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# A Novel Synthesis Route of [1,2,5]Oxadiazolo [3,4-e] [1,2,3,4] tetrazine-4,6-Di-N-oxide

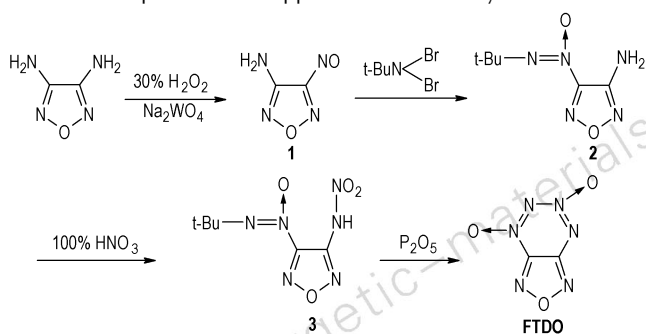
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## 1 Introduction

An energetic material, [1,2,5] oxadiazolo [3,4-e] [1,2,3,4] tetrazine-4,6-di-N-oxide (FTDO), whose density (tested) was  $1.85 \text{ g} \cdot \text{cm}^{-3}$ <sup>[2]</sup>, enthalpy of formation was  $1010 \text{ kcal} \cdot \text{kg}^{-1}$ <sup>[3]</sup>, calculated detonation velocity pressure was  $9802 \text{ m} \cdot \text{s}^{-1}$ , and detonation pressure was 44.78 GPa, was firstly synthesized and reported by Russian scientists in 1995<sup>[1]</sup>. The five-step synthetic route of FTDO, which was synthesized from 3,4-diaminofurazan (DAF) via the reactions of oxidation, amino protection, condensation, hydrolysis and cyclization with a total yield of 14.63%, had been reported<sup>[1]</sup>. However, there were many shortcomings in that synthetic route, including reaction conditions rigorous, difficult separation and purification of FTDO and expensive  $\text{NO}_2\text{BF}_4$  reagent.

A novel synthetic route of [1,2,5] oxadiazolo [3,4-e] [1,2,3,4] tetrazine 4,6-di-N-oxide (FTDO) was designed and FTDO was synthesized from 3,4-diaminofurazan (DAF) via the reactions of oxidation, condensation, nitrification and cyclization with a total yield of 30.89% (Scheme 1). FTDO and its intermediates were characterized by  $^{13}\text{C}$  NMR,  $^{14}\text{N}$  NMR,  $^{15}\text{N}$  NMR,  $^{17}\text{O}$  NMR, IR, MS and EA etc. Compared with the five-step route in reference, this new route simplifies the synthetic route with milder reaction conditions, more convenient separation and purification of FTDO and lower-cost reagents, which offers potential for application in industry.



Scheme 1 The novel synthetic routes of FTDO

## 2 Synthesis of 3-amino-4-nitrosofurazan (1)

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, 180 mmol) being added dropwise at 5 ~ 10 °C, and then DAF (1), was stirred at 15 °C for 1.5 h. The organic layer was separated, washed with water and dried by anhydrous magnesium sulfate. After the drying agent being filtered, the solvent was removed to obtain 5.19 g yellow solid, yield 91.05%. m. p. 76 ~ 78 °C.  $^1\text{H}$  NMR (DMSO, 500 MHz)  $\delta$ : 6.86 (s, 2H); IR (KBr,  $\text{cm}^{-1}$ )  $\nu$ : 3421, 3318, 1628, 1531, 1482, 1409, 1284, 1014; Anal. Calcd for  $\text{C}_2\text{H}_2\text{N}_4\text{O}_2$ : C 21.06, H 1.77, N 49.12; Found: C 20.82, H 1.77, N 48.95.

## 3 Synthesis of 3-amino-4-(tert-butyl-NNO-azoxy) furazan (2)

A suspension solution of *N,N*-dibromo-tert-butylamine (11.5 g, 50 mmol), CuCl (10 g, 100 mmol), compound (1) (0.57 g, 50 mmol) in methylene chloride (500 mL) was stirred at 15 ~ 25 °C for 15 h. The reaction mixture was poured into ice-water (500 mL), and then sodium thiosulfate was added. The organic layer was separated, washed with water and dried by anhydrous magnesium sulfate, filtered and the solvent was removed to obtain 6.8 g yellow solid, yield 73.50%. m. p. 156 ~ 158 °C.  $^1\text{H}$  NMR (DMSO, 500 MHz)  $\delta$ : 1.43 (s, 9H), 6.59 (s, 2H);  $^{13}\text{C}$  NMR (DMSO, 500 MHz)  $\delta$ : 25.06, 59.99, 150.77, 151.55; IR (KBr,  $\text{cm}^{-1}$ )  $\nu$ : 3472, 3356, 2980, 1624, 1566, 1453, 1367, 1183; MS (EI)  $m/z$  (%): 185 ( $\text{M}^+$ , 5), 112 (20), 102 (20), 57 (100), 41 (35), 29 (28); Anal. Calcd for  $\text{C}_6\text{H}_{11}\text{N}_5\text{O}_2$ : C 38.92, H 5.99, N 37.82; Found: C 39.36, H 5.96, N 35.60.

