Unsymmetrically Substituted Furoxans. Part 6.[1] 3-Nitro-4-phenylfuroxan: Reaction with Sodium Methoxide and *X*-Ray Structural Analysis

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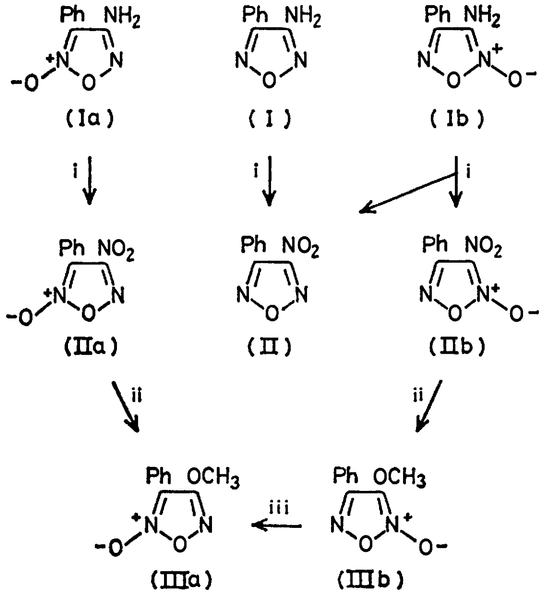
The reaction of sodium methoxide with the by-product obtained by the action of an excess of 85% hydrogen peroxide in trifluoroacetic acid on 3-amino-4-phenylfuroxan suggests, for this derivative, the 3-nitro-4-phenylfuroxan structure. *X*-Ray analysis confirms this deduction.

FEW data have been reported on nitrofuroxan derivatives. The best known compounds are 3-methyl-4-nitrofuroxan[2,3] and 4-nitro-3-phenylfuroxan.[4,5] The syntheses of some other nitrofuroxans have also been reported[6,7] but the structures of these derivatives are uncertain. Recently[5] some of us studied the action of an excess of 85% hydrogen peroxide in trifluoroacetic acid on 4-amino-3-phenylfuroxan (Ia), 3-amino-4-phenylfurazan (I), and 3-amino-4-phenylfuroxan (Ib) (see Scheme).



SCHEME Reagents: i, H_2O_2; ii, CH_3O^-; iii, heat

From (Ia) and (I) the expected 4-nitro-3-phenylfuroxan (IIa) and 3-nitro-4-phenylfurazan (II) respectively were obtained, while (Ib) gave two compounds with similar chromatographic behaviour [t.l.c., silica gel 60 F_{254} (E. Merck), light petroleum (b.p. 40—60°)–benzene (7 : 3) as eluant]. The molecular formula of one (*ca.* 36%), m.p. 41—42°, is $C_8H_5N_3O_3$, of the other (*ca.* 5%), m.p. 106°, $C_8H_5N_3O_4$.

The $C_8H_5N_3O_3$ compound was identical (i.r., mixed m.p.) with (II). The mass spectrum of the $C_8H_5N_3O_4$ derivative suggested the structure as 3-nitro-4-phenylfuroxan (IIb) [characteristic peaks due to fission of the nitrofuroxan moiety: $(M - NO)^+$, $(M - NO_2)^+$, $(M - N_2O_2)^{+\cdot}$, $(M - NO_2 - NO)^{+\cdot}$, $(M - N_2O_2 - NO_2)^+$, $(NO)^+$], but its i.r. spectrum showed a remarkable anomaly: in the 1 570—1 500 cm^{-1} region, where the strong ν_{NO_2}(as) absorption is expected, only a weak band was present (see Figure 1).

