Nitroanilinodinitrobenzofuroxans—synthesis, characterisation, thermal stability and explosive properties

Mehilal, A. K. Sikder,* R. B. Salunke and N. Sikder

High Energy Materials Research Laboratory, Sutarwadi, Pune- 411 021, India. E-mail: ak_sikder@yahoo.com; Fax: +91 5881 1316

Received (in Montpellier, France) 19th April 2001, Accepted 25th July 2001
First published as an Advance Article on the web

Three new derivatives of 4,6-dinitrobenzofuroxan: 7-(4-nitrophenylamino)-4,6-dinitrobenzofuroxan, 7-(3,5-dinitrophenylamino)-4,6-dinitrobenzofuroxan and 7-(2,4,6-trinitrophenylamino)-4,6-dinitrobenzofuroxan, have been synthesised by condensing 4-nitroaniline, 3,5-dinitroaniline and 2,4,6-trinitroaniline with 7-chloro-4,6-dinitrobenzofuroxan, respectively. The characterisation of the compounds by IR, ^{1}H-NMR, mass spectrometry and elemental analysis is described along with some of the evaluated preliminary explosive properties. The compounds were found to exhibit acceptable hazards properties. Furthermore, the thermal stability measurements indicated acceptable stability.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are well-established and important military explosives of unusual stability due in part to their cyclic structures.[1] Explosives for military use must be able to withstand extreme climatic conditions and are required to give acceptable functionality responses to impact and friction tests.

In order to meet these requirements, a primary strategy has been the development of polymer bonded explosives (PBXs), low vulnerability propellants (*i.e.*, having a low flame temperature and good mechanical properties) and thermally stable explosives. The thermal stability of a molecule can be achieved by approaches such as the introduction of amino groups into a nitroaromatic ring,[2] condensation of picryl chloride with an appropriate triazole moiety,[3,4] or through the introduction of conjugation.[5] Further developments towards low sensitivity and greater thermal stability have been made with benzofuroxans, an extremely fruitful class of compounds for use as new explosives. The furoxan ring results in increased density compared to nitro analogues whereas imino groups tend to reduce sensitivity, which in turn increases overall stability and performance, and also in many cases contributes to the heat of formation. Of course, the performance of an explosive also depends on several physical properties, including oxygen balance and heat of formation.[6–9]

Bearing these requirements in mind, we were interested in developing new explosive molecules based on benzofuroxan, possessing the energy of heterocyclic nitramines but having the intrinsic stability of an aromatic cyclic configuration, as found in well-known thermally stable explosives having high detonation velocities and power.

In the following sections, we report the synthesis, characterisation, thermal and explosive behaviour of three new benzofuroxan derivatives, which may be used as strong energetic fillers with reduced vulnerability in insensitive munition.

Experimental

Methods and materials

Unless otherwise stated, all common reagents and solvents were used as supplied from commercial sources without further purification. Melting points were determined in open capillaries and are uncorrected. The IR spectra were recorded on a Perkin–Elmer infrared spectrometer using KBr matrices. ^{1}H-NMR spectra were recorded on a Brucker 90 MHz instrument. Chemical shifts were recorded in ppm with reference to tetramethylsilane (TMS) as internal standard. Elemental analyses were performed on a Carlo–Erba EA 1108 elemental analyzer. Mass spectra were determined by electron ionisation at 70 eV on a Finnigan Mat 1020B GC/MS with a solid probe.

The deflagration temperature[10] was determined by heating 0.02 g of sample in a glass tube in a Wood's metal bath at a heating rate of 5 °C min^{-1}; the temperature at which the sample ignited/decomposed was recorded as the deflagration temperature. Differential thermal analysis (DTA) was recorded on a micro-DTA apparatus fabricated in our laboratory by heating 10 mg of sample at a rate of 10 °C min^{-1} in the presence of static air. The impact sensitivity was determined by the falling hammer method using a 2.0 kg drop weight, and friction sensitivity was determined on a Julius Peter apparatus following standard methods.[11] The velocity of detonation[12] and detonation pressure[13] were calculated by methods reported in the literature.

