

SHORT COMMUNICATION

Synthesis and Characterisation of Diaryl Furoxans

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ABSTRACT

The paper discusses the synthesis, characterisation, and performance evaluation of diaryl furoxans namely, bis-phenyl-3,4-furoxan (**5**) and bis-(4'-nitrophenyl)-3,4-furoxan (**6**). The molecules have been synthesised on the lines of reported method by cyclodimerisation of the nitrile oxides generated from benzaldoxime and *p*-nitro benzaldoxime, respectively. The synthesised furoxans (**5**) and (**6**) were characterised by the elemental analysis, UV, IR, and ¹H NMR spectroscopy. The hazard characteristics (impact and friction sensitivity) confirm that the compounds are safe to handle. The oxygen balance, velocity of detonation and detonation pressure have been computed. The detonation velocity and pressure along with oxygen balance increased with the substitution of nitro group in the benzene ring, as expected. The thermogravimetric studies on promising compound (**6**) brings out that maximum weight loss occurs at decomposition temperature of 259–260 °C.

Keywords: Furoxans, high energetic molecules, synthesis, characterisation, HEMs, diaryl furoxans, high energy materials

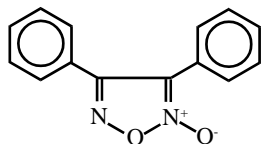
1. INTRODUCTION

Energetic materials are generally compounds containing nitro/nitrate/nitramino and azide groups in the molecules. The widely used current high energetic molecules (HEMs) are nitroglycerine (NG), cyclo trimethylene trinitramine (RDX), cyclo tetramethylene tetranitramine (HMX), trinitro toluene (TNT), and lead azide. These are made up of carbon, hydrogen, oxygen, and nitrogen. In general, HEMs produce energy by the process of oxidation as the internal energy of the reactant molecule is higher than that of the products. The highest oxidation state of carbon, obtained during combustion in oxygen is CO₂ and that of hydrogen is H₂O. The nitrogen being at a lower state of internal energy than that of its oxides in the reactant, is evolved as N₂ gas in the products.

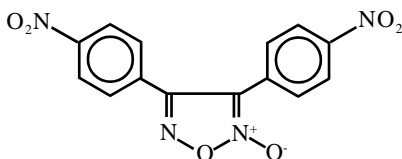
Furazans and furoxans are emerging as prospective high energy materials¹. These molecules have typical structural features. The aromatic ring confers thermal stability and augments density. Furoxans contain two additional oxygen atoms contributing to a latent nitro group inside the ring structure. The working oxygen atom, ie, oxygen atom not bonded to carbon or hydrogen atoms, is able to oxidise these atoms more efficiently during combustion. Another advantage of these molecules is positive enthalpy of formation emanating from ring strain.

The report^{2,3} on poly nitro aryl furoxans indicated that (**6**) is a potential thermally stable high density HEM. Thereby, it was planned to synthesise it during this study. The compound (**5**) of this class was also studied as it is structurally similar to (**6**)

and a key precursor for potential HEMs. The synthesised compounds were characterised by elemental analysis and spectroscopic techniques and were also subjected to thermal analysis.



Compound (5): bis-phenyl-3,4-furoxan



Compound (6): bis-(4'-nitrophenyl)-3,4-furoxan

In view of the ease of preparation of furoxan² by 1,3-dipolar addition of nitrile oxides at ambient temperatures, an attempt was made to synthesise furoxans (Scheme 1) by following similar approach during this study. Benzaldoxime and *p*-nitro benzaldoxime were used for generation of nitrile oxides. The nitrile oxides, being generally unstable, were used immediately after their preparation *in situ*.

2. EXPERIMENTAL PROCEDURE

2.1 Methods

The melting point of the recrystallised product was measured using Thomas Hoover capillary melting point apparatus. The elemental analysis was carried out on Perkin Elmer instrument. Ultra violet spectra of the compounds was recorded on Perkin Elmer model. The IR spectra were determined as Nujol mull on a Perkin Elmer-1600 Fourier transformer IR spectrophotometer. Proton magnetic resonance (¹H NMR) spectra were recorded on Varian 300 MHz spectrometer with tetramethyl silane as an internal standard. The thermal analysis (2 mg samples) was performed on Mettler Toledo Star Simultaneous thermogravimetry-differential thermal analyser (TG-DTA) system at 10 °C/min in nitrogen atmosphere at the flow rate of 80 cm³/min.

