Structure of the Asymmetric Diarylfuroxans Obtained by Reaction of *p*-Chloro- with *p*-Methoxy-benzonitrile *N*-oxide

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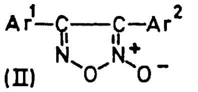
Summary An equimolar mixture of *p*-chloro- and *p*-methoxy-benzonitrile-*N*-oxide in carbon tetrachloride gives the four possible products, in nearly equal amounts.

SPONTANEOUS dimerization of benzonitrile *N*-oxides (I) in neutral medium leads to diarylfuroxans (II).[1] The mechanism of this reaction is under investigation.[2]

$Ar{-}C{\equiv}\overset{+}{N}{-}O^{-}$

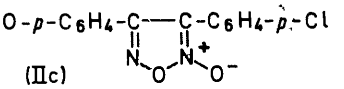
(I)



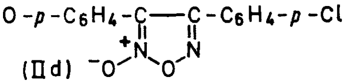
(II)

Following this research, the reaction of equimolar amounts of *p*-chlorobenzonitrile *N*-oxide (Ia) and *p*-methoxybenzonitrile *N*-oxide (Ib) in carbon tetrachloride at 40° was studied and analysed for the four possible furoxans, the two dimers ($Ar^1 = Ar^2$) and the two asymmetric derivatives ($Ar^1 \neq Ar^2$).

After the disappearance, as shown by ν(C≡N), of the total amounts of the previously-isolated nitrile-oxides, the crude reaction mixture was chromatographed over silica gel (70—325 mesh, ASTM, Merck) with benzene–light petroleum (1 : 2) to give three species: 3,4-di-*p*-chlorophenylfurazan *N*-oxide (IIa) m.p. 144—145° (144—145°[3]), 3,4-di-*p*-methoxyphenylfurazan *N*-oxide (IIb) m.p. 110—111° (112°[4]), and a third substance, shown by its spectroscopic characteristics and analytical data to be either asymmetric furoxan (IIc) or (IId), or a mixture of these; the m.p. of the third substance was 142—143° (from ethanol) unchanged by several crystallizations in different solvents. The relative yields of (IIa), (IIb), and (IIc, IId) were respectively 24, 24, and 52% under the outlined reaction conditions, but were substantially different at lower percentages of conversion. The ^1H n.m.r. spectrum (Figure 1) of (IIc, IId) shows the presence of two peaks for the methoxy-group; the separation between the two signals being 0·6 at 56·4 MHz. and 1·2 at 100 MHz. This unambiguously shows the presence of two nonequivalent methoxy-groups and suggests that (IIc, IId) is a mixture of two asymmetric furoxans in one of which the methoxyphenyl group is on the same side of the extra-annular oxygen (IId) and in the second one in the opposite situation (IIc). *X*-Ray crystal structure analysis of the product confirms this result.



(IIc)



(IId)

The crystal data for the species $C_{15}H_{11}N_2O_3Cl$ (IIc, IId) were: monoclinic, $P2_1/a$, $a = 12{\cdot}62(2)$, $b = 10{\cdot}20(2)$, $c = 12{\cdot}83(2)$ Å, $\beta = 122{\cdot}51(0{\cdot}10)^\circ$, M 303, $U = 1393{\cdot}1$ Å^3, $D_m = 1{\cdot}42$, $D_c = 1{\cdot}44$ g cm^{-3}. The intensities of 1152 independent non-zero reflections ($0kl$ through $9kl$) were taken with a multiple-film equi-inclination Weissenberg technique (Cu-K_α radiation) and recorded with a Joyce–Loebl microdensitometer. The reciprocal layers were brought on the same scale using nearly 400 reflections collected with a Siemens diffractometer. Absorption correlations were deemed to be unnecessary ($\mu = 25{\cdot}4$ cm^{-1}).

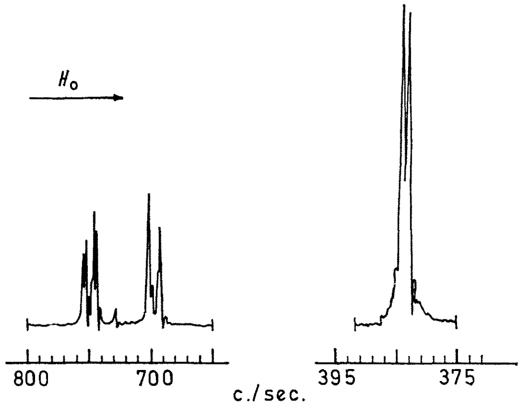


FIGURE 1. *^1H n.m.r. spectrum at* 100 *MHz of* (IIc, IId) *in* $CDCl_3$, *with* Me_4Si *as internal reference. The* 395—375 *c./sec. region is recorded on an expanded scale.*

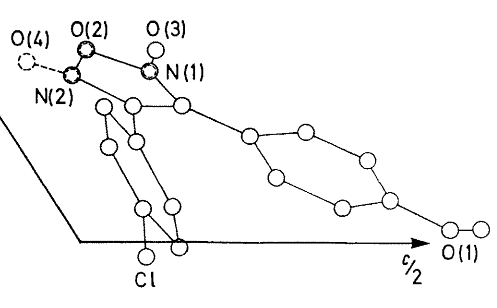


FIGURE 2. *Projection down the* b *axis of the mixture* (IIc, IId). *The dotted circles indicate the overlapping atoms of two different molecules.*

The crystal structure was solved by direct methods and confirmed by Fourier synthesis (F_0 and ΔF) and refined by a full matrix least-squares method with individual isotropic temperature factors to $R = 0{\cdot}14$. The structure consists of a build-up of the two different types of molecules, statically distributed in a ratio 47% of (IId) to 53% of (IIc). [These values were obtained from the relative weights of O(3) and O(4) in the refinement (Figure 2)].

The individual temperature factors of the atoms O(2), N(1), and N(2) are considerably higher than those of the remaining atoms (*ca.* 7 against 4 $Å^{-2}$). This is due to some statistical disorder in overlapping of these atoms. The bond lengths of the two benzene rings are normal with mean C–C = 1·40 ± 0·01 Å. The mean of the two extra-annular N–O distances is 1·07 ± 0·05 Å.

These results show that after complete reaction the distribution of the products obtained from benzonitrile *N*-oxides bearing substituents of opposite electronic effect in the phenyl ring is practically equal.

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[1] A. Werner and H. Buss, *Ber.*, 1894, **27**, 2193; J. V. R. Kaufman and J. P. Picard, *Chem. Rev.*, 1959, **59**, 429.

[2] A. Dondoni, A. Mangini, and S. Ghersetti, *Tetrahedron Letters*, 1966, 4489; G. Barbaro, A. Battaglia, and A. Dondoni, *J. Chem. Soc.*, in the press.

[3] A. Quilico, "Five- and six-membered compounds with Nitrogen and Oxygen," ed. R. H. Wiley, Interscience, New York, 1962, p. 21.

[4] C. R. Kinney, E. W. Smith, B. L. Walley, and A. R. Willey, *J. Amer. Chem. Soc.*, 1933, **55**, 3418.