1,3-Dichloro-2,4,6-trinitrobenzene[14] (as prepared from styphnic acid by treatment with pyridine followed by phosphorus oxychloride, mp 129–130 °C), 4-nitroaniline (mp 149–151 °C), 3,5-dinitroaniline (prepared by nitration of benzoic acid *via* the Schmidt reaction, mp 161–163 °C) and 2,4,6-trinitroaniline[15] (also prepared from picric acid by treatment with pyridine and phosphorus oxychloride followed by amination, mp 189–191 °C) were prepared in our laboratory and used as starting materials. Sodium azide was obtained commercially and used as received. Methyl alcohol, acetic acid and dichloromethane from Qualigen were used as solvents.

Synthesis

1-Azido-3-chloro-2,4,6-trinitrobenzene, 1. 1,3-Dichloro-2,4,6-trinitrobenzene (styphnyl chloride; 5 g, 17.73 mmol) was transferred into a three-necked round-bottom flask fitted with a mechanical stirrer and dropping funnel. To this, 25 ml of dimethylformamide (DMF) was added slowly and sodium azide (1.30 g, 0.02 mol), dissolved in 10 ml of distilled water, was added dropwise to the reaction flask under stirring

DOI: 10.1039/b103537c

at 20–22 °C over half an hour. After complete addition of sodium azide, the stirring was continued for another 3 h while maintaining the same temperature. The reaction mixture was poured into crushed ice and left overnight to precipitate. The product, which settled out, was filtered off, washed thoroughly with distilled water and finally dried at room temperature. Yield 4.2 g (92%). The compound was recrystallised from methanol and was found to melt at 45–47 °C. IR (KBr) cm^{-1}: 3089 (m, Ar–H str), 2165 (s,$-N_3$) 1616 (m, C=C str), 1545 and 1335 (s, NO_2 asym and sym str). ^{1}H-NMR (DMSO-d_6, TMS) δ: 8.5 (s, 1H, aromatic proton). Anal. calc. for $C_6HN_6O_6Cl$ (MW 288): C, 25.00; H, 0.34; N, 29.17; found: C, 24.89; H, 0.46; N, 29.01%.

7-Chloro-4,6-dinitrobenzofuroxan, 2. **1** (5 g, 17.33 mmol) was carefully transferred into a two-necked flask fitted with a reflux condenser and acetic acid (20 ml) was added. The reaction mixture was refluxed for 2 h over an oil bath; the mixture was then cooled to ambient temperature and subsequently poured into crushed ice. The yellow precipitate thus obtained was filtered off and washed with distilled water until it was acid-free. The product was crystallised from methanol. Yield 3.5 g (77%); mp 110–112 °C; DTA: 114 °C (endotherm) and 205 °C (exotherm). IR (KBr) cm^{-1}: 3096 (m, Ar–H str), 1620 and 1580 (m, C=C and C=N str), 1535 and 1345 (s, NO_2 asym and sym str), 815 (s, C–Cl str). ^{1}H-NMR (DMSO-d_6, TMS) δ: 8.75 (s, 1H, aromatic proton). Anal. calc. for $C_6HN_4O_6Cl$ (MW 260): C, 27.69; H, 0.38; N, 21.53; found C, 27.51; H, 0.26; N, 21.30%.

7-(4-Nitrophenylamino)-4,6-dinitrobenzofuroxan, 3. To a 250 ml three-necked round-bottom flask fitted with mechanical stirrer, dropping funnel and reflux condenser, **2** (5.21 g, 20 mmol) was transferred and 4-nitroaniline (5.6 g, 40.57 mmol) was added along with 125 ml of methanol. The reaction mixture was refluxed for 5 h and subsequently cooled down to ambient temperature. The reaction mixture was placed into ice-cold water. The off-yellow precipitate thus obtained was filtered off on a Buchner funnel and washed with water. The product was crystallised from dichloromethane. Yield 5.6 g (77.3%); the compound did not melt but decomposed at 172 °C (DTA exotherm). IR (KBr) cm^{-1}: 3266 (m, N–H str), 3116 (m, Ar–H str), 1636, 1594, 1495, 1250 (mw, furoxan ring), 1526 and 1346 (s, NO_2 asym and sym), 940 (m, substituted benzene ring). ^{1}H-NMR (chloroform-d_1, TMS) δ: 8.9 (s, 1H, aromatic proton), 8.1 (s, 2H, aromatic proton), 7.7 (s, 2H, aromatic proton), 6.8 (br s, 1H, NH). EI-MS (70 eV) *m/z*: 279, 264, 235, 189, 164, 138 (100%), 152, 107, 91. Anal. calc. for $C_{12}H_6N_6O_8$ (MW 362): C, 39.77; H 1.65; N, 23.20; found: C, 39.54; H, 1.83; N, 22.96%.