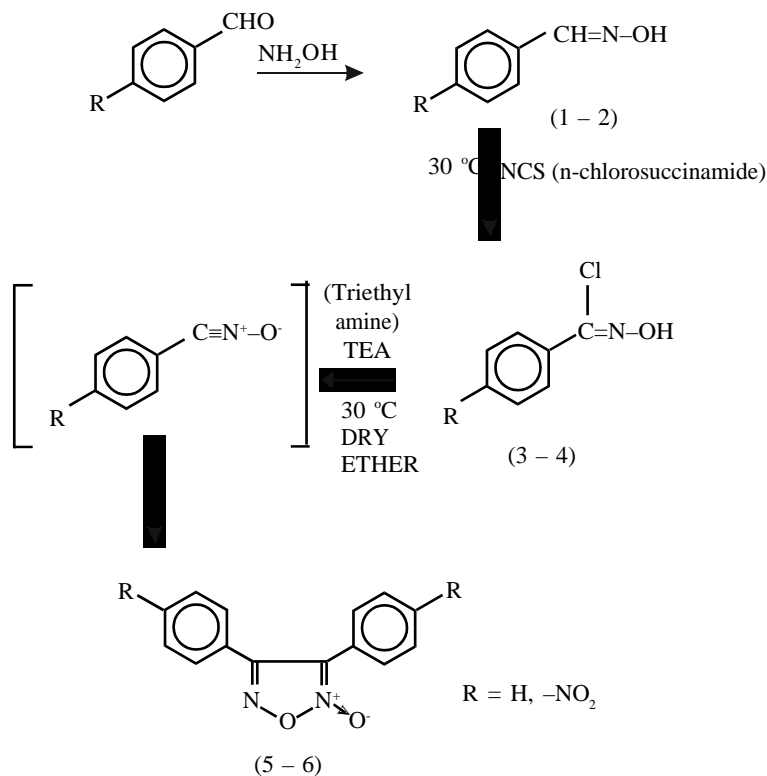
The impact test was conducted using a setup similar to that used in Naval Ordnance Laboratory (NOL), USA. The test specimens (30-35 mg of powder) were kept between two hardened stainless steel anvils and a 3 kg drop weight was allowed to fall freely from different heights. Both open and aluminum foil-encapsulated specimens were used for evaluation. Ten tests were conducted for each compound. The results are reported in terms of height for 50 per cent probability of explosion ($h_{50\%}$) of the sample. The impact sensitivity studies on benchmark explosives such as RDX and TNT were also carried out under identical conditions to validate the experimental setup.

2.1.1 Preparation of Benzohydroxamoyl Chloride (3)

A solution of benzaldoxime (0.242 g, 0.002 mol) in dimethyl formamide (5 cm³) was taken in a 100 cm³ round-bottom flask equipped with a guard tube and *N*-chlorosuccinimide (0.332 g, 0.0024 mol) was added to it in small portions with vigorous stirring. The stirring was continued overnight. After all the starting material was consumed, water was added to the reaction mixture. Subsequently, the product was extracted with ether (10 cm³ × 2). The organic layer was washed with water and dried over sodium sulphate. The solvent was evaporated to obtain the compound (0.3 g). Yield: 80 per cent; m.p.: 47-50 °C (m.p. 48-52 °C)⁴; IR (Nujol): 689 cm⁻¹ (*C-Cl*), 3224 cm⁻¹ (*OH*); analysis per cent found: C-54.19, H-3.87; C₇H₆ClNO; per cent calc.: C-54.20, H-3.85; ¹H NMR (90 MHz, CDCl₃, δ): 7.2-8.2 m, 5 H, *ArH*; 8.2-8.4 bs, 1H (exchangeable with D₂O), *OH*.

2.1.2 Preparation of 4-Nitrobenzohydroxamoyl Chloride (4)

A solution of *p*-nitro benzaldoxime (0.332 g, 0.002 mol) in dimethyl formamide (5 cm³) was transferred to a 100 cm³ round-bottom flask equipped with a guard tube, and *n*-chlorosuccinimide (0.332 g, 0.0024 mol) was added to it in small portions with vigorous stirring. The stirring was continued overnight. The progress of reaction was monitored by thin layer chromatography (TLC). After all the starting



Scheme 1. Synthesis of furoxans

material was consumed, water was added to the reaction mixture. The product was extracted with ether (10 cm³ × 2). The organic layer was washed with water and dried over sodium sulphate. The compound (4) obtained was used as such for further reaction.

