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Benzofuroxan (Benzo[1,2-c]1,2,5-oxadiazole *N*-oxide) Derivatives as Potential Energetic Materials: Studies on Their Synthesis and Properties

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Abstract: The objective of this work was to prepare benzofuroxan derivatives as new, dense, potentially energetic materials and to investigate their properties, with the main focus being on 5,6-dinitrobenzofuroxan (5,6-DNBF). 5,6-DNBF was prepared by a 3-step reaction sequence: a) 1-azido-3-nitrobenzene was synthesized by diazotation of 3-nitroaniline with sodium nitrite and subsequent reaction with sodium azide in acetic/sulfuric mixed acids; b) it was nitrated with HNO_3/H_2SO_4 to 1-azido-2,4,5-trinitrobenzene; c) thermal cyclization of the latter compound in a polar solvent gave the desired 5,6-DNBF (m.p. 177 °C). It was fully characterized by UV/VIS, FT-IR and NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. The density of the compound (X-ray) was found to be comparatively high (1.88 g/cm^3), and to be superior to the previously known, isomeric energetic material − 4,6-dinitrobenzofuroxan (4,6-DNBF) (1.76 g/cm^3). Furthermore, the synthesis of some other benzofuroxan derivatives, potentially interesting as high energy, density materials (HEDMs), has been carried out. The densities of the compounds obtained were calculated using ACD Labs software (version 4.0). Based on the results obtained, it could be concluded that 5,6-DNBF is one of the densest nitro derivatives of the benzofuroxan series, comparable to CL-14, CL-17, CL-18, and thus could have potential applications as an HEDM.

Keywords: heterocyclic nitro compounds, X-ray diffraction, structure analysis, density, HEDM, 5,6-DNBF

Introduction

Since the beginning of the era of benzofuroxan chemistry, the structure of this compound and its intriguing chemistry has been a considerable challenge to organic chemists [1, 2].

At first benzofuroxans were thought to have the dioxime peroxide structure [3, 4], then that of an o-dinitroso-system [2], and only in 1912 were they given the correct structure by Green and Rowe [5].

Benzofuroxan derivatives can exist as a pair of positional isomers. NMR spectroscopy and X-ray crystallography have proved unequivocally that the compounds have the basic structure of benzo[1,2-c]1,2,5-oxadiazole *N*-oxide [6, 7]. The controversy over furoxan and benzofuroxan structures and their reactivity has been exhaustively reviewed [8-10].

A number of nitro-furoxan and -benzofuroxan derivatives attracted attention as high-energy materials in the early 1980s when some primary explosives e.g. potassium [11] and hydroxylamine [12] salts of 4,6-dinitrobenzofuroxan (DNBF) and the potassium salt of hydroxynitrobenzodifuroxan [13]), as well as some secondary nitro-substituted explosives e.g. 4-amino-5,7-dinitrobenzofuroxan (ADNBF), 4,6-diamino-5,7-dinitrobenzofuroxan (CL-14), 4-amino-5,6,7-trinitrobenzofuroxan (CL-17), aminonitrodibenzofuroxan, (CL-18) ('CL' is the assignation for Naval Air Weapons Station, China Lake, USA) and benzotrifuroxan (BTF) were developed [11, 14-16]. The largest part of the work in this field has been carried out in the USA, the USSR, Australia and China. We have previously assessed the physico-chemical parameters of benzofuroxan compounds and examined their biochemical, biomedicinal, electrochemical and ecotoxicological properties [17-21]. Herein is reported an investigation of the structural peculiarities and densities of nitro-substituted benzofuroxan derivatives as HEDMs, with particular attention being paid to 5,6-DNBF as a potential HEDM.

Materials and Methods

Chemical reagents and materials

All chemical reagents and solvents were obtained from Sigma-Aldrich, Fluka and Merck, and were used as supplied.

Samples of benzofuroxan [5], 4- and 5-nitrobenzofuroxans [22, 23], 4,6- and 4,7-dinitrobenzofuroxans [8, 24], amino-/ nitroderivatives of benzofuroxan, i.e. CL-14 and CL-17 [25], CL-18 [26] were synthesized and characterized in

our laboratory according to the conventional procedures as reported previously [17-21]. Benzodifuroxan (BDF), nitrobenzodifuroxan and benzotrifuroxan (BTF) were prepared as described in [24, 27, 28].

The preparation of 5,6-dinitrobenzofuroxan (5,6-DNBF), which has still received insufficient study, is described in detail in the experimental part of this paper. The synthesis of 5,6-DNBF provided below *via* a 3-step reaction sequence is a modification of Bailey and Case's method [24].

Experimental

General

The melting points of the compounds synthesized were determined in open capillaries. The purity of the compounds was monitored by TLC using silica gel 60 F254 aluminium plates (Merck). UV-VIS spectra of the compounds were recorded using a Perkin-Elmer Lambda 25 UV-VIS spectrophotometer. IR spectra were recorded in KBr on a Perkin-Elmer spectrophotometer (FT-IR Spectrum BX II). NMR spectra were recorded using a Varian Unity Inova (300 MHz for ^{1}H NMR). HRMS spectra were obtained on a mass spectrometer Dual-ESI Q-TOF 6520 (Agilent Technologies).

Gas chromatography-mass-spectrometry (GC-MS) analyses were performed using a gas chromatograph (Agilent 6890N; Agilent technologies, CA, USA) and a mass spectrometer (Autospec Premier; Waters-Micromass technologies, USA) equipped with a MS detector (HRMS Autospec Premier). The temperature-programmable gas chromatograph, suitable for split-less injection, was equipped with a 30 m × 0.25 mm fused-silica capillary column (J&W Scientific DB-5MS), with 0.25 μm coating thickness and helium as the carrier gas at a flow rate of 1 ml/s. The column temperature was set at 100 °C for 1 min, then increased at 5 °C/min to 220 °C and held for 4 min. The sample injection temperature was set at 220 °C. During the full-scan acquisition, the mass spectra were collected over a scanning mass range 40 to 500 amu every 1 s or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

For X-ray analysis a 'Bruker-Nonius' diffractometer with a 'KappaCCD' detector was used. In the crystal structure hydrogen atoms were located and refined.

