 \quad (1)$$

$$c_{p,m}^\theta = -0.00006T^2 + 0.127T + 23.02 \quad (2)$$

$$S_{p,m}^\theta = -0.00004T^2 + 0.171T + 76.62 \quad (3)$$

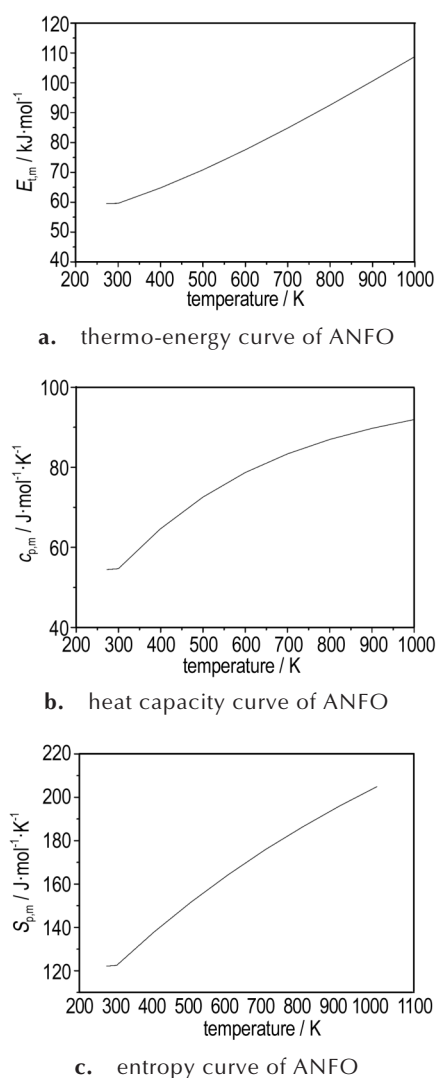


Fig. 5 The relationships of thermodynamics properties of ANFO with temperature.

Correlation coefficients were 0.999, 0.998 and 0.999, respectively. In addition, it can be concluded the increase values of  $c_{p,m}^\theta$  is small with the increase of the temperature in the range of 273 K to 1000 K. When  $T > 2117$  K,  $d c_{p,m}^\theta / d T < 0$ ,  $c_{p,m}^\theta$  will decrease with the increase of temperature.

### 3.11 Density and Enthalpy of Formation

On the basis of optimization by B3LYP/6-31G\*\*, the Monte-Carlo method was used to calculate the molecular volume with higher precision, and then the density of the compound was calculated by the formula  $\rho = M/V$ . The calculated density is  $1.85 \text{ g}\cdot\text{cm}^{-3}$ .

Hess' law of constant heat summation (equation 2) was used to obtain the solid-phase enthalpy

of formation [ $\Delta H_f(\text{solid}, 298 \text{ K})$ ] basis on the gas-phase enthalpy of formation [ $\Delta H_f(\text{gas}, 298 \text{ K})$ ]. The enthalpy of sublimation were calculated by equations 2 to 6, which was firstly presented by Politzer<sup>[27]</sup>. The standard molar enthalpies of formation for gas phase and the electrostatic potential of the molecule surface were calculated by B3LYP/6-31G\*\*.

$$\Delta H_f(\text{solid}, 298 \text{ K}) = \Delta H_f(\text{gas}, 298 \text{ K}) - \Delta H_{\text{sub}}(298 \text{ K}) \quad (4)$$

$$\Delta H_{\text{sub}}(298 \text{ K}, \text{kJ/mol}) = 0.001986A^2 + 8.8591(\nu\sigma_{\text{tot}}^2)^{0.5} - 9.405 \quad (5)$$

$$\sigma_{\text{tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m [V^+(r_i) - \bar{V}_s^+]^2 + \frac{1}{n} \sum_{j=1}^n [V^-(r_j) - \bar{V}_s^-]^2 \quad (6)$$

$$\nu = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{tot}}^2]^2} \quad (7)$$

Where  $V^+(r_i)$  and  $V^-(r_j)$  denote the positive and negative values of the electrostatic potential at any point on the surface of the molecule, respectively, and  $\bar{V}_s^+$  and  $\bar{V}_s^-$  represent their mean values, In formulae 5 and 6,  $A$  represents the molecular surface area ( $\text{\AA}^2$ ).

$$\bar{V}_s^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (8)$$

$$\bar{V}_s^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j) \quad (9)$$

The calculated enthalpy of formation of ANFO was  $630 \text{ kJ}\cdot\text{mol}^{-1}$ .

