

## Synthesis and Crystal Structure of Bis-3,3'-(nitro-*NNO*-azoxy)-4,4'-azofurazan

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During the recent decades, high-nitrogen heterocyclic compounds have been recognized as one class of promising energetic materials.<sup>1-3</sup> These energetic compounds with high nitrogen content have high heat of formation due to the large number of N-N and C-N bonds.<sup>4,5</sup> A number of heterocycle-based energetic compounds were reported as potential materials for military and space applications.<sup>6-9</sup> Of these, furazan ring served as an efficient build-block. The combination of furazan ring with energetic substituents, such as amino (-NH<sub>2</sub>),<sup>10</sup> nitro (-NO<sub>2</sub>),<sup>11,12</sup> azide (-N<sub>3</sub>)<sup>13</sup> and nitramine (-NHNO<sub>2</sub>)<sup>14</sup> have been investigated.

An unconventional explosophoric group, namely nitro-*NNO*-azoxy, through the destructive *N*-nitration of an *XNO*-azoxy compound (X=Ac, *t*Bu) with nitronium was first reported by Churakov *et al.*<sup>15</sup> After that, Sheremetev A. B. *et al.*<sup>16</sup> synthesized bis-3,3'-(nitro-*NNO*-azoxy)-difurazanyl ether, which has high crystal density and excellent detonation properties. In this paper, a novel compound, bis-3,3'-(nitro-*NNO*-azoxy)-4,4'-azofurazan (BNOAF, **5**), was designed and synthesized from 3,4-diaminofurazan (DAF, **1**) *via* four steps, such as the reactions of oxidation,<sup>17</sup> condensation,<sup>18</sup> oxidation and nitrolysis (Scheme 1). The structure of title compound was confirmed by IR, <sup>13</sup>C NMR, <sup>14</sup>N NMR, MS and elemental analysis. The X-ray crystal structure of BNOAF was also studied. Furthermore, the performance of BNOAF was calculated.

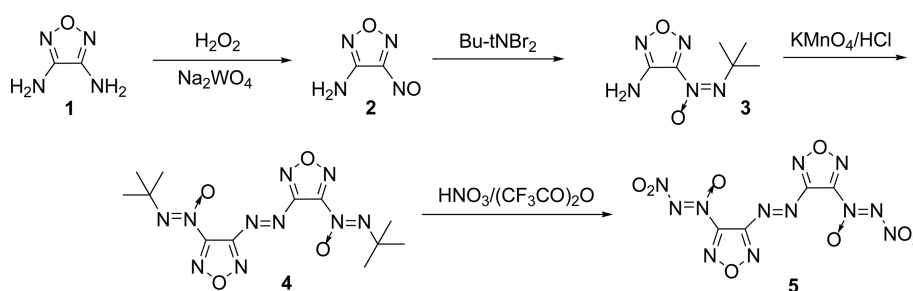
### Results and Discussion

Churakov<sup>15</sup> and Sheremetev<sup>16</sup> synthesized the compound containing nitro-*NNO*-azoxy group through nitrolysis using NO<sub>2</sub>BF<sub>4</sub> as nitrolysis agent, but this method could not be

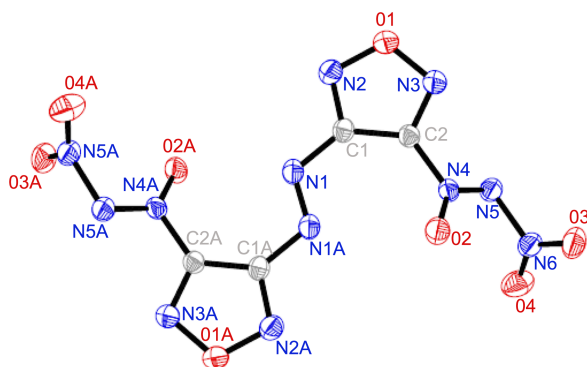
performed successfully in synthesis of the BNOAF. The reaction was monitored by TLC, it was found that the reaction mixture contained only the bis-3,3'-(*t*-Bu-*NNO*-azoxy)-4,4'-azofurazan(BAOAF, **4**) and there was no new product spot during the whole experiment. The effects of different nitrolysis agents on the yield of the BNOAF was studied and the results were given in Table 1. The nitrolysis of the *tert*-butyl group with anhydrous nitric acid or a mixture of anhydrous nitric acid in acetic anhydride give no product. The mixture of pure nitric acid in trifluoroacetic anhydride is a much stronger nitrolysis agent and gives BNOAF in a yield of 17.4%.

