Sulphone Structures. Part III.[1] Crystal and Molecular Structure of 5,5'-Dichloro-2-hydroxy-2'-(phenylsulphonyl)azoxybenzene

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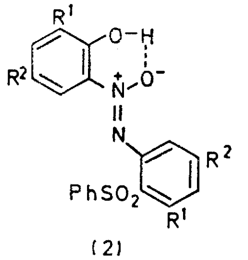
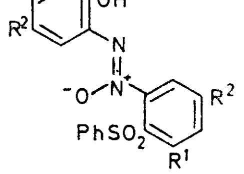
The crystal structure of the title compound (4) has been determined by a direct method. Crystals are monoclinic, $a = 14.68 \pm 0{\cdot}01$, $b = 12.07 \pm 0.01$, $c = 21.27 \pm 0.02$ Å, $\beta = 91.5° \pm 0.1°$, space group $A2/a$, $Z = 8$; visual data, R 0.11 for 2 079 independent reflections. The molecule contains a bifurcated hydrogen bond, and the orientation of the substituent to the phenylsulphonyl group is as expected.

DURING an investigation into base-catalysed rearrangements of aryl hydroxylamines, it was observed[2] that the major product from the reaction of a 2-hydroxyaminoaryl phenyl sulphone (1a, b, c) with sodium hydroxide or sodium methoxide in methanol was a 2-hydroxy-2'-(phenylsulphonyl)azoxybenzene (2) or (3). The ^{1}H n.m.r. spectra of the products indicated the presence of an intramolecular hydrogen bond, and for this reason structure (2) was preferred. Since the mechanism of this reaction is being studied[3] it was decided to establish the structure of the major product by an X-ray analysis of the compound derived from the hydroxylamine (1b).

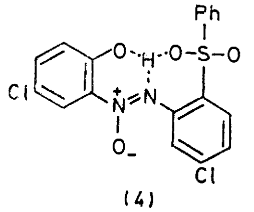
(1) a; $R^1 = R^2 = H$
b; $R^1 = H, R^2 = Cl$
c; $R^1 = Cl, R^2 = H$



(2)



(3)



(4)

RESULTS AND DISCUSSION

Interatomic distances are given in Table 1 and final atomic parameters in Table 2. A detail of the structure is shown in Figure 1, and the packing of the molecules in the unit cell is given in Figure 2.

The crystal contains isolated molecules not of structure (2) with a single intramolecular hydrogen bond, but of structure (4), with a bifurcated hydrogen bond. The molecule is in the shape of a contorted letter Y. Two phenyl rings, one from the phenyl sulphone and the other containing the hydroxy-group, make the arms of the Y and the third phenyl group forms the stem. In the unit cell the bulk of each molecule lies near a 004 plane with the stems in the zone of the b axis; the molecules pack, therefore, with the stem of one fitting between an arm from each of two adjacent molecules, one on either side along the a glide.

The molecular dimensions are much as expected, the

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[1] Part II, T. S. Cameron, K. Prout, B. Denton, R. Spagna, and E. White, *J.C.S. Perkin II*, 1975, 176.

[2] M. F. Grundon, D. J. Maitland, and W. L. Matier, *J. Chem. Soc.*, 1964, 654, and refs. therein.

[3] R. J. Cummings, University of Ulster, Ph.D. thesis, 1976.

most noticeable deviations are those required to accommodate the intramolecular hydrogen bond. The distances O(2) · · · O(4), N(1) · · · O(2), and N(1) · · · O(4) are 3.08, 2.96, and 2.63 Å, which suggests the presence of a bifurcated hydrogen bond between the three atoms.

TABLE 1

Interatomic distances and selected interbond angles (°)