7-(3,5-Dinitrophenylamino)-4,6-dinitrobenzofuroxan, 4. **2** (25.21 g, 20 mmol) and 3,5-dinitroaniline (7.4 g, 40.43 mmol) were carefully transferred into a 250 ml three-necked round-bottom flask fitted with mechanical stirrer and reflux condenser, followed by 130 ml of methanol. The reaction mixture was refluxed for 5 h, then cooled down to ambient temperature and poured into crushed ice. The yellow precipitate thus obtained was filtered off and washed with distilled water and was crystallised from dichloromethane. Yield 6.5 g (79.8%); the product did not melt, however, the DTA was recorded and the endotherm found at 95 °C and the exotherm at 260 °C. IR (KBr) cm^{-1} : 3378 (m, N–H str), 3088 (m, Ar–H str), 1640, 1588, 1490,1294 (mw, furoxan ring), 1538 and 1342 (s, NO_2 asym and sym str), 956 (m, substituted benzene ring). ^{1}H-NMR ($CDCl_3$, TMS) δ: 9.1 (s, 1H, benzofuroxan ring), 8.37 (s, 1H, phenyl), 7.75 (s, 2H, phenyl ring), 7.15 (br s, 1H, NH). EI-MS (70 eV) *m/z*: 285, 283, 264, 247, 183 (100%), 169, 154, 137, 124, 107, 91. Anal. calc. for $C_{12}H_5N_7O_{10}$ (MW 407): C, 35.38; H, 1.22; N, 24.07; found : C, 35.16; H, 1.10; N, 23.85%.

7-(2,4,6-Trinitro-1-iminophenyl)-4,6-dinitrobenzofuroxan, 5. In a three-necked round-bottom flask fitted with reflux condenser and dropping funnel, **2** (5.21 g, 20 mmol) was introduced with 2,4,6-trinitroaniline (9.20 g, 40.35 mmol) to which 150 ml of methanol was added. The reaction mixture was refluxed for 5 h, cooled down to ambient temperature and finally poured into crushed ice. The yellow precipitate thus obtained was filtered off, washed with water and dried in a water-jacketed oven at 60 °C. The product was further recrystallised from dichloromethane to yield 7.5 g (83%) of pure product; mp 179–80 °C. The DTA results showed no exotherm up to 400 °C. IR (KBr) cm^{-1}: 3322 (m, N–H str), 3082 (m, Ar–H str), 1636, 1590, 1495, 1274 (mw, furoxan ring), 1528 and 1274 (s, NO_2 asym and sym str), 934 (m, substituted benzene ring). ^{1}H-NMR ($CDCl_3$, TMS) δ: 9.4 (s, 1H, benzofuroxan ring), 9.0 (s, 2H, trinitrophenyl ring), 7.30 (br, 1H, NH). EI-MS (70 eV) *m/z*: 264, 228 (100%), 212, 198, 166, 152, 137, 107, 91. Anal. calc. for $C_{12}H_4N_8O_{12}$ (MW 452): C, 31.85; H, 0.88; N, 24.77; found: C, 31.75; H, 1.06; N 24.56%.