Chemical software ACD Labs (Toronto) (version 4.0, 2000) was used for the calculation of the molecular properties and densities of 4-nitrobenzofuroxan, 5-nitrobenzofuroxan, and 4,7-dinitrobenzofuroxan, for which experimental densities were not available.

CAUTION! 1-Azido-3-nitrobenzene and 1-azido-2,4,5-trinitrobenzene are dangerous energetic materials with increased sensitivities towards various stimuli. Extra safety precautions should be taken, especially when 1-azido-2,4,5-trinitroderivative is prepared on a large scale.

Synthesis

Synthesis of 1-azido-3-nitrobenzene

3-Nitroaniline (10.00 g, 71 mmol) was added in portions to a vigorously stirred mixture of acetic acid (99%) (80 ml) and H_2SO_4 (98%) (40 ml) at 10-15 °C. Stirring was continued until all of the solids had completely dissolved.

Any insoluble material was filtered off and the resultant clear, yellow solution was cooled in an ice-water bath to 0 °C. $NaNO_2$ (5.65 g, 81.65 mmol) dissolved in H_2O (15 ml) was then added with stirring at 4-6 °C during 30 min. A solution of urea (0.63 g, 10 mmol) in H_2O (2 ml) was added. The reaction mixture was then stirred again for an additional 30 min. Subsequently a solution of NaN_3 (5.2 g, 80 mmol) in H_2O (27 ml) was added drop-wise and stirring was continued for another l h at 6-9 °C. The yellowish solid produced was filtered off on a porous glass filter and dried in the dark. The product, 1-azido-3-nitrobenzene, which consisted of yellowish, lustrous crystals in the form of needles, had m.p. 53-54 °C (yield: 11.35 g, 97%).

FT-IR (KBr tablet, ν/cm^{-1}) 2124 (s, br, asym, N_3), 1529 (s, br, asym, NO_2), 1350 (s, br, sym, NO_2).

^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.00-7.96 (m,1H), 7.88 (t, J= 2.1Hz, 1H), 7.52 (t, J= 8.0 Hz, 1H), 7.33 (dd, J=1.8, 7.6 Hz, 1H);

Synthesis of 1-azido-2,4,5-trinitrobenzene

1-Azido-3-nitrobenzene (10 g, 61 mmol) was carefully added in small portions and dissolved with stirring in HNO_3 (98%) (150 ml) which was cooled to 3-5 °C in an ice-water bath. H_2SO_4 (98%)(200 ml) was added portion-wise to the resultant solution at 0-5 °C and the mixture was stirred and cooled for an additional 3 h. It was then poured onto crushed ice (750 g) and the resultant solid was collected and washed with cold water. The 1-azido-2,4,5-trinitrobenzene obtained was re-crystallized from methanol to yield yellow crystals (12.9 g, 83%), m.p. 74 °C, which can be used in the next step without further purification.

FT-IR (KBr tablet, ν/cm^{-1}): 2147 (s, br, asym, N_3), 1553 (s, br, asym, NO_2), 1376 (s, br, sym, NO_2).

Synthesis of 5,6-dinitrobenzofuroxan (5,6-DNBF)

1-Azido-2,4,5-trinitrobenzene (3 g, 11.81 mmol) was dissolved in acetic acid (30 ml) and heated (3 h) at 105-115 °C. The yellow solution obtained was concentrated *in vacuo* (80-85 °C) until the first crop of crystals started to separate, and then allowed to cool to room temperature. Repeated recrystallization of the product from acetic acid gave 5,6-dinitrobenzofuroxan (5,6-DNBF) (yield 2.08 g, 78%, m.p. 177 °C).

Spectral characteristics:

UV-VIS: λ_{max} = 202 nm (ε_{202} = 4980 M^{-1} cm^{-1}); λ_{max} = 260 nm (ε_{260} = 14500 M^{-1} cm^{-1}); λ_{max} = 382 nm (ε_{382} = 21700 M^{-1} cm^{-1}).

FT-IR (KBr tablet, ν/cm^{-1}): 1783w, 1624s (br), 1607s, 1541s,1528s (br, asym, NO2), 1471m, 1407w, 1349s (s, br, sym, NO2), 1224w, 1192m, 1102w, 1026m, 898s, 856s, 815w, 780s, 747s, 722w, 684m, 657m, 651m, 608w.

^{1}H NMR spectrum (300 MHz, $CDCl_3$): singlet at 8.29 ppm (H4 and H7).

EI MS *m/z*: (relative abundance, %): 228, (12.5), (227) (8.1), 226 (76.3), 212 (13.8), 210 (65.6), 196 (29.7), 166 (3.9), 136 (7.5), 118 (16.3), 106 (15), 89 (10), 88 (78,1), 87 (38.8), 76 (56.9), 75 (29.4), 74 (41.3), 73 (21.2), 68 (10), 67 (11.3), 64 (11.6), 63 (30), 62 (100), 61 (87.7), 53 (29.9), 52 (16.9), 51 (18.1), 50 (18.7), 46 (21.9).

Results and Discussion

Synthesis of benzofuroxan compounds

The preparation of benzofuroxan and many of its nitro derivatives has been extensively described in previous papers and reviewed by Katritzky and Gordeev (1993) [29].

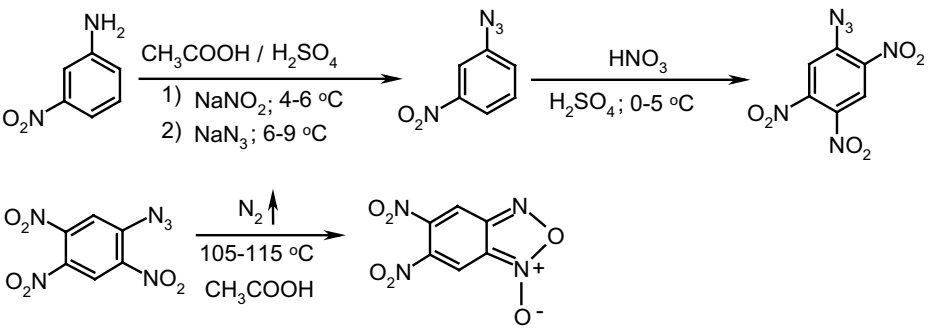
However 5,6-dinitrobenzofuroxan (5,6-DNBF) is a very uncommon substance in the scientific literature. A number of incorrect structures for this compound were suggested prior to the modern era of NMR spectroscopy [1, 30]. Previous authors had actually obtained not 5,6- but the isomeric 4,6-dinitrobenzofuroxan (it must be noted that the melting points of these two isomers differ by only 5 degrees: 172 °C (for 4,6-DNBF) [31] and 177 °C (for 5,6-DNBF). For this reason, 5,6-DNBF was synthesized and its structure re-investigated by mass-spectrometry and X-ray diffraction methods. The synthesis of 5,6-DNBF described here is a modification of the method of Bailey et al. [24].

