The Crystal and Molecular Structure of 4,4'-Dichlorodiphenyl Sulfone

By J. G. Sime

Chemistry Department, The University, Glasgow W. 2, Scotland

and S. C. Abrahams

Bell Telephone Laboratories, Murray Hill, New Jersey, U.S.A.

4,4'-dichlorodiphenyl sulfone forms monoclinic crystals, space group $I2/a$, in a cell with

$$a = 20 \cdot 204 \pm 0 \cdot 010, \quad b = 5 \cdot 009 \pm 0 \cdot 010, \quad c = 12 \cdot 259 \pm 0 \cdot 010 \text{ Å}, \quad \beta = 90° \ 34' \pm 15',$$

containing four molecules. The crystal structure has been solved by two-dimensional Patterson and by trial-and-error methods. The position and thermal vibration parameters were initially refined by use of double Fourier series. Final refinement was obtained by a complete anisotropic least-squares analysis of the 1158 observed and 548 unobserved structure factors. The three position and six thermal parameters of all atoms except hydrogen have been determined. The bond distances of interest include $S-C = 1 \cdot 765 \pm 0 \cdot 006$, $S-O = 1 \cdot 432 \pm 0 \cdot 005$, $C-C = 1 \cdot 380 \pm 0 \cdot 003$, $Cl-C = 1 \cdot 736 \pm 0 \cdot 007$ Å; among the bond angles are $C-S-O = 107° \ 39' \pm 17'$, $C-S-C = 104° \ 48' \pm 24'$, $O-S-O = 120° \ 24' \pm 25'$. The dihedral angle between the planes of the aromatic rings is $79° \ 27' \pm 18'$ and between the plane of each ring and the common C–S–C plane it is $84° \ 25' \pm 18'$.

1. Introduction

The geometrical configuration of the sulfone group, $X-SO_2-Y$, has now been studied in several molecules. The bond distribution about the sulfur atom is found to depart significantly from that of a regular tetrahedron (for a review, see Abrahams, 1956), with some dependence on the substituent atoms X and Y. The sulfone group is of particular interest when linked to two aromatic rings, in view of the molecular orbital investigation of diphenyl sulfone by Koch & Moffitt (1951). These authors predicted overlap of the sulfur atom $3d$ orbitals with the adjacent carbon atom $2p$ orbitals, resulting in an angle of 90° between the normals to the aromatic rings and the common C–S–C plane.

The crystal structure of diphenyl sulfone has not yet been solved. However, two-dimensional studies of the isomorphous crystals, 4,4'-dichlorophenyl sulfone (Toussaint, 1948), 4,4'-dibromodiphenyl sulfone (Toussaint, 1948) and 4,4'-diiododiphenyl sulfone (Keil & Plieth, 1955) have been reported. In the case of the chloro- and iodo-compounds, Fourier series projected along one axis only were computed; a second electron-density projection, along a 12·34 Å axis, was also studied for the bromo-compound. It was not possible to obtain accurate interatomic dimensions in any of these crystals. The present investigation of the chloro-compound has utilized the complete three-dimensional X-ray diffraction data. The subsequent results will provide, *inter alia*, a comparison with a simultaneous neutron diffraction study (Bacon & Curry, 1960) of the same crystal.

2. Crystal data

4,4'-dichlorodiphenyl sulfone, $(p\text{-Cl} \cdot C_6H_4)_2SO_2$; mol.wt. $= 287 \cdot 2$; m.p. $= 147 \cdot 5$ °C, $D_m = 1 \cdot 533$ g.cm.$^{-3}$; $D_x = 1 \cdot 537$ g.cm.$^{-3}$. Monoclinic, with $a = 20 \cdot 204 \pm 0 \cdot 010$, $b = 5 \cdot 009 \pm 0 \cdot 010$, $c = 12 \cdot 259 \pm 0 \cdot 010$ Å, $\beta = 90 \cdot 57 \pm 0 \cdot 25°$ (Toussaint (1948) obtained the values 20·5, 5·01, 12·3 kX, $\beta = 90° \ 31'$, with the a- and c-axes interchanged). Four molecules per unit cell. (hkl) present only when $h + k + l = 2n$, ($h0l$) only when $h = 2n$, $l = 2n$. Space group C_{2h}^6-I2/a or C_s^4-Ia (the body-centered cell chosen by Toussaint in 1948 has been retained here to avoid a conflict in the literature). The $N(z)$ test of Howells, Phillips & Rogers (1950), using the complete three-dimensional intensity data, clearly indicated the most probable space group to be $I2/a$. Molecular symmetry required by this space group in the absence of disorder, 2 or $\bar{1}$. Absorption coefficient for Mo $K\alpha$ radiation ($\lambda = 0 \cdot 7107$ Å), $0 \cdot 718$ mm^{-1}. Volume of the unit cell, 1240·6 Å^3. Total number of electrons per unit cell, $F(000) = 584$.