Results and discussion

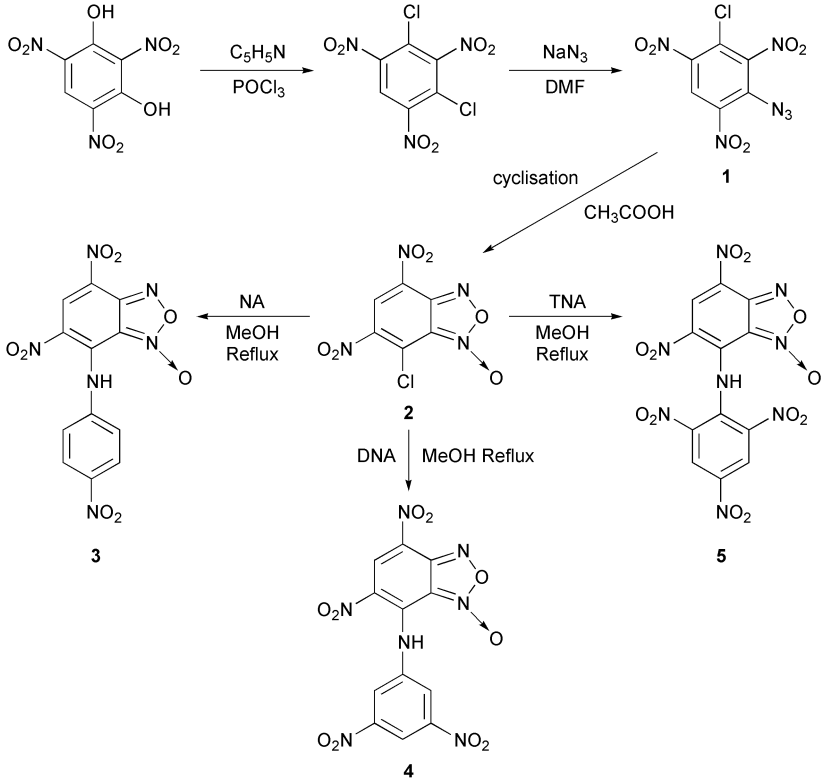
Synthesis and structure

7-Chloro-4,6-dinitrobenzofuroxan, **2**, was synthesised from styphnic acid following an essentially different route from that of Norris *et al.*[16] The reaction steps followed for the preparation of the parent compound **2**, along with compounds **3**, **4** and **5** are outlined in Scheme 1. The dipyridinium styphnate was prepared from styphnic acid by treatment with pyridine; it was then chlorinated using phosphorus oxychloride. Azidation of the chlorinated product and subsequent cyclisation produced **2**, which was subsequently condensed with the nitroaniline derivatives, thus resulting in the target molecules with very good yields and excellent purity. This method of preparation of the nitroanilinobenzofuroxans has been achieved even more conveniently through a simplified method for the preparation of the halide benzofuroxans, **2**, which can be used without further purification. Mention is made here of the possibilities for large-scale synthesis of thermally stable, insensitive energetic molecules and their parent compounds from inexpensive starting materials.

Compounds **3**, **4** and **5** are light yellow to dark yellow solids and the analytical and spectroscopic data unambiguously proved the structures of the compounds with no evidence of isomeric structures. This is further supported by the fact that formation of the furazan oxide involves ring opening to give an "*ortho*-dinitrosobenzene" as a transient intermediate, followed by very rapid interconversion to the cyclised product.[17] The X-ray crystallography[18] and electrospectroscopy for chemical analysis (ESCA)[19] results, together with IR, ^{1}H-NMR and mass spectrometry, further confirmed the structures of the benzofuroxans.

The EI-MS fragmentation species suggested below are tentative in the absence of the use of techniques such as accurate mass measurement, fast atom bombardment and chemical ionisation, as well as the mass spectra of deuterated analogues. The EI-MS of these compounds were expected to show similar patterns; however, on analysing the results we found that the number of nitro groups and their positions in the aromatic ring greatly influence the decomposition pathways and species.