Synthesis of 5,6-DNBF

The starting compound 1-azido-3-nitrobenzene was prepared by the reaction

of 3-nitroaniline with $NaNO_2$ in a cold mixture of acetic and sulfuric acids to yield the diazonium salt. The diazonium salt was then reacted with NaN_3 to yield 1-azido-3-nitrobenzene. The reaction product was isolated as a yellow solid, which after recrystallization from ethanol, gave crystals in the form of pale yellow, thin needles (which subsequently darkened and turned brown on prolonged exposure to daylight).

The 1-azido-3-nitrobenzene was nitrated with mixed acid (HNO_3/H_2SO_4) at 0-5 °C to give 1-azido-2,4,5-trinitrobenzene (Scheme 1).



Scheme 1. Synthesis of 5,6-DNBF.

The latter product was recrystallized from methanol and dried in a vacuum desiccator in the dark. 1-Azido-2,4,5-trinitrobenzene was thermally cyclized in boiling acetic acid until no further N_2 gas evolution was observed (normally about 3.5-4 h). 5,6-DNBF was obtained as a yellow solid, m.p. 177 °C.

Spectroscopic investigation

As shown in Figure 1, the UV-VIS absorbance spectrum of 5,6-DNBF in acetonitrile was characterized by absorbance maxima at 202, 260 and 382 nm, and molar extinction coefficients (ε), (obtained from the linear dependence of the absorbance of the compound at various concentrations), equal to 4.98×10^3, 1.45×10^4, and 2.17×10^4 M^{-1} cm^{-1} respectively. The UV-VIS spectrum of the meta-isomer, 4,6-DNBF recorded under the same conditions, was different, i.e. characterized by absorbance maxima at 210, 257, 277 and 418 nm with ε values of 6.33×10^3, 9.73×10^3, 9.56×10^3 and 1.58×10^4 respectively.

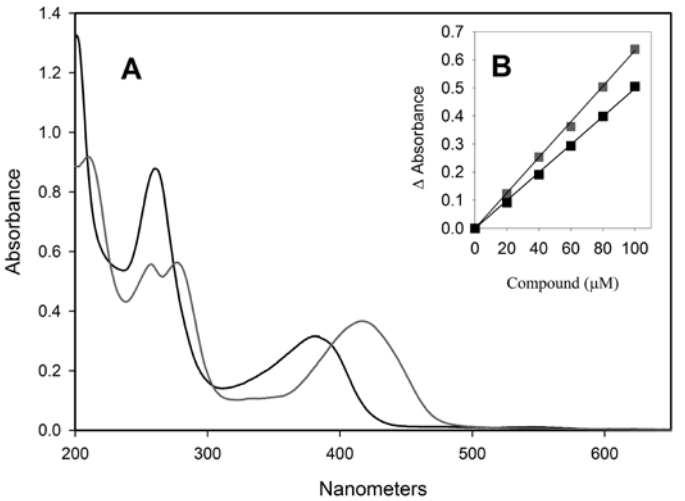


Figure 1. (A)UV-VIS absorbance spectra of 60 μM 5,6-DNBF (black) and 4,6-DNBF (gray). (B) The dependence of absorbance of 4,6-DNBF (black) and 5,6-DNBF (gray) upon concentration, as measured at the absorbance maxima 418 nm and 382 nm as characteristic for 4,6- and 5,6-DNBF respectively.

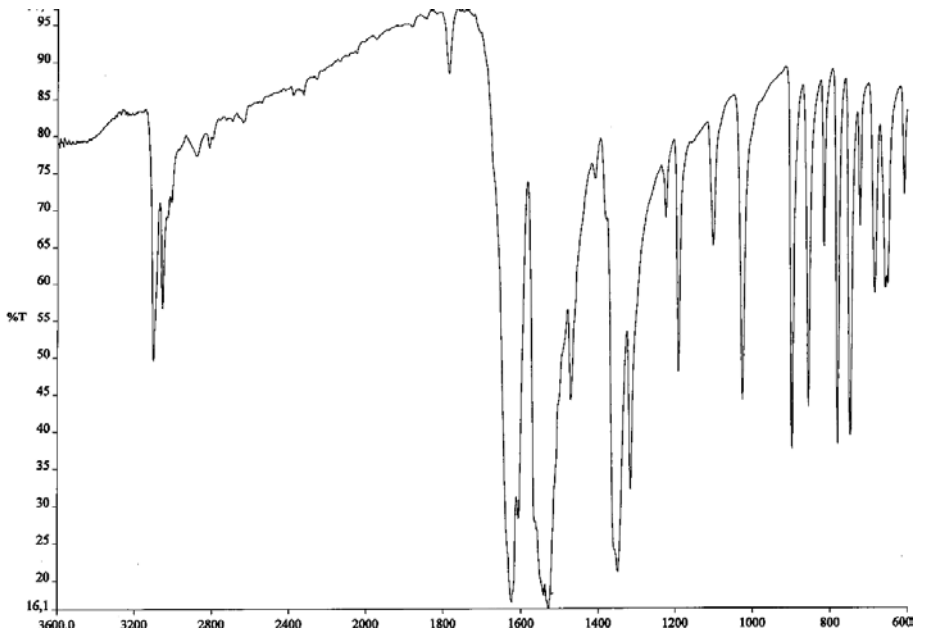


Figure 2. FT-IR spectrum of 5,6-DNBF in KBr tablet (4000-600 cm^{-1}).

The FT-IR spectrum of 5,6-DNBF recorded in the range of 4000-600 cm^{-1} as a KBr tablet is shown in Figure 2.

The FT-IR spectra of the two dinitrobenzofuroxan isomers investigated also contain significant differences between the typical characteristic peaks (the characteristic peaks of both spectra are compared below in Table 1).