(*a*) Distances			
S(1)–O(1)	1.453(7)	C(21)–C(22)	1.39(1)
S(1)–O(2)	1.470(7)	C(21)–C(26)	1.41(1)
S(1)–C(11)	1.775(9)	C(22)–C(23)	1.41(1)
S(1)–C(31)	1.788(9)	C(22)–O(4)	1.37(1)
N(1)–N(2)	1.31(1)	C(23)–C(24)	1.41(1)
N(1)–C(16)	1.43(1)	C(24)–C(25)	1.39(1)
N(2)–O(3)	1.27(1)	C(25)–Cl(2)	1.73(1)
N(2)–C(21)	1.43(1)	C(25)–C(26)	1.38(1)
C(11)–C(12)	1.41(1)	C(31)–C(32)	1.34(1)
C(11)–C(16)	1.42(1)	C(31)–C(36)	1.43(1)
C(12)–C(13)	1.40(1)	C(32)–C(33)	1.43(1)
C(13)–C(14)	1.42(1)	C(33)–C(34)	1.43(2)
C(14)–Cl(1)	1.75(1)	C(34)–C(35)	1.41(2)
C(14)–C(15)	1.37(1)	C(35)–C(36)	1.37(1)
C(15)–C(16)	1.38(1)		
	O(2)–O(4)	3.08(1)	
	O(2)–N(1)	2.96(1)	
	O(4)–N(1)	2.63(1)	
(*b*) Angles			
O(1)–S(1)–O(2)	120.0(4)	C(15)–C(14)–Cl(1)	119.1(9)
O(1)–S(1)–C(11)	107.0(5)	C(14)–C(15)–C(16)	118.3(9)
O(1)–S(1)–C(31)	107.5(4)	C(15)–C(16)–C(11)	120.2(8)
O(2)–S(1)–C(11)	108.3(4)	C(15)–C(16)–N(1)	123.3(8)
O(2)–S(1)–C(31)	108.1(4)	C(11)–C(16)–N(1)	116.3(8)
C(11)–S(1)–C(31)	104.9(4)	N(2)–C(21)–C(22)	123.9(8)
N(2)–N(1)–C(16)	118.3(7)	N(2)–C(21)–C(26)	117.0(8)
N(1)–N(2)–O(3)	123.2(8)	C(22)–C(21)–C(26)	119.2(8)
N(1)–N(2)–C(21)	117.3(8)	C(21)–C(22)–O(4)	124.6(8)
O(3)–N(2)–C(21)	119.5(8)	C(21)–C(22)–C(23)	119.8(9)
S(1)–C(11)–C(12)	118.4(8)	O(4)–C(22)–C(23)	115.5(8)
S(1)–C(11)–C(16)	121.4(7)	C(22)–C(23)–C(24)	120.7(10)
C(12)–C(11)–C(16)	120.1(9)	C(23)–C(24)–C(25)	118.0(10)
C(11)–C(12)–C(13)	120.3(10)	C(24)–C(25)–C(26)	121.9(10)
C(12)–C(13)–C(14)	116.6(10)	C(24)–C(25)–Cl(2)	117.6(8)
C(13)–C(14)–C(15)	124.6(10)	C(26)–C(25)–Cl(2)	120.4(9)
C(13)–C(14)–Cl(1)	116.3(9)	C(25)–C(26)–C(21)	120.4(9)

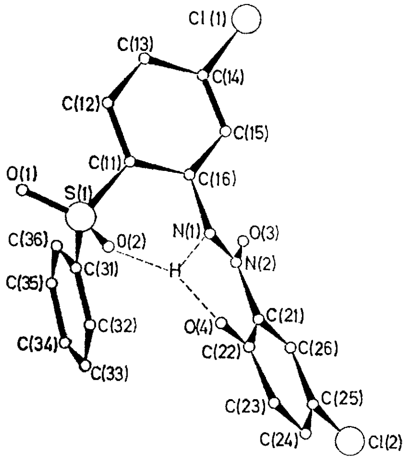

FIGURE 1 The molecule projected along (0, 0, 1)

This is supported by several associated observations. The O(1)–S–O(2) angle [120.0(4)°] is slightly larger than any we have observed in other sulphones [1,4] and the increase brings the oxygen atom O(2) closer to N(1) and O(4), moreover the S–O(2) bond length [1.470(7) Å] is longer than S–O(1) [1.453(7) Å], again indicative [1] of the presence of a hydrogen bond at atom O(2). The angle C(11)–C(16)–N(1) is reduced from the expected value of 120° to 116.3(8)°, this decreases the distance between atoms N(1) and O(2) without greatly altering the N(1) · · · O(4) contact. The N(1)–N(2) bond length [1.31(1) Å] is considerably longer than the equivalent N–N bond [1.218(5) Å] in *p*-azoxyanisole [5] which is consistent with an N · · · H interaction at N(1) particularly as the N(2)–O(3) bond length [1.27(1) Å] compares with N–O 1.279(4) Å in *p*-azoxyanisole.[5] The increase in the N(2)–C(21)–C(22) and C(21)–C(22)–O(4) angles from 120° to 123.9(8) and 124.6(8) increases the separation between atoms N(1) and O(4). The N(1) · · · O(4) distance, however, is still much shorter than the other two: N(1) · · · O(2) or O(2) · · · O(4). The consistent trend through all the angular distortions to balance these three distances, which in conjunction with the bond length changes normally associated with hydrogen bonding, strongly supports the existence of the suggested bifurcated hydrogen bond. Unfortunately the hydrogen atom of this bond could not be located with confidence from a difference-Fourier synthesis (see later).