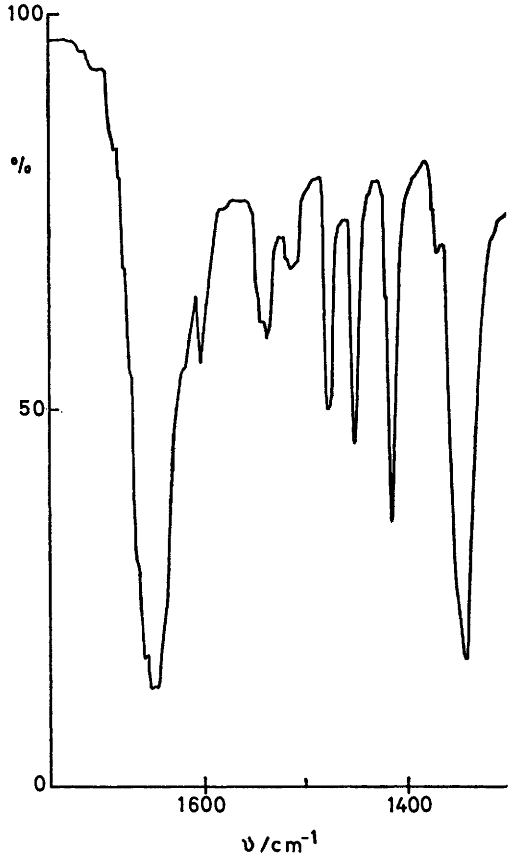


FIGURE 1 I.r. spectrum of 3-nitro-4-phenylfuroxan in the 1 350—1 750 cm^{-1} region

Since a complete chemical characterization of this derivative was difficult because of the small amounts obtained, in the present work we report only its reaction with sodium methoxide and its structure as determined by *X*-ray analysis. The results of this study confirm that, notwithstanding the i.r. spectrum, $C_8H_5N_3O_4$ is 3-nitro-4-phenylfuroxan (IIb).

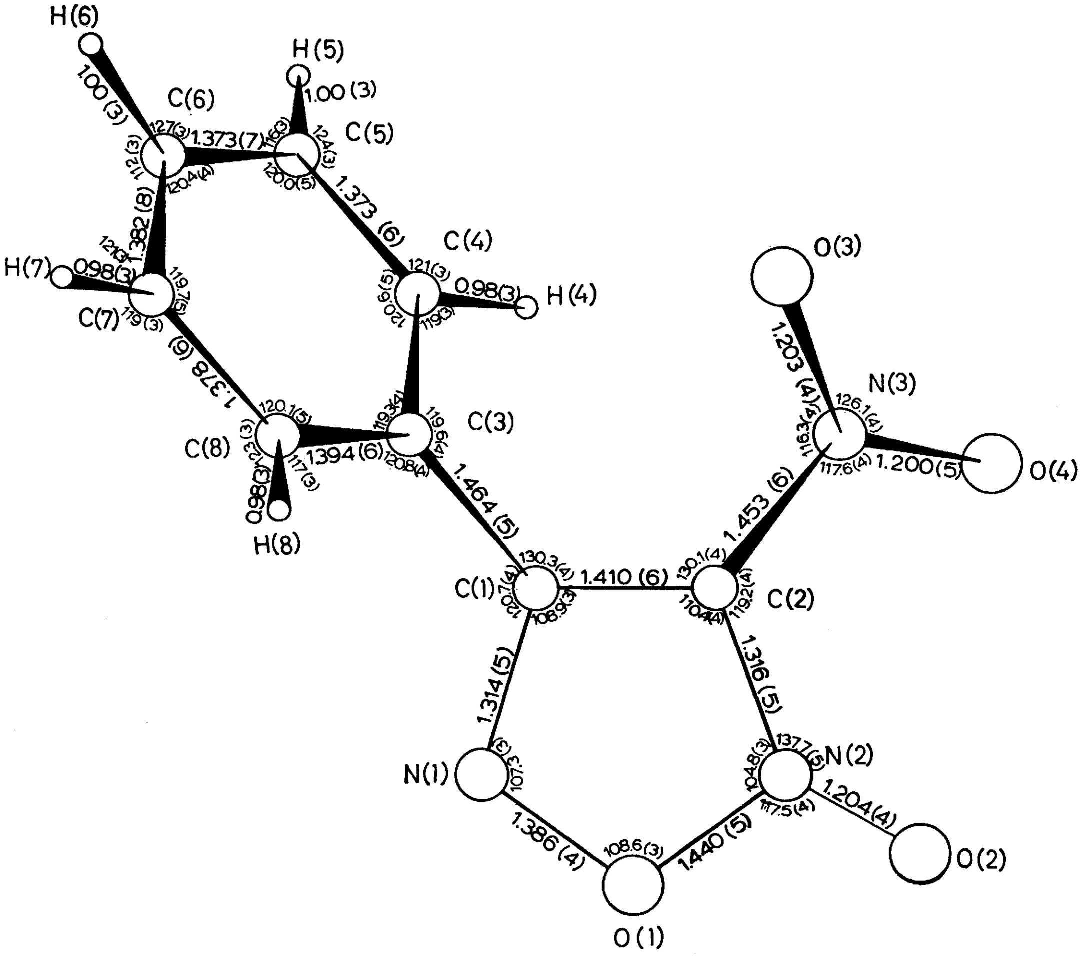


Figure 2 Projection of the molecule on the plane of the oxadiazole ring, showing the unconventional numbering scheme and the bond distances and angles with e.s.d.s in parentheses