3. Experimental

Well formed plates of 4,4'-dichlorodiphenyl sulfone recrystallized from benzene solution, were kindly provided by Dr H. H. Szmant of Duquesne University. All intensity records (Ilford 'Industrial-G' film) were made using Mo $K\alpha$ radiation, except for some preliminary investigations of the ($h0l$) layer by Cu $K\alpha$ radiation which later were discarded. Two crystals were used, of dimensions $0 \cdot 5 \times 0 \cdot 3 \times 0 \cdot 3$ mm and $1 \cdot 0 \times 0 \cdot 5 \times 0 \cdot 5$ mm, the latter only in obtaining the

weakest intensities. The intensity measurements were made visually, with the aid of both the multiple exposure and the multiple-film techniques. Sheets of 0·0008 in. nickel foil were interleaved between films in the second technique, resulting in an intensity reduction of 2·65:1 for normal exposures. In upper layers recorded with the Weissenberg camera, this ratio was modified by the obliquity factor (Rossman, 1956), with $1/(1-c)=1\cdot142$ and $\mu t=0\cdot842$ in Rossman's notation.

The ratio of the strongest to the weakest intensity (taken as unity) was 8,800 in $hk0$; 37,200 in $hk1$; 8,800 in $hk2$; 3,645 in $hk3$ and 3,000 in $hk4$, recorded with the precession camera. In the remaining layers, recorded with a modified Weissenberg camera based on a design by Abrahams (1954), this ratio was 37,950 in $h0l$; 22,300 in $h1l$; 3,905 in $h2l$; 646 in $h3l$; 374 in $h4l$; 315 in $h5l$; 92 in $h6l$ and 4 in $h7l$. Intensities measured on the precession camera were corrected for the Lorentz-polarization factor by use of the Waser (1951) and the Grenville-Wells & Abrahams (1952) charts. Those measured on the Weissenberg camera were corrected in the usual way, including Tunell's (1939) rotation factor for the upper layer lines. Absorption corrections were neglected, since the maximum differences among the corrections were so small. Extinction corrections were not made.

The resulting structure factors were placed on a common scale, using the 351 reflections measured in two different layers. An approximation to the standard deviation in the structure factors was obtained by a comparison of these 351 independent pairs of observations. This standard deviation was very nearly a constant percentage of the magnitude of the structure factor, with $\sigma F_i \simeq 0\cdot092|F_i|$. The complete set of 1706 structure factors on the final, absolute, scale is given in Table 1 under $F_{\text{meas.}}$.

4. Analysis of the structure

The following analysis was carried out without reference to the publication by Toussaint (1948) on 4,4'-dichlorodiphenyl sulfone. Of the two possible space groups, that indicated by the Howells, Phillips & Rogers (1950) test was chosen, and was later justified by the quality of fit obtained among the measured and calculated structure factors. In $I2/a$, assuming no disorder, the molecular symmetry required of the four molecules in the unit cell is 2 or $\bar{1}$, with the sulfur atom in a special position. The known bond arrangements in sulfone groups (Abrahams, 1956) eliminate the center, hence requiring the sulfur atom to have coordinates $\frac{1}{4}, y, 0$; $\frac{3}{4}, \frac{1}{2}+y, \frac{1}{2}$; $\frac{3}{4}, \bar{y}, 0$; $\frac{1}{4}, \frac{1}{2}-y, \frac{1}{2}$.

The x- and z-coordinates of the chlorine and carbon atoms were immediately apparent from an evaluation of the Patterson projection along the b-axis (Fig. 1). The coordinates of the oxygen atom were deduced by assuming a S–O bond distance of 1·43 Å and
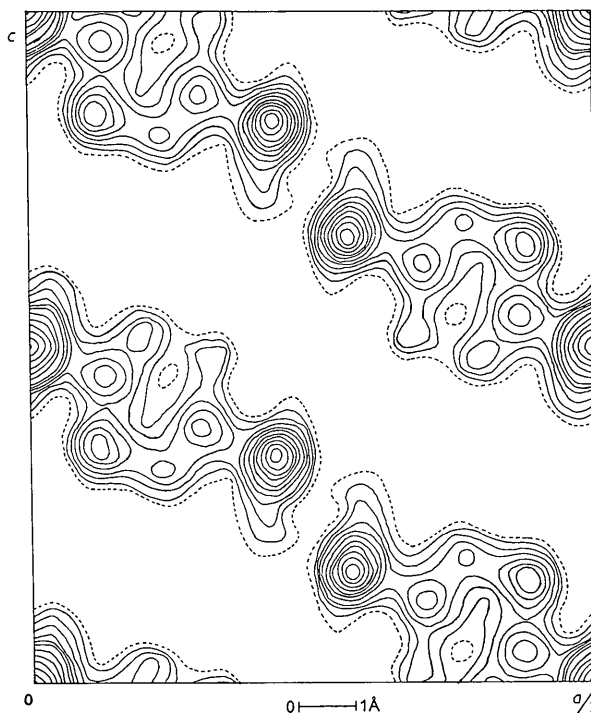

Fig. 1. Patterson projection of one-half unit cell of 4,4'-dichlorodiphenyl sulfone along the b-axis.