In the IR spectra, several main absorption bands around 1627, 1281, 1173, 1039, 848 cm<sup>-1</sup> were attributed to the furazan ring. The absorption bands around 1500 cm<sup>-1</sup> could be assigned to azo (N=N) and the absorption bands around 1552 and 1311 cm<sup>-1</sup> attributed to the nitro group. In the <sup>13</sup>C NMR spectrum of BNOAF, the resonance bands appear at 156.2 ppm and 148.6 ppm. The <sup>14</sup>N spectra of BNOAF showed that two signals were observed at -69.5 ppm and -44.3 ppm respectively.

A perspective view of the title compound, showing the atomic numbering scheme, was given in Figure 1. The complete molecule of BNOAF is located on an inversion center (Symmetry operator: -x, -y, -z) at the mid-point of the central N=N bond which is in *E* configuration. In each molecule, the two furazan ring linked with N=N group are parallel and the distance between two planes is 0.163(2) Å. The dihedral angles between furazan and plane defined by nitro group O3O4N6 and plane O2N4N5, are 54.42(3)° and 43.94(6)° respectively. Meanwhile, the nitro-*NNO*-group involves two planar moieties, namely O3-O4-N6-N5 and



**Scheme 1.** The synthesis routes of BNOAF.



**Figure 1.** Molecular Structure and labeling scheme of BNOAF.

**Table 1.** Effect of nitrolysis agent on the yield of BNOAF

Nitrolysis agent	Yield (%)
NO <sub>2</sub> BF <sub>4</sub> /CH <sub>3</sub> CN	0
anhydrous nitric acid	0
Ac <sub>2</sub> O/anhydrous nitric acid	0
(CF <sub>3</sub> CO) <sub>2</sub> O/anhydrous nitric acid/CH <sub>2</sub> Cl <sub>2</sub>	5.8
(CF <sub>3</sub> CO) <sub>2</sub> O/anhydrous nitric acid	17.4

O2-N4-N5-N6, that are oriented perpendicular to each other (83.55°). The torsion angle C2-N4-N5-N6 is 177.45(1)°. The bond lengths and angles in the molecule are within normal ranges.<sup>19</sup>

The structure of BNOAF was optimized by Gaussian 09<sup>20</sup> and its enthalpy of formation was then calculated. The explosive parameters were obtained by VLW equation of state<sup>21</sup> using crystal density (1.874 g/cm<sup>3</sup>) and enthalpy of formation as basic data. The predicted performance data of BNOAF were as follows: detonation velocity 9466.89 m/s, C-J pressure 44.08 GPa and enthalpy of formation +1169.74 kJ/mol.

In conclusion, a new furazan derivative (BNOAF) was synthesized and well characterized. The crystal structure of BNOAF was determined by X-ray diffraction analysis and the molecular was bridged by *azo* in *E* configuration. Furthermore, the properties of BNOAF were estimated. The target compound exhibits good physical and detonation properties. It might serve as a potential energetic material and be applied in high explosives or environment friendly propellants.

### Experimental Section

<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>14</sup>N NMR were obtained 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 cm<sup>-1</sup>. Elemental analyses (C, H and N) were performed on a VARI-EI-3 elemental analyzer. Mass spectra were obtained on GCMS-QP2010. Differential scanning calorimetry (DSC) was carried out in a platinum sample container using a Shimadzu DSC-60 at a heating rate of 10 °C·min<sup>-1</sup>. 3,4-diaminofurazan (DAF),<sup>22</sup> *N,N*-dibromo-*tert*-butylamine<sup>18</sup> and anhydrous nitric

acid were prepared in our laboratory.

**Synthesis of 3-Amino-4-nitrosfurazan (ANSF, 2).** To a mixture of benzene (200 mL), 30% hydrogen peroxide (145 mL, 1.29 mol) and sodium tungstate dihydrate (16.5 g, 0.05 mol), concentrated sulfuric acid (10 mL) was added dropwise at 5-10 °C, then DAF was added and the mixture was stirred at 15 °C for 1.5 h. The organic layer was separated off, washed with water and dried over magnesium sulfate. After the drying agent was filtered off, the solvent was removed to give 5.19 g of yellow solid in a yield of 91.1%. mp 76-78 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz) δ 6.86 (s, 2H); IR (KBr, v/cm<sup>-1</sup>) v: 3421, 3318, 1628, 1531, 1482, 1409, 1284, 1014 cm<sup>-1</sup>; Anal. Calcd for C<sub>2</sub>H<sub>2</sub>N<sub>4</sub>O<sub>2</sub>: C 21.06, H 1.77, N 49.12; Found: C 20.82, H 1.77, N 48.95.