The mass spectral data (relative intensity $>5\%$) of compounds **3**, **4** and **5** are given in the experimental section. The EI mass spectra show no molecular ions, nevertheless, certain interesting ions that are of diagnostic value offer a means to

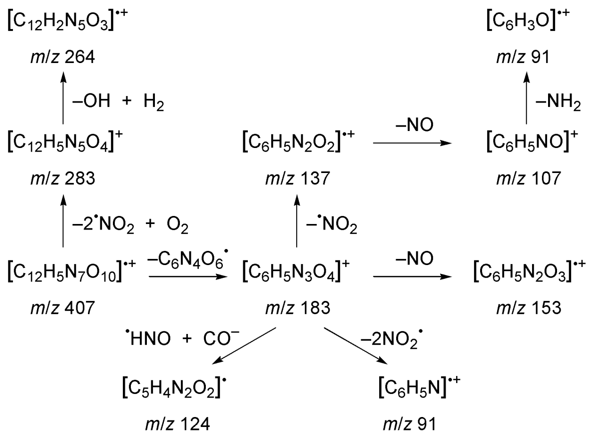


NA: 4-Nitroaniline; DNA: 3,5-Dinitroaniline; TNA: Trinitroaniline

Scheme 1

characterise the compounds. The highest intensity ion is attributed to fission of the dinitrobenzofuroxan moiety linked with condensation derivatives like mono-, di- and trinitroaniline. Most of the other major ions can be explained by the loss of NO_2 or NO, HNO_3 and HNO or, in some cases, CO and O losses.

The mass spectrum of compound **4** is described here in detail as a representative model of this class of compounds and the fragmentation pathways are outlined in Scheme 2. The base peak at m/z 183 constitutes a stable species corresponding to the formation of the nitroaniline moiety through rearrangement involving the imino function. The stepwise loss of NO_2 and NO species from the base peak is evidenced by the formation of peaks at m/z 137 and 107. The fission of NH_2 from m/z 107 resulted in the mass peak 91. The high molecular weight peaks at m/z 283 and 264 correspond to $[M - (2\ NO_2 + O_2)]^+$, followed by the combined loss of molecular hydrogen and hydroxyl radical, respectively. Another daughter ion at m/z 285 (not shown on Scheme 2) could be due to the loss of $(NO_2 + NO)$ followed by loss of NO_2. The peak at m/z 153 may be ascribed to loss of NO from m/z 183.



Scheme 2

Thermal and explosive properties

The thermal and explosive properties of the compounds were evaluated and the results obtained are presented in Table 1. Compound **3** deflagrates at 170 °C, compound **4** at 256 °C while compound **5** does not deflagrate up to 350 °C, as rationalised by the DTA thermograms of the corresponding exotherms and endotherms. Thus, it is evident from the results that the thermal stability of the compounds increases in the order **3** < **4** < **5**. These results undoubtedly confirm the long-term stability of this family of compounds. The study of the explosive properties of compounds **3**, **4** and **5** reveals that the compounds are insensitive to friction and impact, when compared to well-established reference compounds like RDX, HMX and Tetryl. The insensitivity of the compounds increases with the decreasing number of nitro groups in the molecules. The predicted performance parameters such as the velocity of detonation and detonation pressure however, follow the opposite trend. Thus, compound **5** is more powerful when compared to the others, which may be attributed to a higher oxygen balance as well as a low hydrogen content. In addition, the overall performance of compound **5** is more or less comparable to Tetryl (VOD 7700 m s^{-1}), a well-known secondary explosive used as a booster in an explosive train. Even though the present series of new benzofuroxan derivatives exhibits moderate performance with satisfactory thermal properties, they may nevertheless serve as model compounds on which to base further investigations.

Table 1 Some characteristic properties of nitroanilinodinitrobenzofuroxan

Properties	**3**	**4**	**5**
Deflagration temperature/°C	170	256	>350
DTA/°C	172 (endotherm-*cum*-exotherm)	95 (endotherm) 260 (exotherm)	180 (endotherm, no explosion up to 400 °C)
Density/g cm^{-3}	1.89	1.86	1.83
Oxygen balance (CO)/(%)	−30.93	−17.6	−7.07
Impact sensitivity[a] (50% explosion ht)/cm	127	115	92
Friction sensitivity[b] (insensitive up to)/kg	> 36	36	32.4
Velocity of detonation[c] /m s^{-1}	6538	7157	7639
Detonation pressure[c] /kbar	201.97	238.16	266.97

[a] Sensitivity to impact: RDX, 35 cm; HMX, 32 cm; Tetryl, 85 cm. [b] Sensitivity to friction: RDX, 12 kg; HMX, 12 kg; Tetryl, 36 kg. [c] Calculated values (ref. 12, 13)

Conclusions

Three new dinitrobenzofuroxan derivatives, showing moderately powerful explosive properties, have been synthesised and fully characterised. Of the three molecules, compound **5** appears promising and may find applications where thermal stability and high performance are required. Furthermore, the ease with which the starting materials can be prepared from commercially available compounds suggests that the products **3**, **4** and **5** would be economically viable to synthesise on a large scale for applications as explosives.