O–S–O bond angle of 120°. An over-all isotropic temperature factor for B, in the expression

$$\exp\left(-B\,(\sin\theta/\lambda)^2\right),$$

of 3·76 Å² was given by Wilson's (1942) method, using McWeeny's (1951) atomic form factors for carbon and oxygen and James & Brindley's (1931) form factors for sulfur and chlorine. Structure factors calculated with these x-, z- and B-values resulted in an agreement factor R of 0·43 for the 160 $(h0l)$ observations measured with Cu $K\alpha$ radiation. Refinement in this projection was effected by use of difference Fourier syntheses which revealed large anisotropic thermal vibrations of the chlorine and sulfur atoms. The expression used in calculating anisotropic temperature factors was

$$\exp\left[-\{L+M\cos^2(\omega-\beta)\}s^2\right],$$

where $4L=B_{\text{min.}}$, $4M=B_{\text{max.}}-B_{\text{min.}}$, $s=\sin\theta/\lambda$, $\omega=\tan^{-1}l/h$ and $\beta=$ angle between maximum vibration direction and the a-axis (Cochran, 1951). After four difference syntheses based on 189 structure factors measured with Mo $K\alpha$ radiation, $Cl(B_{\text{max.}})=6\cdot40$, $Cl(B_{\text{min.}})=3\cdot80$, $S(B_{\text{max.}})=6\cdot00$, $S(B_{\text{min.}})=3\cdot00$ Å² and $\beta=65°\,50'$: the previous isotropic value, 3·76 Å², of B for carbon and oxygen remained unchanged. The R value at this stage was 0·185. An $F_{\text{meas.}}$ Fourier series projected along the b-axis is shown in Fig. 2(a).

The Patterson projection along the c-axis was not readily interpretable. The y-coordinates were instead obtained by trial and error. The best agreement with

Table 1. *Measured and calculated values of the 4,4'-dichlorodiphenyl sulfone structure factors*

* Unobserved structure factor: maximum value about double that listed.   † Term omitted from least-squares analysis.
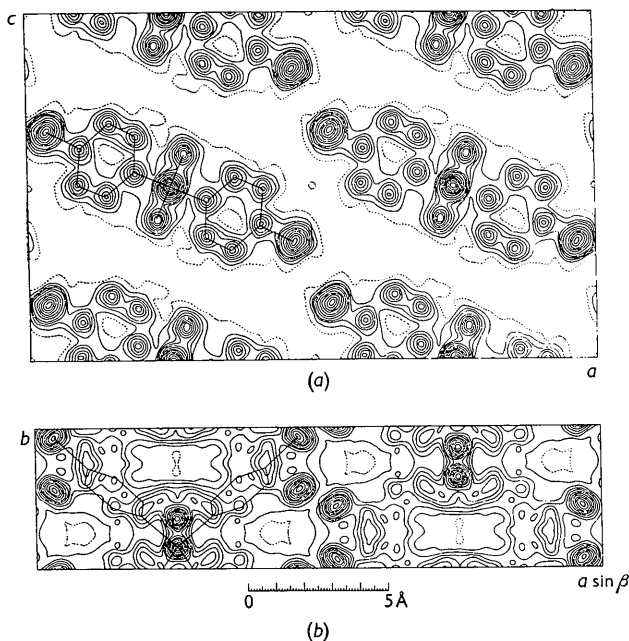
1*

(a)

0   5Å $a\sin\beta$

(b)

Fig. 2. Fourier projection of one unit cell of 4,4'-dichloro-diphenyl sulfone (a) along the b-axis and (b) along the c-axis.

the measured structure factors was obtained for $y_S = 0.135$. The complete set of $(hk0)$ structure factors then gave $R = 0.43$. Examination of one Fourier series projected along the c-axis led to coordinates with $R = 0.344$. The degree of overlap in this projection (Fig. 2(b)) hindered further refinement. The atomic coordinates obtained from the two-dimensional refinement process are given in Table 2.

5. Three-dimensional least-squares refinement

The method of least squares was chosen for refining the parameters, using the three-dimensional data. Initially, 1071 observed and 475 unobserved structure factors, together with those calculated from the coordinates in Table 2, were processed using the $NY\ XR2$ program for the IBM 704 computer. In forming the 1546 conditional equations, unobserved terms were taken as one-half the maximum value. Weights were assigned on the basis of $w^{\frac{1}{2}}_{hkl} \propto 100/|F_{\text{meas.}}(hkl)|$, with $w(\text{max.}) = 25$ for $|F_{\text{meas.}}(hkl)| \leq 20$ (Abrahams, 1955): unobserved terms had a weight of unity (4% maximum