### 3.12 Detonation Performance

The Kamlet-Jacobs formula<sup>[28]</sup> is commonly used to estimate the detonation performances of CHON type high energetic compounds. The detonation velocity and detonation pressure for  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  explosive can be calculated by the following formula:

$$D = 1.01 \left( N \bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho_0) \quad (10)$$

$$p = 1.558\rho_0 N \bar{M}^{1/2} Q^{1/2} \quad (11)$$

Since ANFO satisfies  $b/2 \leq c \leq 2a + b/2$ . Therefore, in the above formula:

$$N = (b + 2c + 2d) / 4M \quad (12)$$

$$\bar{M} = (56d + 88c - 8b) / (b + 2c + 2d) \quad (13)$$

$$Q = \frac{28.9b + 94.05(c/2 - b/4) + 0.239\Delta_f H_m}{M} \quad (14)$$

Where  $D$  and  $p$  are detonation velocity ( $\text{m}\cdot\text{s}^{-1}$ ) and detonation pressure (GPa),  $Q$  is the heat of detonation,  $\text{kJ}\cdot\text{kg}^{-1}$ ,  $\rho_0$  is the explosive charge density,  $\text{g}\cdot\text{cm}^{-3}$ ,  $\Delta_f H_m$  is the standard molar enthalpy of formation,  $\text{kJ}\cdot\text{mol}^{-1}$ .

The calculated detonation velocity of ANFO is  $8660 \text{ m}\cdot\text{s}^{-1}$ , the detonation pressure is 33.81 GPa, and the heat of detonation is  $6725 \text{ kJ}\cdot\text{kg}^{-1}$ .

### 3.13 The Impact Sensitivity ( $H_{50}$ )

The impact sensitivity ( $H_{50}$ ) for ANFO can be predicted by the equation<sup>[29]</sup>.

$$H_{50} = \alpha\sigma_+^2 + \beta\nu + \gamma \quad (15)$$

Where  $\sigma_+^2$  is indicator of the strengths and variabilities of the positive surface potentials and  $\nu$  is the degree of balance between positive potentials and negative potential on the isosurface. The coefficients  $\alpha$ ,  $\beta$  and  $\gamma$  are  $-0.0064$ ,  $241.42$  and  $-3.43$ , respectively<sup>[29]</sup>.

The calculated impact sensitivity ( $H_{50}$ ) of ANFO is 35.2 cm.

## 4 Conclusions

(1) A novel energetic compound 3-azido-3'-nitrodifurazanyl ether (ANFO) was designed and synthesized for the first time with a total yield of 32.7%, and its structure was confirmed by FTIR, NMR, MS and elemental analysis.

(2) The study of molecular orbital and bond order shows that ANFO possesses good thermal stability, and the DSC curves show that the max exothermic peak of ANFO is at  $182.3 \text{ }^\circ\text{C}$  at a heating rate  $2.5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ .

(3) The molecular structure, thermodynamic properties and detonation performances of ANFO were calculated by DFT method. The calculated density is  $1.85 \text{ g}\cdot\text{cm}^{-3}$ , the calculated detonation velocity is  $8660 \text{ m}\cdot\text{s}^{-1}$ , the calculated detonation pressure is 33.81 GPa, the calculated value of  $H_{50}$  of impact sensitivity is 35.2 cm and the calculated heat of detonation is  $6725 \text{ kJ}\cdot\text{kg}^{-1}$ , showing that ANFO is a promising energetic plasticizer.

