Synthesis and Theoretical Studies of a New High Explosive, N,N,-Bis(3-aminofurazan-4-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene

Suming JING, Yucun LIU [*], Dengcheng LIU, Jiahu GUO

School of Chemical Engineering and Environment,
North University of China, Taiyuan 030051, China
[*]*E-mail: j782855067@163.com*

Abstract: A new high energy, low sensitivity material N,N,-bis(3-aminofurazan-4-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BAFDAONAB) was synthesized from 4-chlorobenzoic acid and diaminofurazan. The structure of BAFDAONAB was characterized by FT-IR, NMR and Elemental Analyses and its purity was determined by HPLC. The optimized structure and thermodynamic parameters were obtained at the DFT- B3LYP/6-31+G** theoretical level. Its detonation properties were also predicted by the formulae of Kamlet-Jacobs and the Monte-Carlo method. The results show that the density, heat of formation, detonation velocity, detonation pressure, impact sensitivity and purity were 1.93 g/cm^3, 4487.44 kJ/mol, 9.01 km/s, 35.03 GPa, 63 cm and 99.3%, respectively. In addition, the compound was an insensitive high explosive which could meet the requirements of high energetic materials.

Keywords: BAFDAONAB, density functional theory, detonation properties

1 Introduction

Energetic materials are extensively used for a variety of military purposes and industrial applications [1-6]. It has been confirmed that commonly used high explosives such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) show relatively high sensitivity to impact and shock. Several approaches can be adopted to render a system insensitive, for example (i) synthesis of thermally stable insensitive high explosives, and (ii) development of plastic bonded explosives (PBXs). The most radical solution of all is the synthesis of high energy

density compounds (HEDCs) with low sensitivity. Thus, the development of high-performance explosives with low sensitivity to impact and friction, and good thermal stability is a subject of worldwide intense ongoing research [7-10]. Many HEDCs have been designed and synthesized, such as tetranitroglycoluril (TNGU), 1,2,3-trinitroazetidine (TNAZ), octanitrocubane (ONC), ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF) [11]. However, many problems still exist in the synthesis and scale-up, such as poor water stability (TNGU), high sensitivity (TNAZ, CL-20), and complicated processes (ONC). N,N´-bis(1,2,4-triazol-3-yl-)-4,4´-diamino-2,2´,3,3´,5,5´,6,6´-octanitroazobenzene (BTDAONAB), which is the most thermally-stable explosive, has been synthesized by Mehilal *et al*. [12]. Some congeners of BTDAONAB are stable too [13]. Research has shown that thermal stability and invulnerability of explosive molecules can be achieved by the introduction of amino groups into nitro aromatic rings, the condensation of nitroaryl halides with aminotetrazole, the condensation of nitroaryl halides with aminotriazole, the introduction of conjugation between two nitroaryl compounds or through the introduction of the furoxan group to a nitroaryl compound followed by amino groups [13]. In the present paper an insensitive high explosive, bis(3-aminofurazan-4-yl)-4,4´-diamino-2,2´,3,3´,5,5´,6,6´-octanitroazobenzene (BAFDAONAB) has been synthesized and characterized. BAFDAONAB is a new, thermally stable, insensitive high explosive. Some of the desirable properties of BAFDAONAB are compared with RDX, HMX, CL-20, TNT and LLM-105.
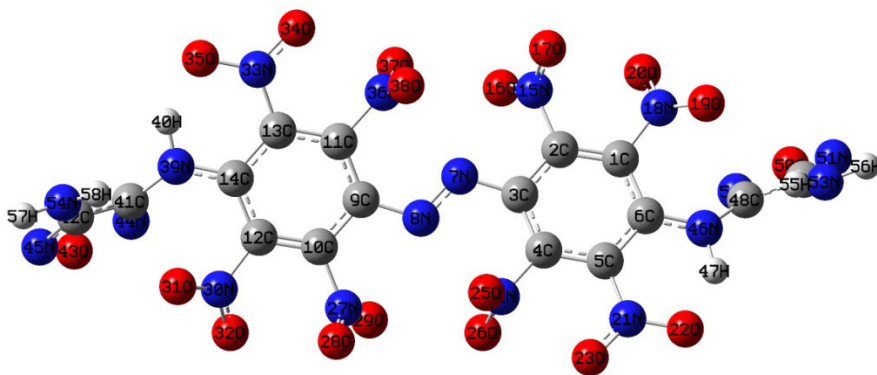