Table 2. *Final two-dimensional positional coordinates*

Atom	x	y	z
Cl	0·0319	0·946	0·1592
S	0·2500	0·135	0
O	0·2250	0	0·9051
C_1	0·1870	0·368	0·0458
C_2	0·1362	0·505	0·9755
C_3	0·0884	0·697	0·0106
C_4	0·0903	0·726	0·1162
C_5	0·1433	0·583	0·1845
C_6	0·1917	0·399	0·1497

value). The atomic form factors used were those of Berghuis *et al.* (1955) for carbon and oxygen and of Viervoll & Øgrim (1949) for sulfur and chlorine. Because the $NY\ XR2$ program is not designed to handle anisotropic thermal vibrations, isotropic values of $B = 5.00$ Å^2 for chlorine and of 4·30 Å^2 for sulfur replaced those found in the $(h0l)$ difference syntheses. In the first three least-squares iterations, the only parameters varied were x_i, y_i, z_i for all i-atoms except hydrogen, and the scale factor. In the following two refinement cycles, the individual values of B_i were also taken as variable, and in the final two cycles the contribution of the hydrogen atoms was included in the calculated structure factors, assuming the hydrogen atoms lie on the extended lines C_2–C_5 and C_3–C_6, with C–H = 1·08 Å. The corresponding values of R' (this differs from the usual agreement factor R in the treatment of the unobserved terms: in R' these are taken as one-half of the maximum value and in consequence $R' \simeq R + 0.03$) and $\Sigma w \Delta^2$ (the quantity minimized in the least-squares process, where w = weight and $\Delta = (|F_{\text{meas.}}| - |F_{\text{calc.}}|)$) are given in Table 3. The rather constant value of R' and of $\Sigma w \Delta^2$ in the final

Table 3. *Course of refinement using*
$NY\ XR2$ program

	R'	$\Sigma w \Delta^2$
Parameters obtained from 2D-refinement	0·446	1,373,060
1st cycle: $x_i y_i z_i$ variable, B_i constant	0·397	988,090
2nd cycle: $x_i y_i z_i$ variable, B_i constant	0·360	804,880
3rd cycle: $x_i y_i z_i$ variable, B_i constant	0·341	700,940
4th cycle: $x_i y_i z_i$ and B_i variable	0·306	545,070
5th cycle: $x_i y_i z_i$ and B_i variable	0·293	462,310
6th cycle: $x_i y_i z_i$ and B_i variable and hydrogen atom contributions included in structure factors, but not varied	0·273	522,667
7th cycle: $x_i y_i z_i$ and B_i variable and hydrogen atom contributions included in structure factors, but not varied	0·269	465,666

Note 1. 1540 observational equations used in this refinement.
Note 2. $w = 25$ for $|F_{\text{meas.}}| \leq 20$, and $w = 10,000 \div |F_{\text{meas.}}|^2$ for $|F_{\text{meas.}}| > 20$.

cycles indicated the refinement process was probably as complete as the $NY\ XR2$ program would permit. An examination of the coordinate shifts ($\Delta \xi_i$) obtained from the 7th cycle and the corresponding standard deviations in these shifts ($\sigma \xi_i$) revealed that many $\Delta \xi_i$ were still significant (Table 4), particularly in the temperature factor for chlorine. To obtain further refinement, it was clear that the anisotropy of thermal vibration present in this crystal had to be determined. The comprehensive least-squares program written by Dr H. A. Levy and Dr W. R. Busing for the ORACLE computer was then made available to us, through the courtesy of Dr Levy and Dr Busing and of the Chemistry Division of Oak Ridge National Laboratory. In this program, temperature factors of the form

$$\exp\left[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{31}lh)\right]$$

Table 4. *Comparison of coordinate-shifts and corresponding standard deviations from 7th NY XR2 least-squares cycle*

	Δx	σx	Δy	σy	Δz	σz	ΔB	σB
C_6	0·00003	0·00048	0·00127	0·00200	0·00083	0·00079	0·105	0·16
C_5	0·00027	0·00048	− 0·00068	0·00200	0·00091	0·00079	0·295	0·16
C_4	0·00037	0·00048	0·00066	0·00200	0·00171	0·00079	0·298	0·16
C_3	0·00004	0·00048	− 0·00063	0·00200	0·00092	0·00079	0·173	0·16
C_2	0·00028	0·00048	0·00127	0·00200	0·00025	0·00079	0·106	0·16
C_1	0·00016	0·00048	0·00080	0·00200	0·00071	0·00079	0·104	0·16
O	− 0·00017	0·00039	0·00023	0·00177	− 0·00058	0·00066	0·192	0·15
Cl	0·00005	0·00020	0·00010	0·00092	0·00019	0·00032	0·319	0·08
S	0	0	− 0·00005	0·00085	0	0	− 0·023	0·07