**Synthesis of 3-Amino-4-(*t*-butyl-*NNO*-azoxy) furazan (ABAOF, 3).** A suspension of *N,N*-dibromo-*tert*-butylamine (11.5 g, 50 mmol), CuCl (10 g, 100 mmol), and ANSF (5.7 g, 50 mmol) in methylene chloride (500 mL) was stirred at 15-25 °C for 15 h. The reaction mixture was poured to ice-water (500 mL), then sodium thiosulphate was added. The organic layer was separated off, washed with water and dried over magnesium sulfate, filtered and the solvent was removed to give 6.8 g of yellow solid in a yield of 73.5%. mp 156-158 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz) δ 1.43 (s, 9H), 6.59 (s, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz) δ 25.06, 59.99, 150.77, 151.55; IR (KBr, v/cm<sup>-1</sup>) v: 3472, 3356, 2980, 1624, 1566, 1453, 1367, 1183 cm<sup>-1</sup>; MS (EI) *m/z* (%): 185 (M<sup>+</sup>, 5), 112 (20), 102 (20), 57 (100), 41 (35), 29 (28); Anal. Calcd for C<sub>6</sub>H<sub>11</sub>N<sub>5</sub>O<sub>2</sub>: C 38.92, H 5.99, N 37.82; Found: C 39.36, H 5.96, N 35.60.

**Synthesis of Bis-3,3'-(*t*-butyl-*NNO*-azoxy)-4,4'-azofurazan (BAOAF, 4).** To a suspension of ABAOF (2.78 g, 15 mmol) in concentrated hydrochloric acid (60 mL), a solution of potassium permanganate (2.84 g, 18 mmol) in water (100 mL) was added dropwise at 0-5 °C, then the mixture was stirred at 55 °C for 5 h. After the reaction mixture was cooled to room temperature, the yellow precipitate was filtered, washed with water and dried to obtain 2.39 g of solid with a yield of 87.0%. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz): 1.36 (s, 18H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz): 156.49, 150.75, 61.28, 24.68; IR (KBr, v/cm<sup>-1</sup>) v: 2979, 1494, 1364, 1316, 1176, 1028, 902, 861 cm<sup>-1</sup>; Anal. Calcd. (%) for C<sub>12</sub>H<sub>18</sub>N<sub>10</sub>O<sub>4</sub>: C 38.23, H 4.95, N 38.23; Found (%): C 38.99, H 5.25, N 37.42.

**Synthesis of Bis-3,3'-(nitro-*NNO*-azoxy)-4,4'-azofurazan (BNOAF, 5).** BAOAF (0.36 g, 1 mmol) was added to a mixture of trifluoroacetic anhydride (6.7 mL) and anhydrous nitric acid (1.7 mL, 0.04 mol), then the mixture was stirred at 30 °C for 6 h. The reaction mixture was poured to ice-water (50 mL), then extracted five times with CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The extraction were washed with water and dried over magnesium sulfate, filtered and the solvent was removed to give yellow oil. The title compound was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (R<sub>f</sub> = 0.45, 10:1, V/V) as an eluent, affording 60 mg of orange solid in a yield of 17.4%. T<sub>m</sub> 83.7 °C (DSC). T<sub>d</sub> 132.1 °C (DSC). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125

MHz): 156.26, 148.64;  $^{14}\text{N}$  NMR (DMSO- $d_6$ , 36 MHz): -44.27, -69.54; IR (KBr,  $\text{v}/\text{cm}^{-1}$ ): 1627, 1552, 1500, 1311, 1281, 1173, 1039, 954, 848  $\text{cm}^{-1}$ ; MS (EI)  $m/z$  (%): 298 (0.51), 282 (0.92), 252 (1.33), 208 (0.49), 44 (78.07), 30 (100.00). Anal. Calcd. (%) for  $\text{C}_4\text{H}_6\text{N}_{12}\text{O}_8$ : C 13.96, H 0, N 48.84; Found (%): C 13.80, H 0.00, N 49.05.

Block-like single crystals suitable for X-ray diffraction studies were obtained after 7 days by slow evaporation from a solution of the title compound in  $\text{CHCl}_3$  at room temperature. A yellow crystal of title compound with dimensions of 0.15 mm  $\times$  0.15 mm  $\times$  0.10 mm was chosen for X-ray diffraction analysis performed on Bruker SMART APEXII CCD X-ray diffractometer with a  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) by using a  $\varphi$ - $\omega$  scan mode at 296(2) K. In the range of  $2.52 \leq \theta \leq 28.40^\circ$ , a total of 3654 reflections were collected including 1488 unique ones ( $R_{\text{int}} = 0.0276$ ). The structure was solved by direct methods using SHELXS program of the SHELXL-97 package and refined with SHELXL package.<sup>23</sup> The final refinement was performed by full-matrix least-squares method with anisotropic thermal parameters on  $F^2$  for the non-hydrogen atoms.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-903494). The data can be obtained free of charge via [www.ccdc.cam.ac.uk/deposit](http://www.ccdc.cam.ac.uk/deposit) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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