2.1.3 Dimerisation of Benzonitrile Oxide (Preparation of bis-phenyl-3,4-furoxan (5))

A solution of benzohydroxamoyl chloride (3) (0.155 g, 0.001 mol) in dry ether (5 cm³) was transferred to a 100 cm³ round-bottom flask equipped with a guard tube. Triethyl amine (0.101 g, 0.001 mol) was added drop-wise to the solution with vigorous stirring. In this step, the reaction mixture became viscous. The stirring of the reaction mixture was continued overnight, and the progress of the reaction was monitored by TLC. After consumption of the starting material, the reaction mixture was extracted with dichloromethane (10 cm³ × 2). The organic layer was washed with water and dried over sodium sulphate. A white crystalline solid was obtained on

chromatographic separation. Yield: 75 per cent; m.p.: 116-117 °C. (m.p. 117 °C)⁵; UV (CHCl₃): λ_{max} 240 nm and 278 nm; IR (Nujol): 1224 cm⁻¹ (N-oxide); analysis per cent found: C-70.39; H-4.09; C₁₄H₁₀N₂O₂; per cent required: C-70.58, H-4.20; ¹H NMR (200 MHz, CDCl₃, δ): 7.4-8.4 m 10H, ArH.

2.1.4 Preparation of bis-(4'-nitrophenyl)-3,4-furoxan (6)

A solution of (4) (0.155 g, 0.001 mol) in dry ether (5 cm³) was placed in a 100 cm³ round-bottom flask equipped with a guard tube. Triethyl amine (0.101 g, 0.001 mol) was added to the solution drop wise with vigorous stirring. During the addition, reaction mixture become highly viscous. The stirring of the reaction was continued overnight and the progress of the reaction was monitored by TLC. After completion of the reaction, water was added and the reaction mixture was extracted with dichloro methane (10 cm³ × 2). The organic layer was washed with water and dried over sodium sulphate. A white crystalline solid was obtained on chromatographic

separation. Yield: 75 per cent; m.p.: 196 °C; (m.p. 197-198 °C)¹¹; UV(CHCl₃): λ_{max} 242 nm and 280 nm; IR(Nujol): 1440 cm⁻¹ and 1300 cm⁻¹ (C-NO₂), 1228 cm⁻¹ (N-oxide); analysis per cent found: C-51.09, H-2.29; C₁₄H₈N₄O₆; per cent required: C-51.21, H-2.43; ¹H NMR (300 MHz, CDCl₃, δ): 7.4–8.4 2 x d J=8.4 Hz, 4 x 2 H, ArH.

2.2 Theoretical Calculations

The velocity of detonation (VOD) of the synthesised molecules was estimated based on the empirical calculations developed by Rothstein⁶. Detonation pressure and density (ρ) values were calculated by Chapman-Jouguet (C-J) and Eremenko methods,⁶ respectively. The equation used for calculation of VOD is given below:

$$D' = (F - 0.26)/0.55$$

where

$$F = [100(\phi + \psi) / MW] - G$$

$$\phi = n(O) + n(N) + n(F) - [n(H) - n(HF)] / 2n(O)$$

$$\psi = A/3 - n(B/F)/1.75 - n(C)/2.5 - n(D)/4 - n(E)/5$$

where, A=1, if compound is aromatic, otherwise A = 0; G = 0.4, for liquid explosives, and G = 0 for solids;

- $n(O)$ Number of oxygen atoms in molecules
 $n(N)$ Number of nitrogen atoms in molecules
 $n(H)$ Number of hydrogen atoms in molecules
 $n(F)$ Number of fluorine atoms in molecules
 $n(HF)$ Number of hydrogen fluoride molecules that can possibly be formed from available hydrogen
 $n(C)$ Number of oxygen atoms doubly-bonded directly to carbon as in ketone or ester
 $n(B/F)$ Number of oxygen atoms in excess of those available to form CO₂ and H₂O and/or the number of fluorine atoms in excess of those available to form HF
 $n(D)$ Number of oxygen atoms singly-bonded directly to carbon as in C-O-R and where R can be -H, NH₄, -C

$n(E)$ Number of nitro groups existing either as a nitrate ester or as a nitric acid salt.