are assumed for each atom, and in the least-squares process the complete normal equation set, including off-diagonal terms, is solved. For the general positions in $I2/a$, all symmetry related atoms have the same coefficients β_{ij} except for a sign change in β_{12} and β_{23} for atoms related by the 2-fold axis: for sulfur, β_{12} and β_{23} are zero (cf. Levy (1956)). The Viervoll & Øgrim (1949) atomic form factors for sulfur and chlorine previously used were replaced in the ORACLE refinement. The factor of Tomiie & Stam (1958), based on Slater atomic wave-functions, was taken for sulfur. A modified Berghuis et al. (1955) Cl⁻-curve was used for chlorine, in which $f_{Cl} = 17·0$ at $\sin \theta/\lambda = 0$ and $f_{Cl} = f_{Cl^-}$ at $\sin \theta/\lambda \geq 0·2$. The weights used were as in the NY XR2 refinement, except for those of the unobserved terms (which were again taken as one-half maximum value): these now were assigned the maximum weight of 25. The hydrogen atom contributions were included in the calculated structure factors throughout, using Bacon's (1957) isotropic values of B (Table 5). The initial hydrogen atom coordinates, also given in Table 5, were Bacon's (1957) x- and z-values together with y-values obtained by solving these x-, z-coordinates against the equation of the benzene ring plane found from the 7th NY XR2 cycle.

Table 5. *Initial hydrogen atom coordinates*

Atom	x	y	z	B
H_2	0·1375	0·3452	0·8944	6·1
H_3	0·0447	0·6703	0·9558	6·9
H_5	0·1489	0·7183	0·2708	6·9
H_6	0·2319	0·4152	0·2044	6·1

The total number of terms used in the ORACLE program was increased to 1706, of which 1158 were observed structure factors. A requirement was placed on each term that rejected it from inclusion in an observational equation if $3F_{calc.} < F_{meas.}$. Structure factors based on the coordinates from the 7th NY XR2 cycle contained 141 such rejected terms. Those based on the final ORACLE coordinates contain 126 rejected terms, and are indicated by a dagger in Table 1. Of these, 76 refer to unobserved terms and need not have been rejected.

The ORACLE is able to solve a determinant of order not exceeding 48, so the 78th-order determinant resulting from the 25 position, 52 thermal and 1 scale

factor parameters was solved in two, overlapping, parts. In all, six cycles of refinement were computed: no significant changes in R' or $\Sigma w \Delta^2$ occurred after the 4th cycle. More important, all subsequent $\Delta \xi_j$'s were less than their $\sigma \xi_j$. The final two cycles then completely ensured convergence. The variation in R' and in $\Sigma w \Delta^2$ in the course of the ORACLE refinement is shown in Table 6. In splitting the 78th-order deter-

Table 6. *Course of refinement using ORACLE program*

	R'	$\Sigma w \Delta^2$
Final NY XR2 coordinates: variables	0·2562	406,987
1st cycle: $x_i y_i z_i$, $\beta_{,11}$ β_{22}, β_{33}, β_{12}, β_{23}, β_{31}	0·1759	183,484
	0·1589	140,496
2nd cycle: $x_i y_i z_i$, β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}	0·1467	116,892
	0·1430	112,371
3rd cycle: $x_i y_i z_i$, β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}	0·1419	109,379
4th cycle: $x_i y_i z_i$, β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}	0·1415	107,434
5th cycle: $x_i y_i z_i$, β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}	0·1415	107,548
6th cycle: $x_i y_i z_i$, β_{11}, β_{22}, β_{33}, β_{12}, β_{23}, β_{31}	0·1414	107,481

Note 1. 1706 observational equations used in this refinement.
Note 2. Final R' corresponds to $R = 0·108$ with unobserved $F_{meas.}$ taken as one half maximum value.

minant, all parameters of any atom were kept as a group, and in general, nearest neighbor atoms were included in each cycle. After the 3rd cycle, new hydrogen atom coordinates (Table 7) were deduced,

Table 7. *Final deduced hydrogen atom positional coordinates*

Atom	x	y	z
H_2	0·1321	0·3557	0·8943
H_3	0·0473	0·6646	0·9568
H_5	0·1463	0·7257	0·2685
H_6	0·2310	0·4210	0·2042

based on C–H $= 1·08$ Å and being located on the extended C_2–C_5 and C_3–C_6 lines. Hydrogen atom parameters were not refined at any stage. It is interesting to note the large reduction of nearly 4:1 (Table 6) in $\Sigma w \Delta^2$, obtained on going from an isotropic analysis using the diagonal approximation in solving the determinant, to a complete anisotropic least-squares analysis.

6. Final coordinates

The final values of x_i, y_i, z_i, β_{ij} resulting from the 6th ORACLE refinement cycle are given in Table 8.