Table 1. The characteristic vibration peaks of the FT-IR spectra of 5,6- and 4,6-DNBF

Dinitrobenzofuroxan	ν (cm^{-1})
5,6-DNBF	3112m, 3052m, 1783w, 1624s, 1607s, 1541s, 1528s, 1471m, 1407w, 1389s, 1349s, 1224w, 1192m, 1102w, 1026m, 898s, 856s, 815w, 780s, 747s, 722w, 684m, 657m, 651m, 608w.
4,6-DNBF	3090m, 1806w, 1629s, 1611s, 1562s, 1538s, 1490w, 1457m, 1415w, 1393w, 1345s, 1329s, 1278w, 1220w, 1193w, 1092w, 1067m, 1035w, 987w, 931w, 906w, 847w, 817w, 791w, 764w, 733m, 697m, 652w.

As can be seen from Table 1, the main differences are in the regions of the vibration peaks of the aromatic protons, i.e. two separate peaks at 3112 and 3052 cm^{-1} (Ar-H) for 5,6-DNBF and only one broader peak for 4,6-DNBF at 3090 cm^{-1}. The two pairs of bands of the stretching vibrations of the nitro groups also differs substantially, i.e. 1541s, 1528s and 1389s, 1349s for 5,6-DNBF, and 1562s, 1538s and 1345s, 1329s cm^{-1} for 4,6-DNBF.

The ^{1}H NMR spectrum of 5,6-DNBF (300MHz, $CDCl_3$, δ, ppm) showed that the compound contains only one singlet peak at 8.29 ppm (H4 and H7), while the spectrum of 4,6-DNBF, recorded under the same conditions was characterized by peaks at 9.17 (H5) and 8.87 ppm (H7), with coupling constant $^{4}J_{5/7}$ = 1.8 Hz.

Different crystal fractions of the synthesized 5,6-DNBF were investigated by scanning electron microscopy (SEM).

Figures 3a and 3b demonstrate the SEM investigation of two samples of the product obtained .

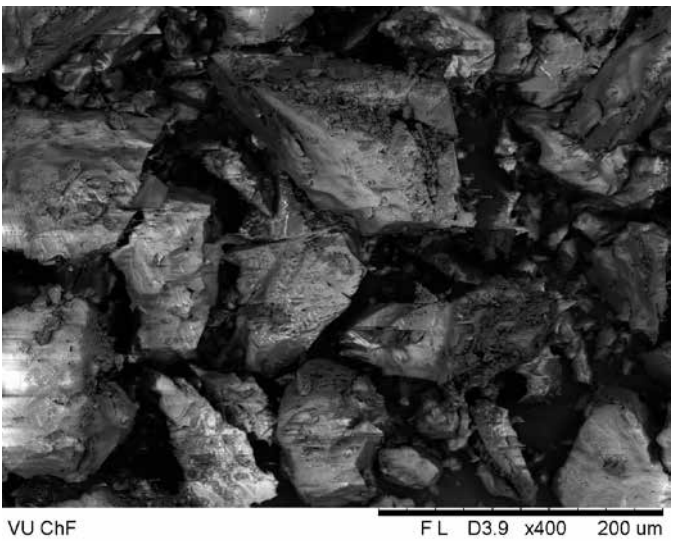


Figure 3a. SEM image of 5,6-DNBF crystals obtained directly from the thermolysis reaction medium (magnification ×400).

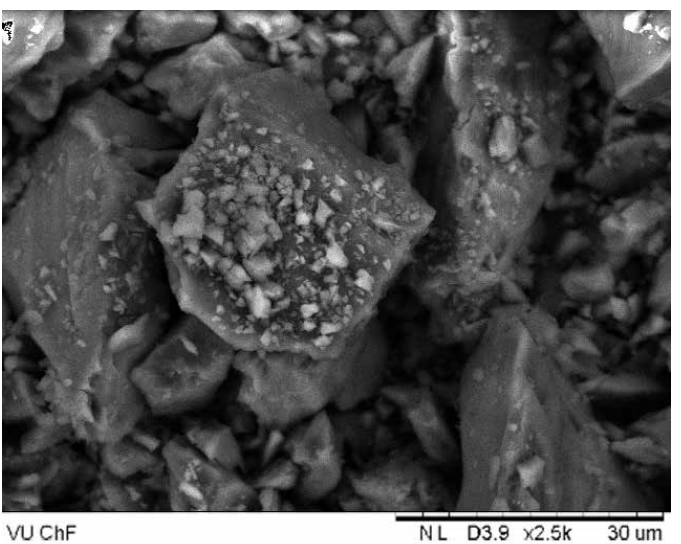


Figure 3b. SEM image of 5,6-DNBF crystals obtained from the third recrystallization from acetic acid (magnification ×2500).

The SEM images obtained (Figures 3a and 3b) clearly demonstrate the typical crystallization habit of 5,6-DNBF, as massive, dense, prismatic crystal chunks.

The final sample (shown in Figure 3b) was re-crystallized from acetic acid and yellow, well-ordered crystals (prisms), suitable for X-ray analysis, were obtained. Separate crystals were selected under a microscope at a magnification ×40.

Identification of nitrobenzofuroxans by GC-MS spectrometry

In order to confirm the structures of benzofuroxan and its isomeric nitro-substituted derivatives, including 5,6-DNBF (Figure 4), high-resolution GC-MS was applied. The spectra obtained are presented in Figures 5-9.

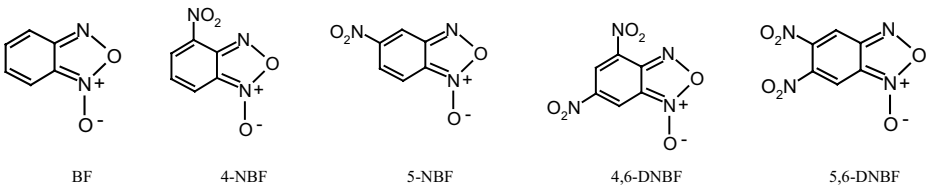


Figure 4. Formulae of selected benzofuroxans analyzed by mass-spectrometry.