Figure 1. Molecular modelled structure of BAFDAONAB.

2 Experimental and Calculation Procedures

2.1 Materials

4-Chlorobenzoic acid, as the starting compound for the preparation of BAFDAONAB, oleum 65% (> 98%, HPLC), fuming nitric acid 100% (> 98%, HPLC), concentrated sulfuric acid 98% (> 98%, HPLC), sodium azide (> 98%, HPLC), chloroform, ethanol, carbon tetrachloride, acetone and ethyl acetate were purchased from Tian Jin Fuyu Corporation (China). 3,4-Diaminofurazan (purity 99%) was supplied by North University of China.

2.2 Experimental methodology

Melting points were determined in open capillaries. Densities were determined experimentally using Archimedes' principle. The IR spectra were recorded on a Perkin Elmer Spectrum 100 (FTIR) instrument (USA). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-Avance DRX 500 MHz instrument (Switzerland). Elemental analyses were performed on a HERAEUS 1106 elemental analyzer (Germany). The impact sensitivity was tested at room temperature using an ERL type 12 drop hammer apparatus with a sample mass of 35 ± 1 mg and a drop weight of 5 ± 0.002 kg. The friction sensitivity tests were carried out according to the explosion probability method of GJB-772 using a Swing Friction Sensitivity Tester.

2.3 Synthesis

2.3.1 4-Chloro-3,5-dinitrobenzoic acid

Fuming sulfuric acid (65%, 50 mL) was transferred to a 500 mL three-necked, round-bottomed flask fitted with a mechanical stirrer, dropping funnel and reflux condenser, at 0-5 °C (ice-water cooling bath), fuming nitric acid (40 mL, 0.95 mol) was added by drop-wise addition with stirring, controlling the temperature to remain below 30 °C, and 4-chlorobenzoic acid (10 g, 0.064 mol) was then added slowly. After the addition was complete, the reaction mixture was heated to 95-98 °C, and was maintained at this temperature for 6 h with continuous stirring. The reaction mixture was allowed to cool to room temperature and poured into saturated salt water to yield a pale yellow compound. The precipitate was collected by suction filtration, washed with water and recrystallized from ethyl acetate to give 14.2 g 4-chloro-3, 5-dinitrobenzoic acid (yield 90.1%). IR: 3444, 3090, 1712, 1644, 1561, 1363, 1120, 931, 752 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$, 25 °C, ppm) δ: 1.15 (s, COOH proton), 8.2 (s, 2H aromatic protons); Elemental analysis for

$C_7H_3N_2O_6Cl$, Calcd: C 34.07, H 1.21, N 11.35, Cl 14.40%; Found: C 33.99, H 1.02, N 11.21, Cl 14.56%.

2.3.2 4-Chloro-3,5-dinitroaniline

Fuming sulfuric acid (65%, 50 mL) was transferred to a three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser and dropping funnel. 4-Chloro-3,5-dinitrobenzoic acid (20 g, 0.081 mol) was added portion-wise with stirring, and after complete dissolution, chloroform (80 mL) was also added through a dropping funnel and the addition speed was controlled so that the reaction temperature would not exceed 40 °C. Sodium azide (8 g, 0.122 mol) was added portion-wise and slowly, with continuous stirring, followed by refluxing for 5 h. The reaction mixture was allowed to cool to room temperature and poured into saturated salt water and cooled to 0 °C. The dark yellow mass thus obtained was filtered off and washed with water. The yield was 16.9 g (91.1%). IR: 3488, 3093, 1722, 1544, 1311, 763 cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d$_6$, 25 °C, ppm) δ: 7.7 (s, 2H, aromatic), 5.6 (br, 2H, NH$_2$); Elemental analysis for $C_6H_4N_3O_4Cl$, Calcd: C 33.01, H 1.83, N 19.31, Cl 16.32 %; Found: C 33.01, H 1.88 %, N 18.99, Cl 16.11%.