The angle between the plane through the three sulphone atoms [O(1), S(1), and O(2)] and that through atoms S(1), C(11), and C(12) is 57.6°, within the range (53—65°) observed [1] for the angle between the SO_2 and SNC(R) planes in substituted aminosulphones ($PhSO_2NHR$) but well outside that (83.98°) observed [1,4] for iminosulphones ($PhSO_2N{:}CR^1R^2$). In the former, when the hydrogen of the NHR group could be located, the nitrogen atom was coplanar with the three atoms bonded to it and it is not surprising that the replacement of NHR by a phenyl group does not affect the orientation of the substituent plane. The two S–C bond lengths are not significantly different and represent [1] a π bond-order of *ca.* 0.25.

Carbon atoms C(16) and C(21) are 0.25 and 0.19 Å respectively on opposite sides of the plane of the azoxy-group. The planes of the two phenyl groups [that containing chlorine atom Cl(1) and that containing Cl(2)] are inclined at angles of 54° and 7° to the azoxy-plane. As had been noted earlier, the azoxy-group has distinctly different dimensions from those of *p*-azoxyanisole.[5] The C–N distances have shortened from 1.496(6) to 1.43(1) Å and the N–N distance increased. This is a result of the reduction in π bond-order along the N–N bond, and the consequent increase in charge separation along the C–N bond. The N–O bond is apparently unaffected, the length [1.27(1) Å] being not significantly different from that in *p*-azoxyanisole (1.279 Å), and similar to the mean length in 1,8-dinitrosonaphthalene [6] (1.264 Å) or to that in a monomeric nitroso compound [7] such as 4-nitroso-5-triphenylphosphoranylideneaminobenzo[1,2-*c*:3,4-*c*′]difurazan [1.265(8) Å].

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[4] J. Tickle and C. K. Prout, *J. Chem. Soc.* (*C*), 1971, 3401.

[5] W. R. Krigbaum, Y. Chatani, and P. G. Barber, *Acta Cryst.*, 1970, **B26**, 97.

[6] T. S. Cameron, C. K. Prout, R. M. A. Dunn, O. J. R. Hodder, and D. Viterbo, *Acta Cryst.*, 1971, **B27**, 1310.

[7] T. S. Cameron and C. K. Prout, *J. Chem. Soc.* (*C*), 1969, 2285.

TABLE 2

Final atomic parameters * (× 10^4), with estimated standard deviation in parentheses

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	5 385(1)	5 079(1)	2 058(1)	35	42	13	−16	−9	4
Cl(1)	2 910(2)	1 306(1)	923(1)	80	63	36	−34	−4	−87
Cl(2)	1 206(2)	9 197(1)	350(1)	90	79	22	30	−22	28
O(1)	6 285(4)	4 593(3)	2 141(3)	35	68	27	−17	−19	30
O(2)	4 950(5)	5 630(3)	2 589(3)	61	43	13	−17	−3	5
O(3)	2 901(6)	5 475(3)	665(3)	106	81	8	−32	−20	42
O(4)	3 208(5)	7 035(2)	2 437(2)	55	86	10	−20	−18	32
N(1)	3 412(4)	5 338(3)	1 678(3)	24	63	10	−13	−2	−1
N(2)	2 999(5)	5 870(3)	1 215(3)	48	20	15	−18	−7	−5
C(11)	4 649(6)	4 013(4)	1 777(4)	37	44	13	−2	−1	12
C(12)	5 003(8)	2 928(5)	1 727(5)	55	66	17	−5	−4	−3
C(13)	4 457(8)	2 071(5)	1 482(5)	67	52	17	−9	12	−26
C(14)	3 566(7)	2 366(4)	1 268(4)	56	60	15	−14	0	−57
C(15)	3 203(7)	3 412(4)	1 305(4)	42	50	16	−8	4	−14
C(16)	3 741(6)	4 245(4)	1 562(4)	33	53	12	−2	6	−1
C(21)	2 637(6)	6 944(4)	1 351(4)	30	41	11	−4	3	−9
C(22)	2 760(6)	7 478(4)	1 926(4)	40	44	14	−9	−8	4
C(23)	2 368(7)	8 531(5)	2 019(5)	47	74	18	−5	0	−7
C(24)	1 887(8)	9 073(5)	1 524(5)	54	49	24	−7	2	−7
C(25)	1 778(7)	8 518(4)	957(4)	42	71	17	17	2	−14
C(26)	2 136(7)	7 477(4)	865(4)	44	44	14	8	−5	−15
C(31)	5 435(6)	6 048(3)	1 424(3)	32	43	11	−14	1	−11
C(32)	5 206(7)	7 110(4)	1 504(4)	47	49	15	−4	12	2
C(33)	5 270(9)	7 885(5)	999(5)	64	71	24	21	−9	3
C(34)	5 585(9)	7 466(5)	416(5)	68	123	20	9	25	−25
C(35)	5 814(10)	6 342(5)	340(5)	93	79	18	−2	25	−35
C(36)	5 745(8)	5 630(5)	837(5)	65	67	20	−30	9	−23

* The temperature factor $T = \exp[-2^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{23}klb^*c^* + U_{13}hla^*c^* + U_{12}hka^*b^*)]$.