(*Assignations*: BF (benzofuroxan), 4-NBF (4-nitrobenzofuroxan), 5-NBF (5-nitrobenzofuroxan), 4,6-DNBF (4,6-dinitrobenzofuroxan) and 5,6-DNBF (5,6-dinitrobenzofuroxan)).

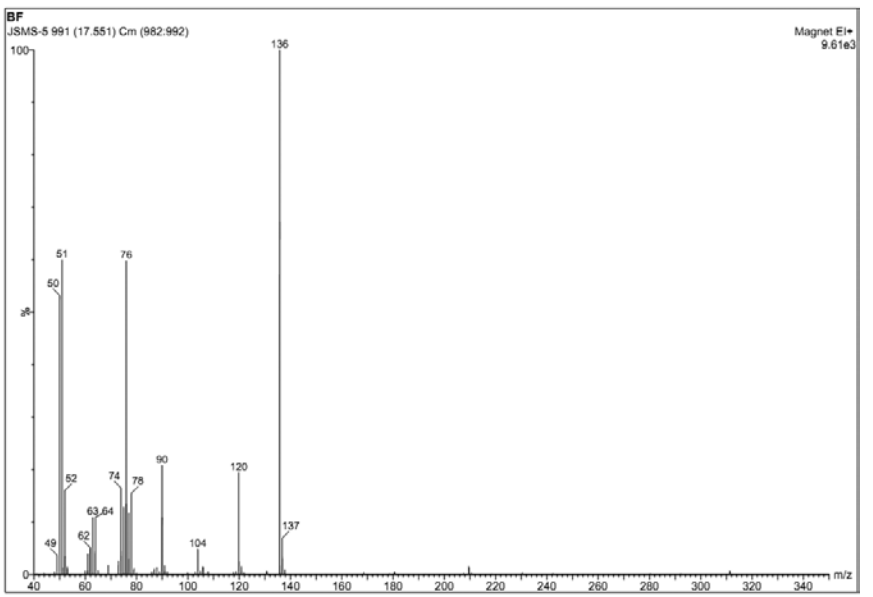


Figure 5. EI mass spectrum of benzofuroxan (BF) (M^+=136).

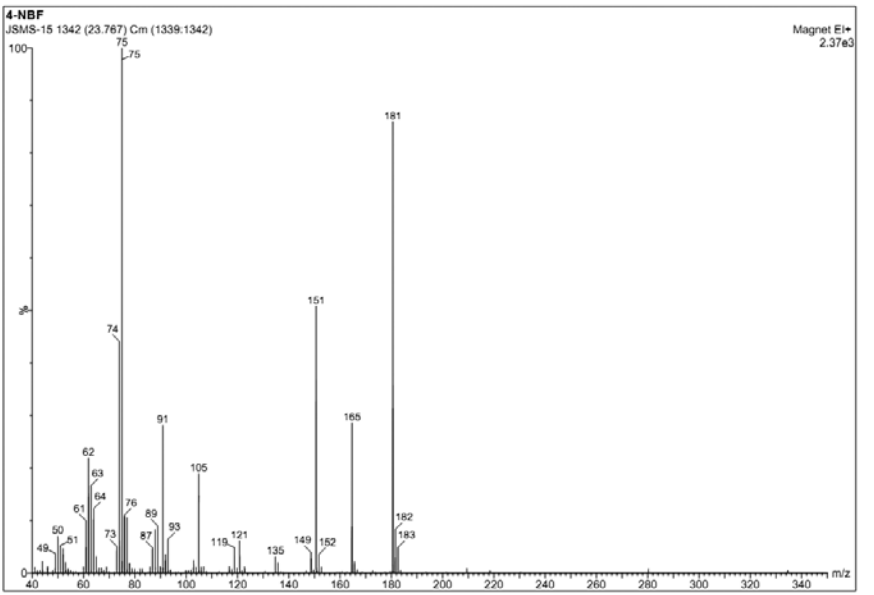


Figure 6. EI mass spectrum of 4-nitrobenzofuroxan (4-NBF) (M^+=181).

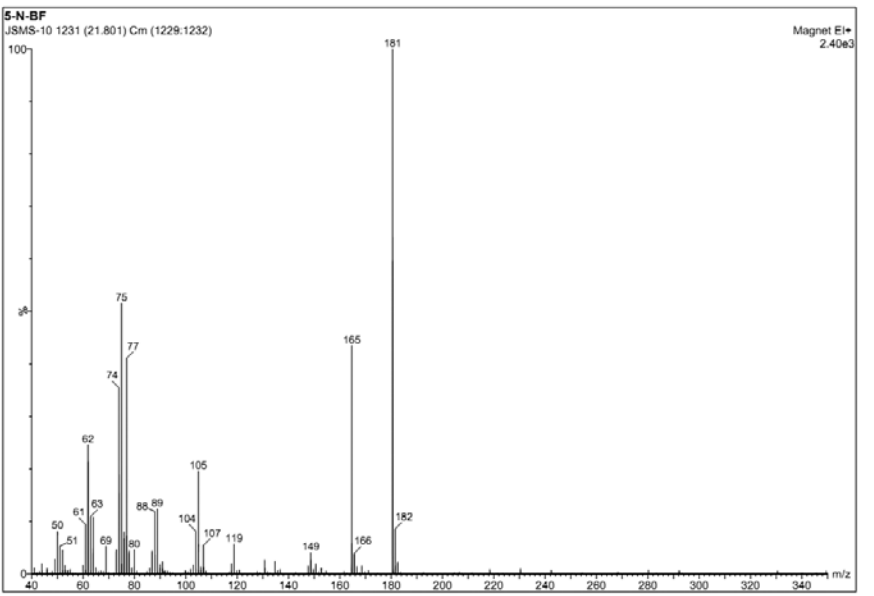


Figure 7. EI mass spectrum of 5-Nitrobenzofuroxan (5-NBF) (M^+=181).