## 4 Synthesis of 3-nitramino-4-(tert-butyl-NNO-azoxy) furazan (3)

Pure nitric acid (2.72 g, 21.6 mmol) was added to a stirred and cooled (0 °C) solution of carbon tetrachloride (2 g, 10.8 mmol). After being warmed to room temperature gradually, the mixture was stirred for 2 h and the solvent was removed by vacuum. Methylene chloride (100 mL) was added, the solution was washed with ice-water (20 mL) and aqueous layer was extracted with methylene chloride (2 x 50 mL). The combined organic layer was dried by anhydrous magnesium sulfate, filtered and the solvent was removed to obtain 2.47 g yellow solid, yield 99.54%. m. p. 92 ~ 94 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 1.52 (t,  $J = 64 \text{ Hz}$ , 9H),  $\delta$ : 11.34 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$ : 25.34,  $\delta$ : 61.90,  $\delta$ : 142.91, 150.35; IR (KBr,  $\text{cm}^{-1}$ )  $\nu$ : 3291, 2983, 1621, 1510, 1488, 1315, 1164; MS (EI)  $m/z$  (%) EI: 230 ( $\text{M}^+$ , 40), 212 (97), 172 (35), 154 (28), 119 (18), 98 (20); Anal. Calcd for  $\text{C}_6\text{H}_7\text{N}_6\text{O}_3$ : C 31.30, H 4.35, N 36.52;

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Found: C 31.73, H 4.41, N 36.12.

## 5 Synthesis of [1,2,5]oxadiazolo [3,4-e] [1,2,3,4] tetrazine-4,6-di-N-oxide (FTDO)

At the temperature of 0 °C, the solution of 3-nitramino-4-(tert-butyl-NNO-azoxy) furazan (1 g, 4.35 mmol) in acetonitrile (160 mL) was added to phosphoric anhydride (20 g), and then keep this temperature for 0.5 h. After being warmed to 55 °C, the mixture was stirred for 5 h and the solvent was poured into ice-water (200 mL). The product was extracted with methylene chloride (10 × 20 mL) and dried by anhydrous magnesium sulfate, filtered and the solvent was removed to obtain 0.70 g yellow oil, the yellow oil was decolorized with active fluridin and obtain 0.315 g bright yellow crystal, yield 46.37%. m. p. 109 ~ 111 °C; <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>, 500 MHz) δ: 156.81, 144.71; <sup>14</sup>N NMR (acetone-*d*<sub>6</sub>, MeNO<sub>2</sub> as the standard, 500 MHz) 37.6 ( $\nu_{1/2}$  = 519 Hz) (N-1,3), 10.0 ( $\nu_{1/2}$  = 458 Hz) (N-5), -42.2 ( $\nu_{1/2}$  = 9 Hz) (N-6), -50.7 ( $\nu_{1/2}$  = 9 Hz) (N-4), -104.7 ( $\nu_{1/2}$  = 279 Hz) (N-7); <sup>15</sup>N NMR (acetone-*d*<sub>6</sub>, MeNO<sub>2</sub> as the standard, 500 MHz) 35.6, 38.8 (N-1,3), -42.3 (N-6), -50.9 (N-4), -104.7 (N-7); <sup>17</sup>O NMR (acetone-*d*<sub>6</sub>, MeNO<sub>2</sub> as the standard, 500 MHz) 532.3 ( $\nu_{1/2}$  = 251 Hz), 504.2 ( $\nu_{1/2}$  = 186 Hz), 441.7 ( $\nu_{1/2}$  = 441 Hz); IR (KBr, cm<sup>-1</sup>)  $\nu$ : 1589, 1543, 1514, 1460, 1418, 1317, 1148, 1018, 939; MS (EI) *m/z* (%): 156 (M<sup>+</sup>, 25), 84 (4), 68 (45), 52 (13), 30 (100); Anal. Calcd for C<sub>2</sub>N<sub>6</sub>O<sub>3</sub>: C 15.38, N 53.47; Found: C 15.38, N 53.85.

## 6 Performances of physical and detonation for FTDO

The performances of physical, such as density, melting point and dissolubility, were obtained by test, detonation velocity and detonation pressure were calculated by VLW method<sup>[4]</sup>. The datas were shown in the Table 1.

A new type of energetic material, [1,2,5]oxadiazolo [3,4-e] [1,2,3,4] tetrazine-4,6-di-N-oxide (FTDO), was synthesized by a novel route, and its performances of physical and detonation were tested or calculated by VLW method. The results showed that FTDO was a new type of energetic material

with a novel structure, and would have the potential for application in industry.

**Table 1** The performances of FTDO

properties	results	test condition
appearance	yellow crystal	eyeballing
density/g · cm <sup>-3</sup>	1.85	experimental method
melting point/°C	110 ~ 112	melting point apparatus
nitrogen content/%	52.47	elemental analysis
dissolubility	soluble in CH <sub>2</sub> Cl <sub>2</sub> and CH <sub>3</sub> COCH <sub>3</sub>	experimental method
detonation velocity/m · s <sup>-1</sup>	9802 ( <i>d</i> = 1.85 g · cm <sup>-3</sup> )	VLW method
detonation pressure/GPa	44.78	VLW method
enthalpy of formation /kcal · kg <sup>-1</sup>	1010	reference[3]

**Key words:** physical chemistry; modified single base propellant; loading density; combustion progressively; muzzle velocity

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