Table 8. *Final atomic coordinates for 4,4'-dichlorodiphenyl sulfone*

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0·0327	0·9381	0·1621	0·00454	0·07857	0·01700	0·00883	0·00281	0·01043
S	0·2500	0·1546	0	0·00312	0·03686	0·00755	0	−0·00025	0
O	0·2244	0·0126	0·9073	0·00403	0·04319	0·00926	−0·00275	−0·00045	−0·00551
C_1	0·1868	0·3696	0·0456	0·00281	0·03571	0·00762	−0·00069	−0·00047	0·00373
C_2	0·1352	0·4367	0·9760	0·00272	0·05968	0·00808	−0·00053	−0·00048	0·00333
C_3	0·0877	0·6117	0·0112	0·00296	0·07263	0·01019	0·00207	−0·00011	0·00680
C_4	0·0926	0·7173	0·1164	0·00297	0·05671	0·01165	0·00190	0·00143	0·00785
C_5	0·1431	0·6448	0·1867	0·00347	0·06119	0·00922	0·00313	−0·00011	0·00051
C_6	0·1910	0·4743	0·1503	0·00331	0·04502	0·00773	0·00192	−0·00006	0·00073

These coordinates correspond to $R'=0\cdot1414$ (Table 6) or $R=0\cdot108$ if unobserved $F_{\text{meas.}}$ terms are taken as less than double the half-maximum (asterisked) values given in Table 1. The actual calculated structure factors are listed under $F_{\text{calc.}}$ in Table 1.

7. Standard deviations

The standard deviations in the positional coordinates of Table 8 were obtained directly from the least squares derived variance-covariance matrix in the usual way, and these values are listed in Table 9.

Table 9. *Standard deviations ($\times 10^3$) in the final positional coordinates*

Atom	σx	σy	σz
Cl	0·10	0·43	0·18
S	0	0·35	0
O	0·20	0·76	0·32
C_1	0·24	0·91	0·38
C_2	0·26	1·23	0·43
C_3	0·29	1·42	0·51
C_4	0·28	1·23	0·53
C_5	0·29	1·31	0·49
C_6	0·27	1·08	0·42

The standard deviation in derived functions, f, is taken as

$$\left[\sum_i \sum_j \left(\frac{\partial f}{\partial p_i}\right)\left(\frac{\partial f}{\partial p_j}\right) C_{ij} + \sum_i \left(\frac{\partial f}{\partial q_i}\right)^2 \sigma_i^2 \right]^{\frac{1}{2}}$$

where p_i, p_j are the least-squares parameters, C_{ij} is the variance-covariance matrix element, q_i are the cell parameters and σ_i their standard deviations. Values so obtained are stated hereafter with the corresponding function.

8. Rotational oscillations

The effect of rotational oscillations upon the bond lengths has been estimated from the r.m.s. atomic displacements in Table 15, assuming the sulfur atom undergoes purely translational vibrations. The resulting apparent atomic displacement towards the sulfur atom is then 0·002 Å for C_1 and less than 0·006 Å for the remaining atoms, with the exception of chlorine. The chlorine atom is displaced 0·012 Å towards the sulfur atom, resulting in an apparent reduction in the Cl–C_4 bond length of 0·007 Å. The bond length corrections due to rotational oscillation are thus in each case no more than the standard deviation in that bond length, and have not been included in the following sections.

9. Molecular dimensions

The bond lengths, bond angles and dihedral angles within a molecule of 4,4'-dichlorodiphenyl sulfone, together with the standard deviations in these functions, are given in Table 10. The final position coordinates used are those in Table 8.

Table 10. *Molecular dimensions, with standard deviations*

C_1–C_2 = 1·382 ± 0·007 Å	C_6–C_1–C_2 = 121·1 ± 0·52°
C_2–C_3 = 1·373 ± 0·009	C_1–C_2–C_3 = 119·2 ± 0·53
C_3–C_4 = 1·395 ± 0·009	C_2–C_3–C_4 = 119·2 ± 0·55
C_4–C_5 = 1·378 ± 0·009	C_3–C_4–C_5 = 121·8 ± 0·54
C_5–C_6 = 1·367 ± 0·008	C_4–C_5–C_6 = 118·9 ± 0·56
C_6–C_1 = 1·386 ± 0·007	C_5–C_6–C_1 = 120·1 ± 0·52
C_2–C_6' = 3·854 ± 0·011	C_3–C_4–Cl = 119·7 ± 0·49
Cl–C_4 = 1·736 ± 0·007	C_5–C_4–Cl = 118·7 ± 0·52
S–C_1 = 1·765 ± 0·006	S–C_1–C_2 = 119·8 ± 0·47
S–O = 1·432 ± 0·005	S–C_1–C_6 = 119·1 ± 0·40
	C_1–S–O = 107·3 ± 0·29
Plane b | Plane b'= 79·5 ± 0·30°	C_1'–S–O = 108·0 ± 0·28
Plane b | C_1SC_1'= 84·4 ± 0·30°	C_1–S–C_1' = 104·8 ± 0·40
	Cl–S–Cl' = 101·8 ± 0·25
	O–S–O = 120·4 ± 0·42