2.3.3 4, 4'- Dichloro-2,2',3,3',5,5',6,6'-octanitroazobenzene

Fuming sulfuric acid (65%, 250 mL) was placed in a 500 mL three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer and dropping funnel, followed by the slow addition of 4-chloro-3,5-dinitroaniline (10 g, 0.046 mol). Fuming nitric acid (25 mL) was carefully transferred followed by drop-wise addition. The temperature of the reaction mixture was slowly raised to 92 °C and maintained there for 3 hours, then the reaction mixture was cooled to room temperature and poured into saturated salt water and cooled to 0 °C. The filter cake was recrystallized from ethyl acetate and water, to give a light yellow product, which was filtered off and washed with water to yield 12.08 g (78.7%). IR: 1588, 1573, 1555, 1338, 1022, 850, 687 cm^{-1}. ^{13}C NMR (500 MHz, DMSO-d$_6$, 25 °C, ppm) δ: 159, 155, 137, 124; Elemental analysis for $C_{12}N_{10}O_{16}Cl_2$, Calcd: C 23.56, N 22.91, Cl 11.62%; Found: C 23.72, N 23.01, Cl 11.54%.

2.3.4 Bis(3-aminofurazan-4-yl)-4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (BAFDAONAB)

4,4′-Dichloro-2,2′,3,3′,5,5′,6,6′-octanitroazobenzene (2.6 g, 0.041 mmol) was transferred to a 500 mL three-necked, round-bottomed flask equipped with a mechanical stirrer, thermometer and dropping funnel, followed by ethanol

(60 mL). 3,4-Diaminofurozan (7.2 g, 0.100 mmol) was added slowly to the solution with occasional swirling. The reaction mixture was then heated under reflux for 4 h. After completion of the reaction, it was cooled to room temperature and poured into ice-cooled water. The product was filtered off, washed thoroughly with cold distilled water and dried to give the product. This was recrystallized from diethyl ether to remove any impurities and finally air dried. The results of HPLC analysis showed that the purity of the synthesized compound was about 99.3%. IR: 3459, 3353, 2925, 1705, 1652, 1555, 1438, 1343, 1058, 1009, 704 cm^{-1}. ^{13}C NMR (500 MHz, DMSO-d$_6$, 25 °C, ppm) δ: 151, 144, 140, 134, 117, 66; ^{1}H NMR (500 MHz, DMSO-d$_6$, 25 °C, ppm) δ: 6.23 (br, 4H, NH protons of the furazan rings), 3.60 (br, 2H, NH protons attached to the benzene rings); Elemental analysis for $C_{16}H_6N_{18}O_{18}$, Calcd: C 26.03, H 0.82, N 34.15%. Found: C 26.32, H 0.80, N 34.24%.
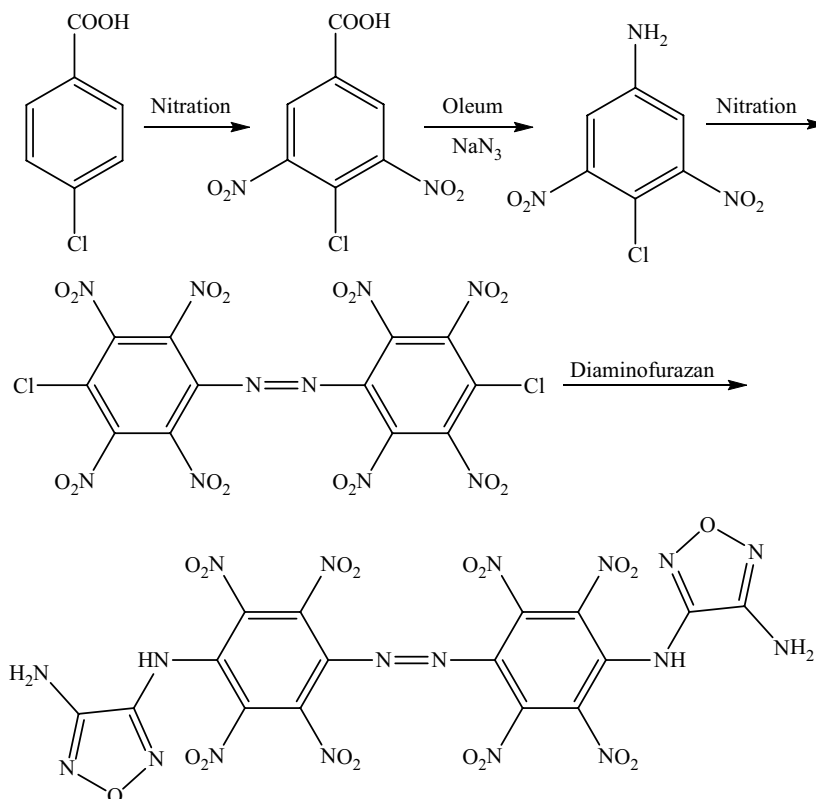