## References:

- [1] Thottempudi V, Shreeve J M, et al. Synthesis and promising properties of a new family of high-density energetic salts of 5-nitro-3-trinitromethyl-1H-1, 2, 4-triazole and 5, 5'-bis (trinitromethyl)-3, 3'-azo-1H-1, 2, 4-triazole [J]. *Journal of the American Chemical Society*, 2011, 133(49): 19982-19992.
- [2] Sheremetev A B, Kulagina V O, Batog L. V, et al. Furazan Derivatives: High energetic materials from diaminofurazan [C]// 22nd International Pyrotechnics Seminar, 1996: 377-388.
- [3] Sheremetev A B, et al. Chemistry of furazan fused to five-membered rings [J]. *Journal of Heterocyclic Chemistry*, 1995, 32(2): 371-385.
- [4] Sheremetev A B, Kulagina V O, Aleksandrova N S, et al. Aminofurazans as key synthons for construction of high energetic material [C]// 21th International Symposium on Pyrotechnics and Explosives, 1995: 249-254.
- [5] WANG Xi-jie, LIAN Peng, GE Zhong-xue, et al. Synthesis, Crystal structure and theoretical research of 3, 3'-dinitrodifurazanyl ether (FOF-1) [J]. *Acta Chimica Sinica*, 2010, 68(6): 557-563.
- [6] Sheremetev A B, Kharitonova O V, Mel'nikova T M, et al. Synthesis of symmetrical difurazanyl ethers [J]. *Mendeleev Communication*, 1996, 4(6): 141-143.
- [7] FAN Yan-jie, WANG Bo-zhou, LAI Wei-peng, et al. Synthesis, characterization and quantum chemistry study on 3, 3'-dicyanodifurazanyl ether (FOF-2) [J]. *Chinese Journal of Organic Chemistry*, 2009, 29(4): 614-620.
- [8] Sheremetev A B, Kulagina V O, Aleksandrova N S, et al. Dinitro trifurazans with oxy, azo and azoxybridges [J]. *Propellants, Explosives, Pyrotechnics*, 1998, 23(3): 142-149.
- [9] ZHAI Lian-jie, WANG Bo-zhou, LI Ya-nan, et al. Crystal structure and thermal behavior of 3, 4-bis (3-cyanofurazan-4-oxy) furazan (FOF-12) [J]. *Chinese Journal of Explosives & Propellants*, 2013, 36(5): 63-67.
- [10] ZHAI Lian-jie, WANG Bo-zhou, HUO Huan, et al. Synthesis, Crystal structure and thermal behaviour of 3, 4-bis (3-nitrofurazan-4-oxy) furazan [J]. *Chinese Journal of Energetic Materials (Hanneng Cailiao)*, 2015, 23(1): 18-22.
- [11] ZHAI Lian-jie, WANG Bo-zhou, XU Kang-zheng, et al. A new synthesis of 3, 3'-bis (fluorodinitromethyl) difurazanyl ether (FOF-13) and Its Energetic Properties [J]. *Journal of Energetic Materials*, 2016, 34(1): 92-102.
- [12] ZHOU Yan-shui, XU Kang-zheng, WANG Bo-zhou, et al. Synthesis, structure and thermal properties of bifurazano [3, 4-b: 3', 4'-f] furoxano [3'', 4''-d]-oxacycloheptatriene (BFFO) [J]. *Bulletin of the Korean Chemical Society*, 2012, 33(10): 3317-3320.
- [13] WANG Xi-jie, XU Kang-zheng, et al. A novel insensitive energetic material trifurazanooxacycloheptatriene (TFO): synthesis and detonation properties [J]. *Propellants, Explosives, Pyrotechnics*, 2015, 40(1): 9-12.
- [14] Sheremetev A B, Mantseva E V, et al. Hydroxyfurazans: outlook to using [C]// Proceedings of the 32th International Annual Conference of ICT, 2001: 103/1-103/4.
- [15] QIU Ling, XIAO He-ming, GONG Xue-dong, et al. Crystal density predictions for nitramines base on quantum chemistry [J]. *Journal of Hazardous Materials*, 2007, 141(1): 280-288.
- [16] LI Hong-zhen, HUANG Ming, LI Jin-shan, et al. Synthesis