The mean length of the aromatic C–C bond is $1\cdot380 \pm 0\cdot003$ Å. The shortest non-bonded C–C contact between the two benzene rings, C_2–C_6', is $3\cdot854 \pm 0\cdot011$ Å. The sum of the internal angles of the benzene ring is $719\cdot9 \pm 0\cdot4°$. By transforming the monoclinic axes to an orthogonal set, with $x'=x+z\cos\beta$, $y'=y$, $z'=z\sin\beta$, the least squares derived equation for the plane of the benzene ring, the sulfur and the chlorine atoms is:

$$x' + 1\cdot4422y' - 0\cdot6327z' - 6\cdot1304 = 0 \qquad (a)$$

In forming this equation, the sulfur and chlorine atoms were given thrice the weight of the carbon atoms. The distances of the atoms from plane (a) are given in Table 11. The equation of the mean plane of the six carbon atoms alone is:

$$x' + 1\cdot4208y' - 0\cdot6327z' - 6\cdot0373 = 0 \qquad (b)$$

The distances of the atoms from plane (b) are also given in Table 11. No carbon atom lies significantly out of plane (b), although three carbon atoms lie out of plane (a).

Table 11. *Out-of-plane distances, in* 10^{-3} Å

Atom	Distance from plane (a)	Distance from plane (b)
S	20 ± 2	62 ± 2
Cl	16 ± 2	12 ± 2
C_1	-24 ± 5	4 ± 5
C_2	-30 ± 6	-8 ± 6
C_3	-15 ± 7	0 ± 7
C_4	3 ± 6	12 ± 6
C_5	-28 ± 6	-15 ± 6
C_6	-16 ± 6	7 ± 6

10. Intermolecular distances

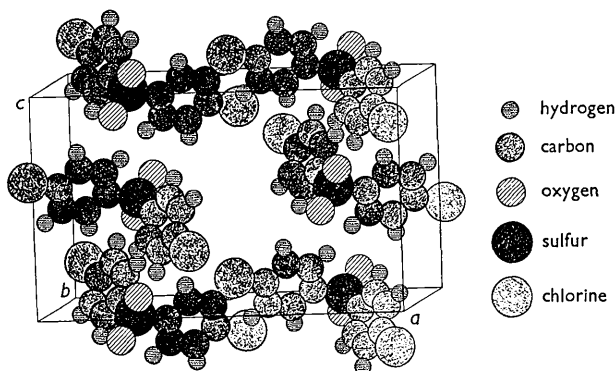All distances less than 4 Å in this crystal were computed in an exhaustive program written by Dr Busing.

Fig. 3. Clinometric view of the structure, showing the outlines of one unit cell.

hydrogen
carbon
oxygen
sulfur
chlorine

Those which lie between molecules are given in Table 12. Three oxygen–carbon contacts of 3·211, 3·243 and 3·272 Å are slightly shorter than the sum of the accepted oxygen–carbon van der Waals radii: the remaining distances are equal to or longer than this sum. A general view of the whole structure is given in Fig. 3.

Table 12. *Intermolecular distances less than 4 Å,*
with standard deviations

$C_6 \cdots O = 3 \cdot 211 \pm 0 \cdot 009$ Å	$C_1 \cdots O = 3 \cdot 721 \pm 0 \cdot 013$ Å
$C_5 \cdots O = 3 \cdot 243 \pm 0 \cdot 010$	$C_1 \cdots O = 3 \cdot 729 \pm 0 \cdot 013$
$C_6 \cdots O = 3 \cdot 272 \pm 0 \cdot 011$	$C_4 \cdots O = 3 \cdot 996 \pm 0 \cdot 011$
$C_5 \cdots O = 3 \cdot 455 \pm 0 \cdot 010$	$C_2 \cdots Cl = 3 \cdot 976 \pm 0 \cdot 010$
$C_2 \cdots O = 3 \cdot 508 \pm 0 \cdot 012$	$C_4 \cdots Cl = 3 \cdot 981 \pm 0 \cdot 010$
$C_3 \cdots O = 3 \cdot 654 \pm 0 \cdot 010$	$Cl \cdots Cl = 3 \cdot 564 \pm 0 \cdot 009$

11. Principal axes of the anisotropic temperature factor

The principal axes of the ellipsoid of thermal vibration were computed from the anisotropic temperature coefficients β_{ij} in Table 8 by the method of Busing & Levy (1958). Table 13 contains $\mu(r)$, the r.m.s. displacement of the atom along the rth principal axis, and $\varphi(r, i)$ the angles made by the rth principal axis with the ith direct-lattice vector. The β_{ii} coefficients in Table 8 are also given in a form directly comparable with the B_i coefficients obtained from the 7th NY $XR2$ refinement cycle, in Table 14. This table very