The detonation pressure (ρ_{CJ}) in k bar was obtained from relationship

$$P_{CJ} = K\rho_0 2NM^{1/2} (-\Delta H_0^d)^{1/2}$$

where, ρ_0 =density, N=number of moles of gas per gram of original explosive, M=grams of gas per mole of gas, ΔH_0^d =heat of detonation in cal/g.

Theoretical maximum density (ρ TMD) was obtained by relationship ρ (TMD)=1.780 – 0.096 H, where H=100 x Wt. of hydrogen/molecular Wt.

3. RESULTS & DISCUSSION

The various approaches effective in improving the thermal stability of the compounds are:

- Incorporation of amino groups
- Condensation with triazole ring
- Salt formation
- Introduction of conjugation

Basically, furoxan is an unstable molecule. Substitution of phenyl groups in the furoxan ring appears to be a viable approach to confer stability on the molecule which is an essential attribute for their application as energy-delivering component in explosives as well as propellant systems. Improved thermal stability simplifies the production procedures, increases the shelf-life of the munitions as well as weapons, and decreases their vulnerability to accidental initiation.

Increase in melting points observed during this study on introduction of aromatic rings or phenyl groups in the molecule, as compared to the parent furoxan is indicative of improved stability. It can be attributed to the extended conjugation involving the aromatic substituents and the furoxan ring. Incorporation of nitro group on the phenyl substituent further increases the stability due to further extension of conjugation. Similar observations have been reported⁷ for 3',4',5'-tris-nitrophenyl-3-nitro furoxan (**7**) as well as bis-(3',4',5'-trinitrophenyl) furoxan (**8**) and

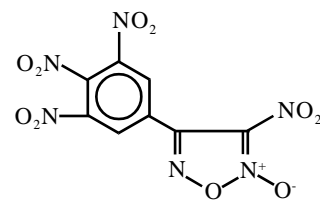
bis (3',5'-dinitrophenyl) furoxan (**9**)⁸⁻¹⁰. The sensitivity studies showed that compounds (**5**) and (**6**) are insensitive towards impact ($h_{50\%} > 100$ cm) and friction (> 36 kg).

The UV of the synthesised compounds (**5**) and (**6**) showed the presence of peaks at ~ 240 nm and 280 nm. The IR spectrum of (**5**) and (**6**) also indicated the characteristic frequency in the range $1224-1228$ cm^{-1} due to *N*-oxide linkage. The title compound (**6**) showed the asymmetric and symmetric stretching frequencies at 1440 cm^{-1} and 1300 cm^{-1} respectively due to nitro group. Aromatic protons in (**5**) and (**6**) resonated at δ 7.4-8.4 in ^1H NMR. The spectral pattern matches with the reported data¹¹.

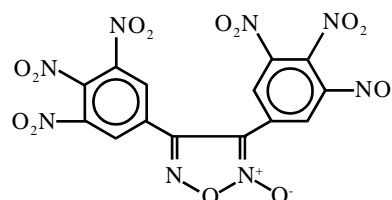
The introduction of nitro group in the phenyl ring also led to the improvement in oxygen balance resulting in a remarkable increase in the energetics in terms of VOD and detonation pressure in case of (**6**) compared to (**5**). (Table 1). This is in line with the higher stability reported⁷ for (**7**), (**8**), and (**9**) in comparison to dinitrofuroxan (**11**).

The compound (**6**) can be considered as a safer substitute for pentaerthrytol tetranitrate (PETN).

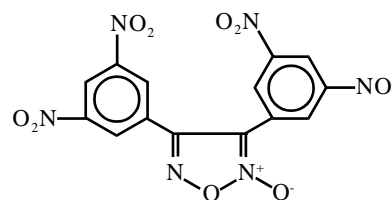
The thermal decomposition of (**6**) commenced at $127-128$ $^{\circ}\text{C}$ and ends at 290 $^{\circ}\text{C}$ in TG. The maximum weight loss occurred at around $259-260$ $^{\circ}\text{C}$. The weight loss studies indicated no residue was left after decomposition despite negative oxygen balance, suggesting the complete breakdown of the molecule to gaseous products. Since the phenyl groups as well as *C*-aryl bonds are stable ones, the decomposition is envisaged to commence with the cleavage of the furoxan ring, followed by further reactions as reported for 3,4-bis-(3',4',5' -trinitrophenyl) furoxan⁸⁻¹⁰.