- and crystal structure of 3-azido-4-aminofurazan [J]. *Chinese Journal of Synthetic Chemistry*, 2007, 15(6): 710-713.
- [17] GE Zhong-xue, WANG Xi-jie, JIANG Jun, et al. Synthesis of 3,4-dinitrofurazan[J]. *Chinese Journal of Synthetic Chemistry*, 2008, 16(3): 260-263.
- [18] Rice B M, Hare J J, Byrd E F, et al. Accurate predictions of crystal densities using quantum mechanical molecular volumes [J]. *The Journal of Physical Chemistry A*, 2007, 111(42): 10874-10879.
- [19] MA Hai-xia, XIAO He-ming, SONG Ji-rong, et al. Theoretical study on the structure and properties of 1,2,4-triazol-5-one [J]. *Chinese Journal of Energetic Materials(Hanneng Cailiao)*, 2005, 13(3): 166-168.
- [20] LAI Wei-peng, LIAN Peng, WANG Bo-zhou, et al. Study of the properties of 3,6-dinitropyrazolo [4,3-c] pyrazoles by quantum chemistry [J]. *Computers and Applied Chemistry*, 2007, 24(8): 1025-1028.
- [21] Frisch M J, Trucks G W, Schlegel H B, et al. Gaussian 09 [CP], rev. A.02, Gaussian, Inc, Wallingford, CT, 2009.
- [22] ZHOU Yan-shui, LI Jian-kang, HUANG Xin-ping, et al. Synthesis and properties of 3,4-bis(4'-aminofurazano-3') furoxan [J]. *Chinese Journal of Explosives & Propellants*, 2007, 30(1): 54-56.
- [23] Aleksandr M, Churakov S L, et al. Synthesis of 4H-[1,2,3]triazolo [4,5-c] [1,2,5] oxadiazole 5-Oxide and its N-and O-Alkyl derivatives [J]. *Tetrahedron Letters*, 1996, 37(47): 8577-8580.
- [24] LIN Zhi-hui, GAO Li, LI Min-xia, et al. Synthesis, crystal, thermal behaviour and prediction of theoretical detonation performance for some energetic compounds derived from furazan [J]. *Chinese Journal of Explosives & Propellants*, 2014, 37(3): 6-10.
- [25] Novikova T S, Melnikova T M, Kharitonova O V, et al. An effective method for the oxidation of aminofurazans to nitrofurazans[J]. *Mendeleev Communication*, 1994, 2(4): 139-140.
- [26] Sheremetv A B, Kharitonova O V, Mel'yana T M, et al. Synthesis of symmetrical difurazanyl ethers [J]. *Mendeleev Communication*, 1996, 4(6): 141-143.
- [27] Politzer P J, Murray S, Grice M E, et al. Calculation of heats of sublimation and solid phase heats of formation [J]. *Molecular Physics*, 1997, 91(5): 923-928.
- [28] Kamlet M J, Jacobs S J, et al. Chemistry of detonations. I. A simple method for calculating detonation properties of CHNO explosives [J]. *Journal of chemical physics*, 1968, 48(1): 23-35.
- [29] QING Hua-zhang, JIA Heng-zhang, XIU Juan-qi, et al. Molecular design and property prediction of high density polynitro [3.3.3]-propellane -derivatized frameworks as potential high explosives[J]. *The Journal of Physical Chemistry A*, 2014, 118(45): 10857-10865.

## 非对称性呋唑醚 3-叠氨基-3'-硝基呋唑醚：合成及量子化学研究

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**摘要:** 以 3-叠氨基-4-氨基呋唑(AAF)为起始原料,经卡罗酸氧化,水解及分子间醚化反应,首次合成了 3-叠氨基-3'-硝基双呋唑基醚(ANFO),总收率 32.7%。采用  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FT-IR, MS 和元素分析表征了 ANFO 和中间体的结构;以过氧化氢(50%)、硫酸、钨酸钠为新的氧化系统,对 ANF 氧化法进行了改进,产率达 75.1%。探讨了氧化和醚化反应的最佳条件,得到最佳反应条件为:氧化体系  $n(\text{H}_2\text{O}_2):n(\text{H}_2\text{SO}_4)=1:1.5$ ,醚化体系反应温度为 30  $^\circ\text{C}$ 。采用 B3LYP/6-31G(d,p)法优化了 ANFO 的结构,在振动分析的基础上计算了 ANFO 在不同温度下的热力学性质。采用差示扫描量热法(DSC)和密度泛函理论(DFT)研究了 ANFO 的物理化学性质和爆轰性能。计算的密度、熔点、爆速、爆压、撞击感度( $H_{50}$ )和爆热分别 1.85  $\text{g}\cdot\text{cm}^{-3}$ , 182.3  $^\circ\text{C}$ (dec.), 8660  $\text{m}\cdot\text{s}^{-1}$ , 33.81 GPa, 35.2  $\text{cm}$ , 6725  $\text{kJ}\cdot\text{kg}^{-1}$ 。

**关键词:** 合成; 3-叠氨基-3'-硝基双呋唑基醚(ANFO); 非对称性呋唑醚; 性能

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