Scheme 1. Synthetic route to BAFDAONAB.

2.4 Physical Properties

2.4.1 Heat of formation (HOF)

HOF is one of the important characteristics for energetic materials and is directly related to the type and number of energetic group in an explosive [14]. All of the calculations were carried out using the program package Gaussian 03 (Revision D.02) [15]. The geometric optimization of the structures and frequency analyses were accomplished by using B3LYP with the 6-31+G** basis set [16], and single point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated by the G2 method [17]. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. The remaining task was to determine the heats of formation, which were computed by using the method of isodesmic reactions or protonation reaction (Scheme 2).
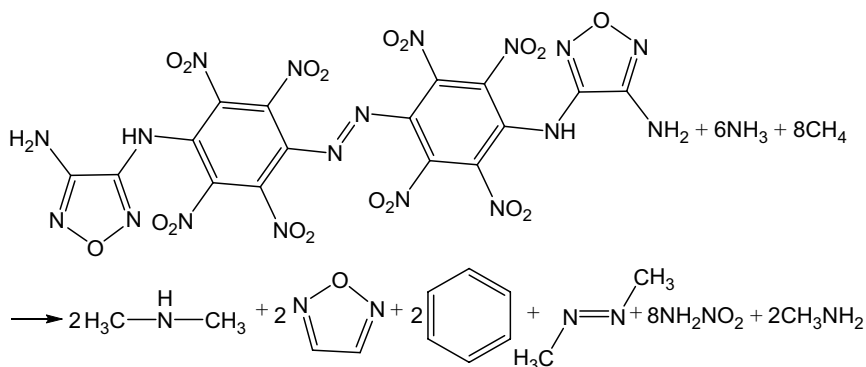
Scheme 2. Isodesmic reaction design for BAFDAONAB.

For the isodesmic reaction, the heat of reaction (ΔH_{298}) at 298 K can be calculated from the following equation:

$$\Delta H_{298} = \sum \Delta H_{f,p} - \Delta H_{f,r}$$

where $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the HOFs of the products and reactants at 298 K, respectively. The experimental HOFs of the reference compounds CH_4, C_6H_6, CH_3NHCH_3, CH_3NNCH_3 and CH_3NO_2 were obtained by combining the MP2/6-311++G** energies. Thus, the HOFs of BAFDAONAB can be calculated once ΔH_{298} is known. The ΔH_{298} can be calculated using the following formula:

$$\Delta H_{298} = \Delta E_0 + \Delta ZPE + \Delta HT + \Delta nRT$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE is the difference between the zero-point energy (ZPE) of the products and the reactants, and ΔHT is the thermal correction from 0 to 298 K. ΔnRT is the work term, which here equals zero.