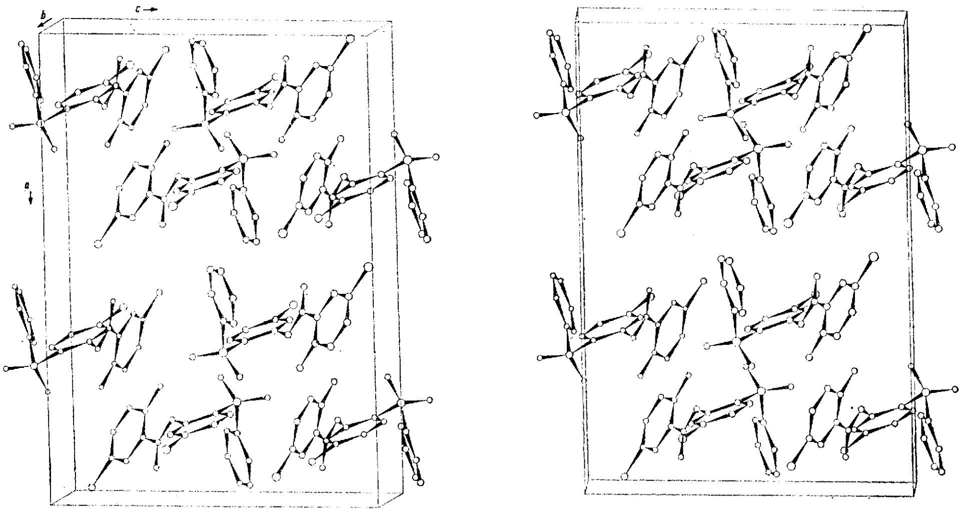

FIGURE 2 Stereoscopic projection of the molecule approximately along (0,1,0)

The C–O bond length [1.37(1) Å] is very similar to those (1.383 and 1.385 Å) reported[8] for the two unique molecules of the stable crystal form of *p*-chlorophenol, where the hydroxy-group is part of two hydrogen bonds. The C–Cl bond lengths for the chlorine atom *para* to the hydroxy-group in the phenol (1.738 and 1.735 Å) are equivalent to those in this present compound: C(14)–Cl(1) 1.75(1) and C(25)–Cl(2) 1.73(1) Å.

EXPERIMENTAL

Crystals were prepared as described in ref. 2 and recrystallised slowly from chloroform.

Crystal Data.—$C_{18}H_{12}Cl_2N_2O_4S$, $M = 423.27$. Monoclinic, $a = 14.68 \pm 0.01$, $b = 12.07 \pm 0.01$, $c = 21.27 \pm 0.02$ Å, $\beta = 91.5 \pm 0.1°$, $D_m = 1.50$, $Z = 8$, $D_c = 1.49$ g cm^{-3}. Space group $A2/a$ (C^6_{2h}, No. 15, alternative setting). Cu-K_α radiation, $\lambda = 1.5418$ Å; μ(Cu-K_α) = 43.7 cm^{-1}. 2 079 independent reflections estimated visually from equi-inclination Weissenberg photographs, layers $h0$—$10l$.

The crystal structure was determined by a direct method using the symbolic-addition procedure. The signs of 220 out of 262 reflections with $E > 1.6$ were determined. All non-hydrogen atoms were located in the resultant E map.

The trial structure, with individual isotropic temperature factors on all atoms and with unit weights was refined by block-diagonal least-squares. After four cycles R was 0.19, and when the interlayer scale factors for each film pack had been refined, R was 0.17. The refinement converged after four more cycles with individual anisotropic temperature factors and a weight w where: $w = \{[1 + (|F_o| - 45)/37]^2\}^{-1}$ with R 0.11. Attempts were made to locate the

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[8] M. Perrin and P. Michel, *Acta Cryst.*, 1973, **B29**, 258.

hydrogen atoms both at the completion of the isotropic and the anisotropic temperature factor refinement. Difference-Fourier syntheses were calculated for the full data and for the data restricted to reflections with a Bragg angle of less than 40° (to increase the proportion of the hydrogen atom contribution to the difference synthesis). In no case was it possible to determine hydrogen atom positions with any confidence.

Observed structure amplitudes and structure factors calculated from the final atomic parameters in Table 2 have been deposited. Atomic scattering factors for neutral atoms [9] were corrected for the real part of the anomalous dispersion. Computation were made by the use of the N.U.U. Crystal system.[10] Diagrams were drawn by the use of STRPL.[10]

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[9] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1969.

[10] T. S. Cameron, University of Ulster Internal Report I, 1973.