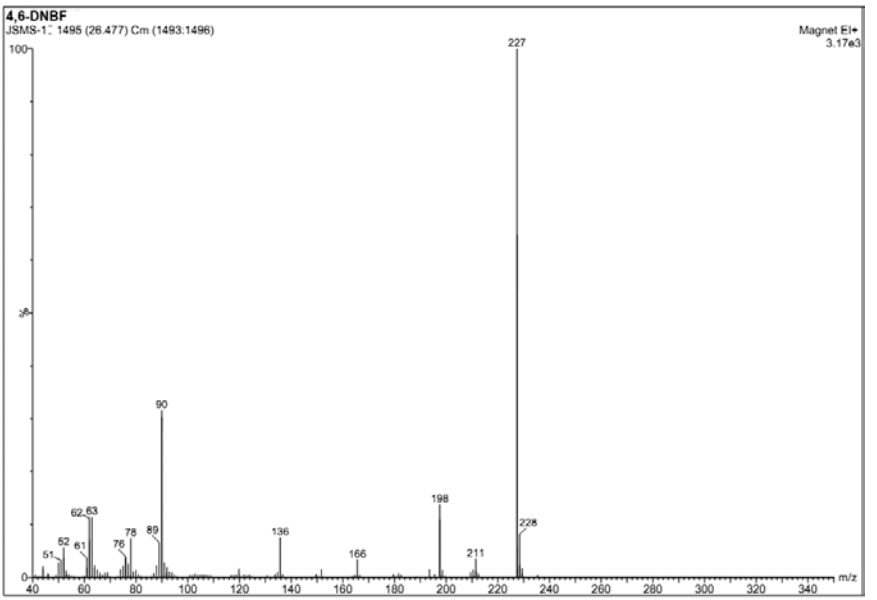


Figure 8. EI mass-spectrum of 4,6-dinitrobenzofuroxan (4,6-DNBF) ($[M+H]^+$=227).

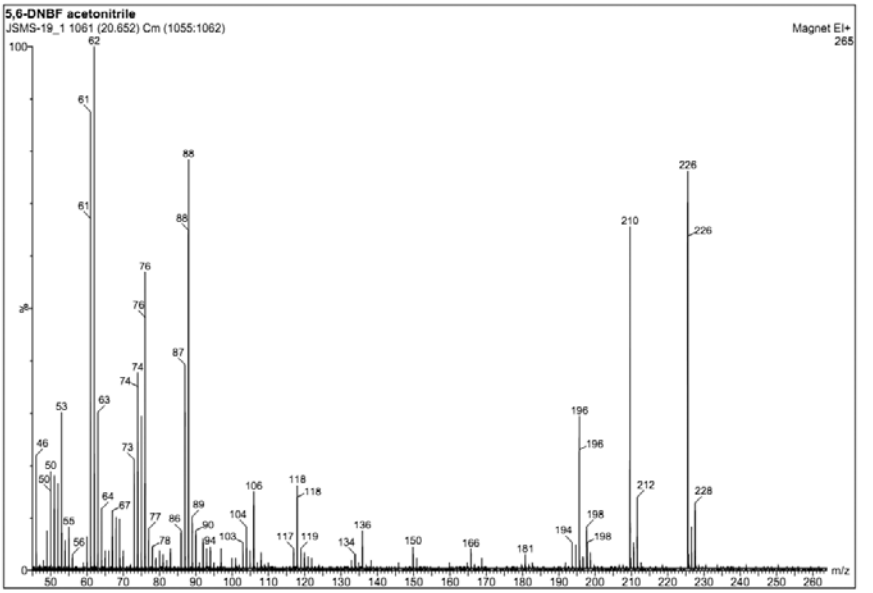
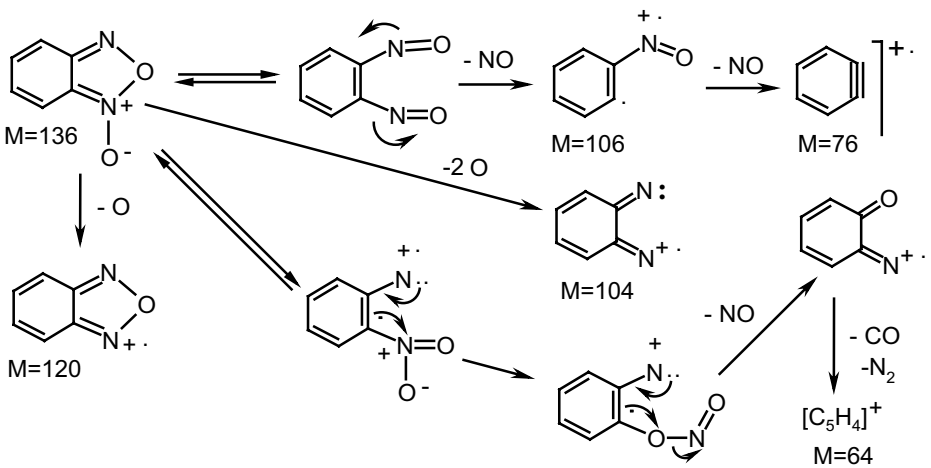


Figure 9. EI mass-spectrum of 5,6-dinitrobenzofuroxan (5,6-DNBF) (M^+=226).

Benzofuroxan was included in the set of materials tested as the parent compound. Its fragmentation scheme is typical and was previously investigated and described in detail by Dyal [32]. However, the author obtained the mass spectrum under conditions which were different from those used in our experiments.

After electron ionization, the fragmentation of the benzofuroxan molecular ion M^+ follows a general pathway i.e. *N*-oxide moiety in position *N*(1) readily loses oxygen (M^+ -16) yielding benzofurazan. The fragmentation of benzofuroxans is concurrent with the elimination of the full fragment (-2NO) of the furoxan moiety (M^+-60). Other possible fragment species are shown in Scheme 2.



Scheme 2. Typical GC-MS benzofuroxan EI fragmentation and possible fragment species involved.

In general, all of the 5 benzofuroxans investigated follow the proposed fragmentation scheme. However, every mass spectrum is unique and it was observed that the peaks generated, registered under identical experimental conditions, were very specific for each compound investigated (Figures 5-9). The mass spectra obtained for the two pairs of isomers: 4- and 5-nitro- benzofuroxans and 4,6- and 5,6-dinitrobenzofuroxans, demonstrate significant differences in their fragmentation patterns as can be seen from the data in Table 2.