Acknowledgement

The authors thank Dr H. Singh, Director of the High Energy Materials Research Laboratory, Pune, for the facilities and encouragement provided during the course of this work.

References

1 B. M. Dobratz and P. C. Crawford, *LLNL Explosives Handbook. Properties of Chemical Explosives and Explosive Stimulants*, Lawrence Livermore National Laboratory, Livermore, CA, USA, UCRL-52997, 1985.

2 J. M. Rosen and J. C. Dacons, *Explosivstoffe*, 1968, **16**, 250.

3 (*a*) M. D. Coburn, *U. S. Pat.*, 3,483,211, 1969; (*b*) M. D. Coburn, *Chem. Abstr.*, 1970, **72**, 55458x.

4 J. P. Agrawal, Mehilal, U. S. Prasad and R. N. Surve, *New J. Chem.*, 2000, **24**, 583.

5 K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, 1966, **31**, 857.

6 A. B. Shermetev and T. S. Pinina, in *27th International Annual Conference of Fraunhofer-Institut fur Chemische Technologie (ICT)*, ed. T. Keicher, Pfinztal, Karlsruhe, Federal Republic of Germany, 1996, pp. 30.1–30.14.

7 W. Naixing, C. Boren and O. Yuxiang, *Propellants, Explos., Pyrotech.*, 1994, **19**, 145.

8 W. P. Norris, *Naval Weapon Center Technical Publication (NWCTP) 6522*, Naval Weapons Center, China Lake, CA, USA, June 1984.

9 W. P. Norris and A. P. Chafin, *Naval Weapon Center Technical Publication (NWCTP) 6598*, Naval Weapons Center, China Lake, CA, USA, June 1989.

10 *Encylopedia of Explosives and Related Items*, ed. B. T. Fedoroff and O. E. Sheffield, Picatinny Arsenal, Dover, NJ, USA, 1st edn., 1960, vol. 1, pp. XVI–XVII.

11 L. Avrami and R. Hutchinson, in *Energetic Materials: Technology of Inorganic Azides*, ed. H. D. Fair and R. F. Walker, Plenum Press, New York, USA, 1st edn., 1977, vol. 2, ch. 4, pp. 111–159.

12 L. P. Rothestein and R. Peterson, *Propellants Explos.*, 1979, **4**, 56.

13 *Explosives, Propellants and Pyrotechnics. Land Warfare: Brasseys New Battlefield Weapon and Technology Series*, ed. A. Bailey and S. G. Murray, Brassey's, Pergamon Press, Oxford, UK, 1st edn., 1989, vol. 2, p. 33.

14 M. Warman and V. I. Siele, *J. Org. Chem.*, 1961, **26**, 2997.

15 R. Boyer, E. Y. Spencer and G. F. Wright, *Can. J. Res.*, 1946, **24**, 200.

16 W. P. Norris, A. Chafin, R. J. Spear and R. W. Read, *Heterocycles*, 1984, **22**, 271.

17 F. B. Malloxy and A. Cammrate, *J. Am. Chem. Soc.*, 1966, **88**, 64.

18 (*a*) R. Hulme, *Chem. Ind.* (*London*), 1962, 42; (*b*) D. Britton and W. E. Noland, *Chem. Ind.* (*London*), 1962, 562.

19 B. Chen and Z. Liao, in *21st International Annual Conference of Fraunhofer-Institut fur Chemische Technologie (ICT)*, ed. H. Schubert and K. Menke, Pfinztal, Karlsruhe, Federal Republic of Germany, 1990, pp 58.1–58.4.