2.4.2 Detonation pressure and velocity

Detonation performance and detonation pressure are two important performance parameters for energetic materials. The empirical Kamlet-Jacobs equations [18-21] are employed to estimate the values of the detonation velocity (D) and detonation pressure (P) for high-energy materials containing C, H, O, and N, as shown in the following equations:

$$D = 1.01(N\overline{M}^{1/2} Q^{1/2})^{1/2}(1+1.3\rho)$$
$$P = 1.558\rho^2 \, N\overline{M}^{1/2} Q^{1/2}$$

D is the detonation velocity (km/s), P is the detonation pressure (GPa), N is the moles of gas produced per gram of explosive, and $\overline{M}$ is the mean molecular weight of the gaseous detonation products. Q is the heat of detonation (cal/g), and ρ the density of the explosive, which in the case of BAFDAONAB is 1.93 g/cm³. For the explosive $C_aH_bO_cN_d$ studied here [$C_{16}H_6O_{18}N_{18}$], $2a + b/2 > c > b/2$. N, M, and Q were calculated according to following formulae:

$$N = (b + 2c + 2d)/4M$$
$$\overline{M} = (56d + 88c - 8d)/(b + 2c + 2d)$$
$$Q = [28.9b + 94.5(c/2 - b/4) + 0.239 \, \Delta_f H_m]$$

where a, b, c and d are the numbers of C, H, O and N atoms in the explosive, respectively; M is the molecular weight.

3   Results and Discussion

3.1 Synthesis

The synthetic route to BAFDAONAB is shown in Figure 1. For the synthesis of BAFDAONAB [13], the first three steps are similar to the methods used by Mehilal *et al.* [12], with some modifications made to increase the yield in each step, *e.g.* use of fuming nitric acid (100%) and oleum (65%), at higher

concentrations than were used in [13]. By pouring the reaction mixture into cooled saturated salt water instead of water, the yield of stage 1 was increased from 12.8 g (81.2%) to 14.2 g (90.1%). The yields of stages 2 and 3 were also improved from 7.4 g (84%) to 8.02 g (91.1%) and 11.3 g (78.7%) to 12.08 g (86%), respectively. In order to increase the purity of the product in stage 3, ethyl acetate and water were used.

3.2 Spectral studies

The product was characterized by elemental analysis and spectral data (IR and NMR), the purity of BAFDAONAB was determined by High Performance Liquid Chromatography (HPLC). The HPLC results showed that BAFDAONAB was pure. The IR spectrum of BAFDAONAB showed the presence of –NH groups at 3543 and 3654 cm^{-1} and the absence of C−Cl groups in the molecule, which supports the complete substitution of 4,4'-dichloro-2,2',3,3',5,5', 6,6'-octanitroazobenzene with diminofurazan. The ^{1}H NMR spectrum of BAFDAONAB reveals a broad peak at δ 6.2 for the –NH$_2$ protons on the furazan rings and a singlet at δ 3.6 for the −NH protons attached to the benzene rings. The ^{13}C NMR spectrum of BAFDAONAB gave 6 different types of carbon, *i.e.* 151, 144, 140, 134, 117 and 66 for 2,2',6,6' (4C), 3,3',5,5' (4C), 1,1' (2C), 4,4' (2C) and positions C3 and C5 in the substituted furazan rings. From the elemental analysis, the percentages of the elements in BAFDAONAB were in good agreement with the calculated values, which indicated high purity of the synthesized product. The X-ray diffraction patterns of BAFDAONAB showed that it was amorphous.