Table 2. Fragmentation of the benzofuroxans investigated (*m/z* value, % of relative abundance) (base peaks are underlined)

Compound	Mol. ion, $M^{+\bullet}$	$M^{+\bullet}$ - O	$M^{+\bullet}$ - NO	$M^{+\bullet}$ - 2O	$M^{+\bullet}$ -NO_2	$M^{+\bullet}$ -CO -NO	$M^{+\bullet}$ - 2NO	Other peaks
BF	<u>136 (100)</u>	120 (19.5)	106(5.0)	104(1.7)	90(20.9)	78(15.6)	76 (59.6)	51(59.8) 50(53.1)
4-NBF	181(89.6)	165 (28.5)	151(50.9)	149(3.9)	135(3.1	123(1.2)	121 (6.1)	<u>75(100)</u>$^{\#}$ ($M^{+\bullet}$-NO_2 -2NO)
5-NBF	<u>181(100)</u>	165 (43.5)	151(1.8)	149(4.0)	135(2.5)	absent	121 (0.7)	75(51.4)$^{\#}$ ($M^{+\bullet}$-NO_2 -2NO)
5,6-DNBF	226 (76.3) 227(8.1) $[M+H]^+$ 228(12.5) $[M+2H]^+$	210 (65.6) 211 (5.0) ($[M+H]^+$-O) 212 (13.8) ($[M+2H]^+$ -O)	196 (29.7); 198(8.1) ($[M+2H]^+$ -NO)	194(5.2)	180 (0.6) 182(0.6) ($[M+2H]^+$ -NO_2)	169(1.9) ($[M+H]^+$ -CO-NO)	166 (3.9)	<u>62 (100)</u> (<u>$NO_3^{\bullet}$</u>)
4,6-DNBF	226(0); <u>227(100)</u> $[M+H]^+$ 228(8.1) $[M+2H]^+$	210 (0.6) 211 (3.4) ($[M+H]^+$-O) 212 (1.3) ($[M+2H]^+$ -O)	196 (0.4) 198(13.7) ($[M+2H]^+$ -NO)	194(1.8)	182(0.6) ($[M+H]^+$ -NO_2)	absent	166 (3.4)	120(1.5); 90(31.7); 62(11.2) (<u>$NO_3^{\bullet}$</u>)

The base peak in the mass-spectrum of 5-nitrobenzofuroxan is the molecular ion ($M^{+\bullet}$, mass 181), whilst in the case of the isomeric 4-nitrobenzofuroxan, it is the benzyne [C_6H_3] fragment with mass 75, which is derived from the parent molecular ion by loss of (NO_2+2NO).

In the case of 4,6-dinitrobenzofuroxan, which is a well-known super-electrophilic nitrocompound [33, 34], there are numerous adduct ions, $[M+H]^+$ (as the base peak, mass: 227) and the less abundant $[M+2H]^+$. Both of these ions fragmented further in the ordinary way by losing O, NO and NO_2 respectively, together with typical fragments such as $[M-2NO]^+$, $[M-(NO+NO_2)]^+$, etc. Similar adduct ions can also be seen with 5,6-DNBF. However, in this case their intensity is much lower. Marked differences in the fragmentation patterns of EI GS-MS spectra could be used to easily distinguish one isomer from another.

X-Ray analysis of 5,6-DNBF

A sample of 5,6-DNBF was re-crystallized three times from acetic acid. The last crystallization was carried out with a slow solution temperature gradient and the crystal suitable for crystallographic analysis was carefully selected by microscopic examination (under magn. ×40). The structure is shown in Figure 10 and selected structural parameters are given in Table 3.

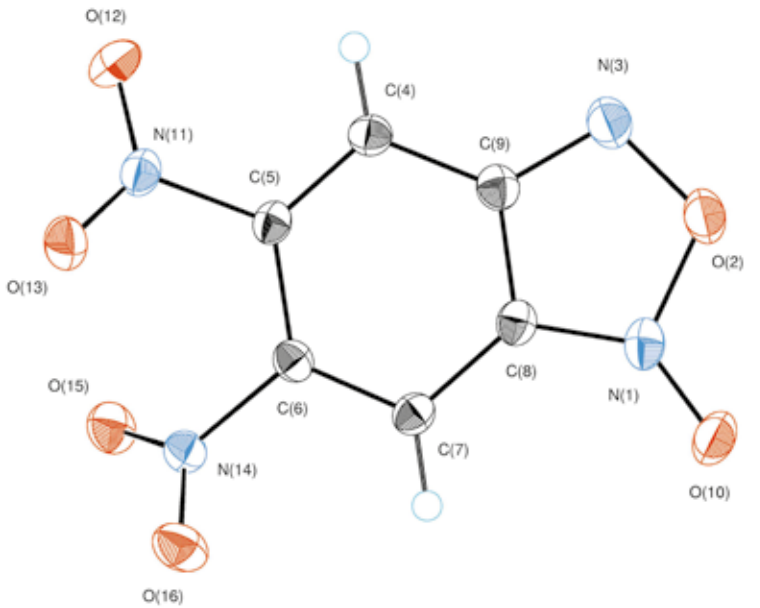


Figure 10. Molecular structure of 5,6-DNBF. Thermal ellipsoids in structure depiction are drawn with 50% probability.

Table 3. 5,6-DNBF X-ray structure determination: selected data and parameters

Formula	$C_6H_2N_4O_6$
Form. weight [g mol^{-1}]	226.103
Crystal system	orthorhombic
Space group	P b c 21
Color/ Shape	yellow prisms
Size [mm]	0.24 x 0.19 x 0.12
a [Å]	5.4751(2)
b [Å]	10.9799(4)
c [Å]	13.2925(5)
α [°]	90.00
β [°]	90.00
γ [°]	90.00
V [Å^3]	799.09(5)
Z	4
$\rho_{calc.}$[g/cm^3]	1.880
μ [mm^{-1}]	0.172
F(000)	456
$\lambda_{MoK\alpha}$ [Å]	0.71073
T [K]	153(2)
Θ Min-Max [°]	3 , 30
Dataset	-7:7; -15:15; -18:18
Reflections collected	2134
Independent reflections	2019
Parameters	152
R_1(obs)	0.0154
wR_2 (all data)	0.0769
GooF	1.038
Device type	'Bruker-Nonius KappaCCD'
Solution	SHELXS-97
Refinement	SHELXL-97
Absorption correction	none

* *More extended results of the X-ray diffraction analysis will be published elsewhere.*

The 5,6-DNBF crystal system is orthorhombic; space group – P b c 21; with a cell volume of 799.09(5) Å^3. The crystal size used for the determination was [mm]: 0.24 × 0.19 × 0.12; color and shape: yellow prisms; density: 1.880 g/cm^3. According to literature data [35], the isomeric 4,6-DNBF crystal system was

monoclinic, space group – $P2_1$ and it consisted of yellow-brown crystals with a density of 1.761 g/cm^3.