Compound (7): 3',4',5'-tris-nitrophenyl-3-nitro-furoxan



Compound (8): bis-(3',4',5'-trinitrophenyl)-furoxan



Compound (9): bis-(3',5'-dinitrophenyl)-furoxan

The sensitivity studies showed that compounds (**5**) and (**6**) are insensitive towards impact ($h_{50\%} > 100$ cm) and friction (> 36 kg). The work on the higher nitrated analogues of (**6**) viz., (**8**) and (**9**) will be taken up in the near-future.

5. CONCLUSIONS

3',4'-aryl and nitroaryl-substituted furoxans have been synthesised by the cyclodimerisation of the nitrile oxides generated from the corresponding benzaloximes. The compounds have been characterised by elemental analysis, UV, IR, and

Table 1. Physical data of 5, 6, 8 and 11

Entry	Mol. formula	Mol. Wt.	m.p. ($^{\circ}\text{C}$)	Max. density (g/cm^3)	Detonation velocity (km/s)	Detonation pressure (k bar)	Oxygen balance (%)
5	$\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$	238	117	1.40	0.702	0.17	-141.17
6	$\text{C}_{14}\text{H}_8\text{N}_4\text{O}_6$	328	197	1.63	4.670	9.70	-87.80
8	$\text{C}_{14}\text{H}_4\text{N}_8\text{O}_{14}$	508	293-5	1.83	7.350	21.12	-42.27
11	$\text{C}_2\text{N}_4\text{O}_6$	176	Liquid	1.95	8.190	32.64	+18.18

^1H NMR spectroscopic studies. The hazard characterisation indicates that the compounds are safe for handling. Theoretical performance predictions as well as sensitivity studies suggest that (6) is a promising alternative to highly sensitive explosive PETN. The work on the higher nitrated analogues of (6), viz., (8) and (9) will be taken up in the near future.

ACKNOWLEDGEMENT

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REFERENCES

1. Krishnamurthy, V.N. The energetic material for new millennium. *In* Proceedings of the 3rd International Conference on High Energy Materials, 2001, pp. 72.
2. Srom, R.C. 1,2,5 - oxadiazole. *In* Comprehensive heterocyclic chemistry II, 1996, **4**, pp. 229-905.
3. Maknova, N.N.; Ovchinhikov, L.I.; Dubonos, V.G. & Khmel'nitskii, L.I. Aminofurazins as key synthons for construction of high energetic materials. *In* Proceedings of International Symposium on Pyrotech Explosives, Beijing, ROC, 1995, **3**, pp. 233.
4. Rajagopalan, P.; Advani, B.G. & Talaty, C.N. Organic synthesis. Coll. Vol. V, John Willey & Sons, 1973. pp. 504.
5. Rappoport, Z. & Topol, A. Nucleophilic attacks on carbon-carbon double bonds. Pt- 39. Nucleophile and nucleofuge effects, catalysis and stereochemistry in vinylic substitution of electrophilic nitro olefins. *J. Org. Chem.*, 1989, **54**, 5967-977.
6. Cooper, P.W. Explosive engineering. VCH Publishers, 1996. pp. 67-71, 160-61.
7. Sitzmann, M.E. 2,5-Dipicryl-1,3,4-oxodiazole: A shock-sensitive explosive with thermal stability (thermally stable substitute for PETN). *J. Energ. Mater.*, 1988, **6**, 129.
8. Ninan, K.N.; Krishan, K. & Krishnamurthy, V.N. Kinetics and mechanics of thermal decompositions of *in situ*-generated calcium carbonate. *J. Therm. Anal.*, 1991, **37**, 1533-545.
9. Lobbecke, S.; Pfeil, A.; Krause, H.; Saucer, J. & Holland, U. Thermo analytical screening of nitrogen-rich substances. *Propell. Explo. Pyrotech.*, 1999, **24**, 1.
10. Lobbecke, S.; Pfeil, A. & Krause, H. Thermal analysis of different nitro furaxans. *In* Proceedings of the 24th International Annual Conference of ICT, Karlsruhe, Federal Republic of Germany, 1999, pp. 168.
11. Kaufman J.V.P. & Picard, T.P. The furoxans. *Chemical Review*, 1959, **59**, 429-61.

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