The action of sodium methoxide on $C_8H_5N_3O_4$ affords a $C_9H_8N_2O_3$ compound with mass, i.r., and n.m.r. spectra consistent with 3-methoxy-4-phenylfuroxan (IIIb). This structure is confirmed by its thermal isomerisation to 4-methoxy-3-phenylfuroxan (IIIa), which is also obtained by the action of sodium methoxide on (IIa).

Atomic co-ordinates with e.s.d.s in parentheses

Atom	*x/a*	*y/b*	*z/c*
C(1)	0.323 0(2)	0.357 0(2)	0.416 5(7)
C(2)	0.268 8(2)	0.378 6(2)	0.563 6(8)
C(3)	0.398 6(2)	0.369 8(2)	0.434 7(7)
C(4)	0.435 0(2)	0.405 5(3)	0.261 5(8)
C(5)	0.506 5(2)	0.412 0(4)	0.268 4(9)
C(6)	0.542 5(2)	0.380 5(3)	0.446 7(11)
C(7)	0.507 0(2)	0.344 7(4)	0.622 7(10)
C(8)	0.435 2(2)	0.339 0(3)	0.616 8(8)
N(1)	0.296 2(2)	0.316 0(3)	0.246 5(6)
N(2)	0.208 3(2)	0.351 4(2)	0.487 1(7)
N(3)	0.270 5(2)	0.430 3(3)	0.763 8(6)
O(1)	0.224 7(1)	0.310 4(2)	0.280 5(6)
O(2)	0.148 0(1)	0.352 7(2)	0.542 7(7)
O(3)	0.325 0(2)	0.465 6(2)	0.806 1(5)
O(4)	0.217 4(2)	0.435 9(3)	0.867 9(7)
H(4)	0.408(2)	0.430(3)	0.138(7)
H(5)	0.535(2)	0.439(3)	0.150(7)
H(6)	0.594(1)	0.385(3)	0.474(9)
H(7)	0.532(2)	0.316(3)	0.741(6)
H(8)	0.408(2)	0.313(3)	0.734(6)

This derivative had been prepared by Wieland[4] from nitro(phenyl)furoxan, a by-product of the reaction of nitrogen oxides with cinnamic aldehyde; the 4-nitro-structure of this compound has been suggested in a previous paper.[5]

The structure of 3-nitro-4-phenylfuroxan was confirmed by *X*-ray analysis. Atomic parameters are listed in the Table. Figure 2 shows the molecule projected on the plane of the oxadiazole ring and also shows the unconventional numbering scheme adopted and the bond distances and angles.* There are no strong intermolecular interactions and packing is governed only by van der Waals contacts.

Both the furoxan and the phenyl groups are planar and the two planes form a dihedral angle of 53°. The angle between the nitro-group and the furoxan plane is only 11°; as a consequence O(4) is close to the extranuclear oxygen O(2) (2.703 Å). The small dihedral angle between the nitro-group and the furoxan ring

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* Observed and calculated structure factors and the components of the anisotropic thermal parameters of the non-hydrogen atoms are deposited as Supplementary Publication No. 23096 (18 pp.). For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1980, Index issue.

allows dipole–dipole interactions, which in turn may be responsible for the anomalies in the i.r. spectrum.

The trend of the bond distances in the five-membered ring is similar to that found in other furoxans [3,8–11] with a rather large difference between the two N–O bonds. The N(2)–O(2) distance is here shorter than in other derivatives, where it ranges between 1.220 and 1.242 Å.

EXPERIMENTAL

M.p.s were recorded on a capillary melting point apparatus and are uncorrected. ^{1}H N.m.r. spectra were recorded on a Varian T-60 instrument in deuteriochloroform with tetramethylsilane as internal standard. I.r. spectra were measured on a Perkin-Elmer 257 spectrometer. Mass measurements were carried out on a Varian CH7 MAT mass spectrometer. 4-Nitro-3-phenylfuroxan (IIa) and its 3-nitro-isomer (IIb) were prepared as reported in ref. 5.

