Tetrahedron Letters No. 31, pp. 2907-2908, 1971. Pergamon Press. Printed in Great Britain.

CRYSTAL AND MOLECULAR STRUCTURE OF BIS-p-CHLOROPHENYLFURAZAN N-OXIDE

A. Battaglia and A. Dondoni*
Laboratorio Composti Carbonio con Eteroatomi del C.N.R., Ozzano Emilia, Italy

C. Panattoni, G. Bandoli and D.A. Clemente
Istituto Chimico, Università di Camerino and Laboratorio Chimica e Tecnologia Radioelementi del C.N.R., Padova, Italy.

(Received in UK 21 June 1971; accepted in UK for publication 2 July 1971)

Recently, Boulton and Katritzky and co-workers have pointed out[1] discrepancies in the melting point quoted for the 1,2,5-oxadiazole 2-oxide (furazan N-oxide) obtained from p-chlorobenzonitrile N-oxide or from its precursor, p-chlorobenzohydroxamoyl chloride treated with bases. The synthesis of bis-p-chlorophenylfurazan N-oxide (I) (R= p-ClC_6H_4) by a different route, and mass spectra, showed[1] that this product has m.p. 143-144°, practically identical with the values reported by Quilico and Speroni[2] (m.p. 144-145°), Truce and Naik[3] (m.p. 139-142°), and by Berg[4] (m.p. 145-146°).

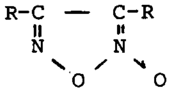
In connection with our studies[5] on the mechanism of the dimerization of nitrile oxides to furazan N-oxides, we have observed that pure p-chlorobenzonitrile N-oxide[6] affords, in high yield, under different conditions, *i.e.* in various solvents (chlorinated hydrocarbons, alcohols, dioxan, acetonitrile), or in carbon tetrachloride in the presence of tertiary amines (triethylamine, pyridine), a product melting at 144-145° (from ethanol). In order to confirm that this compound is the expected bis-p-chlorophenylfurazan N-oxide (I) and lend further support to the previous structural assignements[1-4] by means of another experimental method, we have carried out an X-ray structure determination of it. The crystal data for this species, $C_{14}H_8Cl_2N_2O_2$, were: orthorombic, *Pbcn*, a = 17.675, b = 9.219, c = 16.161 Å, M = 307.2, U = 2633.6 Å^3, Z = 8, D_m = 1.50, D_c = 1.52 g.cm^{-3}. The intensity of 1027 independent non-zero reflections (536 observed) were taken with a Siemens four-circle diffractometer ($\theta \leq 55°$). Absorption corrections were applied (μ = 44.2 cm^{-1}). The crystal structure was solved by direct methods, confirmed by Fourier synthesis (F_o and ΔF to locate hydrogen atoms) and refined by full-matrix least-squares; hydrogen atoms were excluded, chlorine atoms allowed to vibrate anisotropically and other atoms isotropically. The R index was 0.08. A perspective view of the molecule is shown in the Figure, while the most significant bond-lengths in Å (e.s.d's of

---

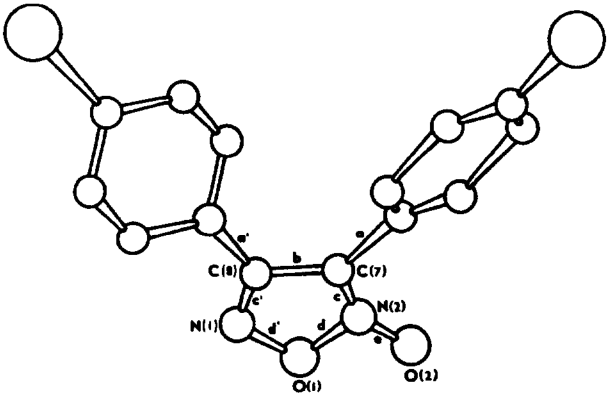
*To whom inquiries should be addressed at the Istituto di Chimica Organica e Chimica Industriale della Università, Viale Risorgimento 4, 40136 Bologna, Italy.

last figures in parentheses) and angles in degrees (e.s.d's in parentheses) are reported in the Table.

The bond distances and angles within the two benzene rings are those normally found in aromatic compounds; the two C-Cl distances are 1.713(9) Å. The pentatomic ring-atoms and the extra-annular oxygen are co-planar, whereas the phenyl rings lie in different planes.



(I)



FIGURE

TABLE

bond-lengths (Å)				angles (°)			
a	1.45(1)	c'	1.45(2)	∠ ab	131.0(0.8)	∠cd	112.3(1.0)
a'	1.45(1)	d	1.31(1)	∠ a'b	132.2(0.8)	∠c'd'	92.4(1.3)
b	1.40(1)	d'	1.29(2)	∠ bc	96.2(1.4)	∠dd'	120.6(1.4)
c	1.41(2)	e	1.16(1)	∠ bc'	118.5(1.3)	∠ce	120.8(1.2)

The present results domonstrate that the product, m.p. 144-145°, prepared by spontaneous dimerization of p-chlorobenzonitrile N-oxide has in fact the structure of bis-p-chlorphenylfurazan N-oxide (I) and confirm the correcteness of the assignements previously reported[1-4]. A similar investigation would be desirable to attribute unambigously the structure of the higher-melting isomers reported[4,7] by other Authors.

References

[1] A.J.Boulton, P.Hadjimihalakis, A.R.Katritzky, and Majid Hamid, J.Chem.Soc.(C), 1901 (1969).

[2] G.Speroni in "Five and Six-membered Compounds with Nitrogen and Oxygen" by A. Quilico, ed.R.H.Wiley, Interscience, New York, 1962, p.21.

[3] W.E.Truce and A.R.Naik, Canad.J.Chem., 44, 297 (1966).

[4] S.S.Berg, private communication cited in ref.1.

[5] G.Barbaro, A.Battaglia, A.Dondoni, J.Chem.Soc.(B), 588 (1970); C.Panattoni, D.A. Clemente, G.Bandoli, A.Battaglia, and A.Dondoni, Chem.Com., 60 (1970).

[6] Prepared from p-chlorobenzohydroxamoyl chloride and Et$_3$N, and recrystallised from ethyl ether-light petroleum at -70°, m.p. 82-83°.

[7] R.H.Wiley and B.J.Wakefield, J.Org.Chem., 25, 546 (1960).