In the 4,6-DNBF molecule, the 6-nitro group is almost coplanar with the ring, whilst in the 5,6-DNBF molecule, both nitro groups are at different angles to the ring plane: 29.7° for 5-NO_2 and 46.5° for 6-NO_2.

Interestingly, the nitro groups in the molecular structure of the fairly similar 1,2-dinitrobenzene, are at almost the same angle, i.e. 41.5 and 41.4° to the benzene ring, but the density of this material is much lower – only 1.573 g/cm^3 [36]. This fact allows us to conclude that the influence of the furoxan fragment on the total density of 5,6-DNBF is very significant.

Experimental and calculated physico-chemical characteristics of benzofuroxans

All of the data concerning the main characteristics of the benzofuroxan compounds were collected for comparison and analysis in Table 4. The densities of 4-nitrobenzofuroxan, 5-nitrobenzofuroxan and 4,7-dinitrobenzofuroxan, which are absent from the databases, were calculated using ACD Labs (Toronto) (vers. 4.0) software and are marked as 'calc.':

Table 4. The main properties of benzofuroxans

No.	Compound	Formula	Mol. weight	Melt. point, °C	Density (g/cm^3), (crystal properties) [lit. refs]
1	Benzofuroxan	$C_6H_4N_2O_2$	136.11	71	1.55*(exp.) (triclinic, SG***: *P*1) [37]
2	4-Nitrobenzo-furoxan	$C_6H_3N_3O_4$	181.11	143	1.62 (calc.)
3	5-Nitrobenzo-furoxan	$C_6H_3N_3O_4$	181.11	73	1.65 (calc.)
4	4,6-Dinitrobenzo-furoxan	$C_6H_2N_4O_6$	226.10	173	1.76*(exp.) (monoclinic, SG: $P2_1$) [35]
5	5,6-Dinitrobenzo-furoxan	$C_6H_2N_4O_6$	226.10	177	1.88** (exp.) (1,91(calc.) (orthorhombic, SG: P b c 21)
6	4,7-Dinitrobenzo-furoxan	$C_6H_2N_4O_6$	226.10	182 (with dec. [7])	1.72 (calc.)

7	4-Amino-5,7-dinitrobenzofuroxan (ADNBF)	$C_6H_3N_5O_6$	241.12	270	1.90* (exp.) [38]
8	4,6-Diamino-5,7-dinitrobenzo-furoxan (CL-14)	$C_6H_4N_6O_6$	256.13	289-294 (with dec.)	1.95* (exp.) [39]
9	5-Amino-4,6,7-trinitrobenzo-furoxan (CL-17)	$C_6H_2N_6O_8$	286.12	175 (with dec.)	1.94* (exp.) [9]
10	4-Amino-5-nitrobenzodifuroxan (CL-18)	$C_6H_2N_6O_6$	254.12	205	1.932* (exp.) (orthorhombic, SG: $P2_12_12_1$) [26]
11	Benzodifuroxan (benzo[1,2-c;3,4-c'] bis[1,2,5]oxadi-azole 1(or 3),6-dioxide) (BDF)	$C_6H_2N_4O_4$	194.11	95	1.76* (exp.) [8]
12	4-Nitrobenzodi-furoxan (NBDF)	$C_6HN_5O_6$	239.10	158	1.840*(SG: Pna21) [28]
13	Benzotrifuroxan (BTF)	$C_6H_6O_6$	252.10	198-200	1.901* (SG: Pna21) [27] 1.912* (SG: P1121/a) [40]

*Density values were taken from the literature sources.
**Density value for 5,6-DNBF was obtained from the experimental X-ray data in the present work.
***SG – assigned crystal space group.

The density of an energetic material is one of the most important characteristics of a high-performance explosive and is closely related to the velocity and pressure of detonation, as is well-known from the literature [39].

The densities of the nitro-substituted benzofuroxans investigated varied from 1.62 (4-nitrobenzofuroxan) to 1.88 g/cm^3 (5,6-DNBF), whilst amino/nitro- derivatives were found to possess slightly higher densities, i.e. from 1.90 (ADNBF) to 1.95 g/cm^3 (CL-14). In comparison, the density of HMX, a classical HEDM, is 1.90 g/cm^3 [25].

Conclusions

Previously studied nitroaromatic compounds, which can be used as energetic materials, differ widely in density, from 1.65 g/cm^3 for TNT to 2.0 g/cm^3 for

HNB (hexanitrobenzene) [28].

Theoretical calculation of density allows us to select the very uncommon dinitrobenzofuroxan isomer, 5,6-DNBF, as a potentially interesting compound for our further in-depth study.

The following conclusions can be drawn from this experimental study:

5,6-DNBF (5,6-dinitrobenzofuroxan or 5,6-dinitrobenzofurazan-*N*-oxide, molecular formula - $C_6H_2N_4O_6$) has been synthesized in 78% yield by thermolysis of 1-azido-2,4,5-trinitrobenzene. The GC-mass-spectra of isomeric mono- and dinitrobenzofuroxans possess marked differences in fragmentation and are very useful for the rapid-analysis of these substances and for isomer characterization.

The crystal structure of 5,6-DNBF was determined, and a high experimental density (1.880 g/cm^3) and a comparatively high melting point (177 °C) were observed, demonstrating great potential for a more detailed investigation of this substance as an HEDM.

A comparison of the crystal properties and experimental densities of two similar molecular structures, both ortho-dinitro benzene derivatives viz. 1,2-dinitrobenzene and 5,6- DNBF, supports the theory that the positive influence of the furoxan fragment on the total density of 5,6-DNBF is very significant (density: 1,2-DNB 1.573 g/cm^3 [36], 5,6-DNBF 1.880 g/cm^3).

It can also be concluded that the denser isomer 5,6-DNBF could be superior, in terms of energetic properties, to the well-known 4,6-DNBF.

Moreover, the data obtained in the present work can be useful for the design of further new HEDMs.

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