4-*Methoxy*-3-*phenylfuroxan* (IIIa).—To a stirred solution of sodium methoxide (1 mmol) in methanol (2.0 ml), compound (IIa) (1 mmol) was added. The mixture, stirred at room temperature for 30 min, was poured into ice and the resulting solid was collected by filtration and dried (yield 85%). A sample was recrystallized from light petroleum (b.p. 40—60°), m.p. 69° [lit.,[4] 69° (from petroleum or alcohol)], δ 4.23 (s, OCH_3) and 7.36—8.33 (m, C_6H_5), m/e 192 $(M)^{+\cdot}$, 162 $(M - NO)^+$, and 132 $(M - N_2O_2)^{+\cdot}$, $\nu_{max.}$ (KBr) 1 600 cm^{-1} (furoxan).

3-*Methoxy*-4-*phenylfuroxan* (IIIb).—This compound was prepared in a similar way to its 4-methoxy-isomer (yield 70%). An analytical sample was recrystallized from light petroleum (b.p. 30—50°), m.p. 50—51° (Found: C, 56.3; H, 3.9; N, 14.5. $C_9H_8N_2O_3$ requires C, 56.25; H, 4.2; N, 14.6%), δ 4.20 (s, OCH_3) and 7.38—8.08 (m, C_6H_5); m/e 192 $(M)^{+\cdot}$, 162 $(M - NO)^+$, and 132 $(M - N_2O_2)^{+\cdot}$, $\nu_{max.}$ (KBr) 1 620 cm^{-1} (furoxan).

Thermal Isomerisation of 3-*Methoxy*-4-*phenylfuroxan*.—A solution of (IIIb) (0.050 g) in benzene (2.0 ml) was refluxed for 4 h. Removal of benzene left 4-methoxy-3-phenylfuroxan (IIIa). A sample recrystallized from light petroleum (b.p. 40—60°) melted at 69° and was identical (i.r., mixed m.p.) with the 4-methoxy-derivative prepared from (IIa). The isomerisation was quantitative.

Suitable crystals of (IIb) for *X*-ray measurements were obtained from light petroleum. The space group and the unit-cell parameters were derived from diffractometer data. The intensities were collected, using graphite-monochromatized Cu-K_α radiation, on a Philips PW 1100 four-circle diffractometer. The intensities of 1 518 unique reflections, in the range $2° \leqslant \theta \leqslant 65°$, were measured by the θ–2θ scanning technique. Lorentz and polarization corrections were applied to yield structure amplitudes $|F_0|$. Only 961 reflections for which $|F| \geqslant 4\sigma(F_0)$, where $\sigma(F_0)$ is the estimated standard deviation, were used in the refinement.

Crystal Data.—$C_8H_5N_3O_4$, $M = 207$. Orthorhombic, $a = 19.142(2)$, $b = 15.301(2)$, $c = 6.089(1)$ Å, $U = 1\,783.42$ Å^3, $Z = 8$, $D_c = 1.543$ g cm^{-3}. Space group *Pbca*, Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu(\text{Cu-}K_\alpha) = 9.90$ cm^{-1}.

Structure Solution and Refinement.—The structure was solved by direct methods using the SHELX [12] routine for centrosymmetric structures. The best set of signs, in terms of figures of merit, produced an E-map showing all 15 non-hydrogen atoms of the molecule. Their position and individual isotropic temperature factors were initially adjusted by three cycles of full-matrix least-squares refinement, using SHELX.[12] The hydrogen atoms were located on a difference map computed after three further cycles in which the components of the anisotropic temperature factors were refined. The hydrogen atoms were then included in the refinement but, in order to maintain them in stereochemically plausible positions, the C–H distances were constrained to their usual values (1.00 ± 0.05 Å); their isotropic temperature factor was refined as a single parameter [final value $B = 7.4(6)$cm^2]. The final cycles with anisotropic temperature factors assigned to all non-hydrogen atoms converged to an R value of 6.6%. The weighting scheme was $w = 1/[\sigma^2(F_0) + q\,F_0^2]$, where q is a variable parameter which is adjusted after each cycle; its final value was 0.0012 and the final weighted R factor was 6.7%.

Atomic scattering factors for carbon, nitrogen, and oxygen were taken from ref. 13 and for hydrogen from ref. 14.

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