3.3 Sensitivity and performance studies

The sensitivity and performance properties of RDX, HMX, CL-20, LLM-105 and BAFDAONAB are presented in Table 1. The BAFDAONAB has sensitivity to temperature at 219 °C, as indicated by the TG-DTA thermogram of the corresponding exotherm at 222.6 °C. The TG-DTA plot of BAFDAONAB is shown in Figure 2. The DTA curve shows that an exothermic peak begins at 219.7 °C with a peak maximum at 222.6 °C. The TG curve shows no weight loss until about 141 °C. Beyond 141 °C, the weight loss is slow up to 222.8 °C. After 222.8 °C, the weight loss continues very slowly and the total weight loss becomes about 62% by 400 °C.

The study of the sensitivity of BAFDAONAB revealed that its sensitivities were close to those of TNT. The calculated performance parameters of BAFDAONAB, such as detonation pressure, detonation velocity and density are greater than RDX and close to HMX, but less sensitive.

Table 1.   Comparison of explosive performance and sensitivity

Explosive	Density [g/cm³]	Velocity [km/s]	Pressure [GPa]	Melting point, [°C]	Impact h$_{50}$, [cm]	Friction P, [%]
RDX	1.81	8.61	32.71	205	29	80
HMX	1.91	9.12	36.17	278	26	100
CL-20	2.04	9.46	42.78	-	14	100
TNT	1.68	7.46	21.40	81	61	41
LLM-105	1.91	8.56	34.11	233	117	32
BAFDAONAB	1.93	9.01	35.03	-	63	38
TATB	1.93	7.86	30.00	360	170	0
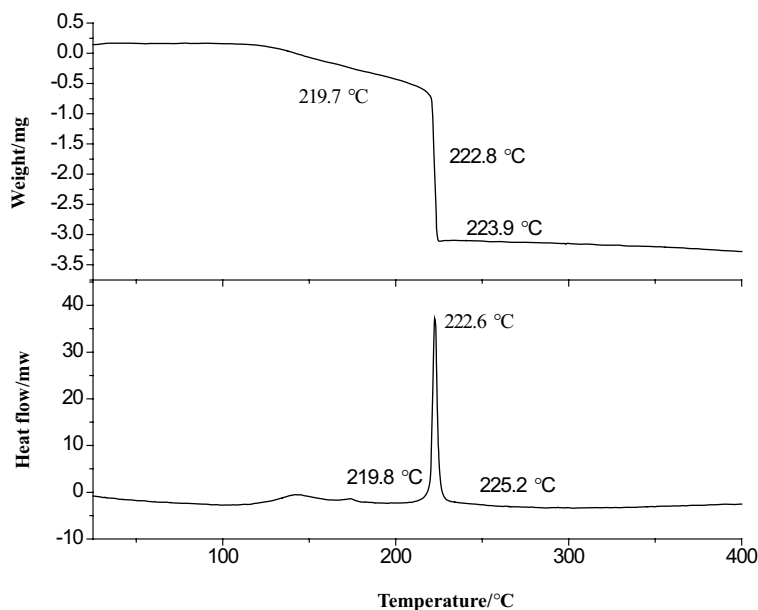
Figure 2.   TG-DTA diagram for BAFDAONAB.

4   Conclusions

We have developed an efficient and straight forward procedure for the synthesis of BAFDAONAB. BAFDAONAB is a new and powerful explosive with the favorable properties of high density, thermal stability and low sensitivity. BAFDAONAB was prepared via a four-step synthetic route and characterized by instrumental techniques including spectral methods. A study of the sensitivity and performance properties of BAFDAONAB shows that its impact sensitivity

is better than most explosives except LLM-105 and TATB, but its detonation velocity and pressure are superior to TATB and LLM-105. Furthermore, the ease with which BAFDAONAB can be prepared from commercially available starting materials suggests that it will be economically valuable for synthesis on a large scale for application in propellant and explosive formulations. Moreover, scale-up of the synthesis of this compound was also examined.

5   References

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