Table 13. *The principal axes r.m.s. displacements and orientations*

Atom	r	$\mu(r)$	$\varphi(r, a)$	$\varphi(r, b)$	$\varphi(r, c)$
Cl	1	$0 \cdot 427 \pm 0 \cdot 003$ Å	$58 \cdot 5 \pm 0 \cdot 52°$	$57 \cdot 2 \pm 0 \cdot 59°$	$49 \cdot 2 \pm 0 \cdot 75°$
	2	$0 \cdot 227 \pm 0 \cdot 002$	$138 \cdot 6 \pm 0 \cdot 78$	$48 \cdot 8 \pm 0 \cdot 85$	$86 \cdot 5 \pm 0 \cdot 92$
	3	$0 \cdot 297 \pm 0 \cdot 002$	$66 \cdot 1 \pm 1 \cdot 05$	$58 \cdot 6 \pm 1 \cdot 00$	$139 \cdot 0 \pm 0 \cdot 76$
S	1	$0 \cdot 257 \pm 0 \cdot 002$	$157 \cdot 2 \pm 3 \cdot 83$	$90 \cdot 0$	$66 \cdot 7 \pm 3 \cdot 83$
	2	$0 \cdot 217 \pm 0 \cdot 002$	$90 \cdot 0$	$180 \cdot 0$	$90 \cdot 0$
	3	$0 \cdot 236 \pm 0 \cdot 002$	$112 \cdot 8 \pm 3 \cdot 82$	$90 \cdot 0$	$156 \cdot 7 \pm 3 \cdot 83$
O	1	$0 \cdot 197 \pm 0 \cdot 004$	$71 \cdot 3 \pm 1 \cdot 79$	$36 \cdot 5 \pm 1 \cdot 91$	$60 \cdot 2 \pm 2 \cdot 07$
	2	$0 \cdot 299 \pm 0 \cdot 004$	$23 \cdot 9 \pm 8 \cdot 27$	$113 \cdot 7 \pm 6 \cdot 56$	$87 \cdot 1 \pm 11 \cdot 44$
	3	$0 \cdot 284 \pm 0 \cdot 004$	$75 \cdot 6 \pm 12 \cdot 53$	$64 \cdot 0 \pm 6 \cdot 23$	$150 \cdot 0 \pm 2 \cdot 47$
C_1	1	$0 \cdot 264 \pm 0 \cdot 005$	$123 \cdot 0 \pm 6 \cdot 82$	$64 \cdot 7 \pm 3 \cdot 86$	$43 \cdot 4 \pm 5 \cdot 15$
	2	$0 \cdot 196 \pm 0 \cdot 005$	$89 \cdot 3 \pm 5 \cdot 89$	$148 \cdot 9 \pm 4 \cdot 47$	$58 \cdot 9 \pm 4 \cdot 35$
	3	$0 \cdot 231 \pm 0 \cdot 005$	$147 \cdot 0 \pm 6 \cdot 83$	$106 \cdot 8 \pm 6 \cdot 56$	$116 \cdot 9 \pm 6 \cdot 79$
C_2	1	$0 \cdot 287 \pm 0 \cdot 006$	$102 \cdot 4 \pm 5 \cdot 40$	$31 \cdot 8 \pm 6 \cdot 05$	$61 \cdot 0 \pm 5 \cdot 24$
	2	$0 \cdot 226 \pm 0 \cdot 006$	$43 \cdot 7 \pm 13 \cdot 16$	$101 \cdot 2 \pm 7 \cdot 93$	$49 \cdot 0 \pm 10 \cdot 88$
	3	$0 \cdot 245 \pm 0 \cdot 006$	$48 \cdot 9 \pm 13 \cdot 39$	$60 \cdot 6 \pm 6 \cdot 95$	$125 \cdot 4 \pm 11 \cdot 63$
C_3	1	$0 \cdot 329 \pm 0 \cdot 007$	$80 \cdot 9 \pm 3 \cdot 70$	$34 \cdot 7 \pm 3 \cdot 52$	$56 \cdot 9 \pm 4 \cdot 04$
	2	$0 \cdot 231 \pm 0 \cdot 006$	$41 \cdot 4 \pm 8 \cdot 57$	$117 \cdot 4 \pm 4 \cdot 26$	$62 \cdot 2 \pm 7 \cdot 19$
	3	$0 \cdot 263 \pm 0 \cdot 006$	$50 \cdot 0 \pm 8 \cdot 70$	$70 \cdot 3 \pm 5 \cdot 75$	$134 \cdot 1 \pm 6 \cdot 74$
C_4	1	$0 \cdot 336 \pm 0 \cdot 007$	$69 \cdot 6 \pm 2 \cdot 62$	$57 \cdot 5 \pm 2 \cdot 81$	$40 \cdot 1 \pm 2 \cdot 63$
	2	$0 \cdot 228 \pm 0 \cdot 006$	$136 \cdot 2 \pm 24 \cdot 52$	$111 \cdot 6 \pm 23 \cdot 15$	$53 \cdot 6 \pm 9 \cdot 18$
	3	$0 \cdot 237 \pm 0 \cdot 006$	$126 \cdot 7 \pm 25 \cdot 66$	$40 \cdot 6 \pm 16 \cdot 40$	$104 \cdot 6 \pm 17 \cdot 39$
C_5	1	$0 \cdot 302 \pm 0 \cdot 007$	$129 \cdot 6 \pm 4 \cdot 64$	$140 \cdot 4 \pm 4 \cdot 66$	$89 \cdot 4 \pm 7 \cdot 82$
	2	$0 \cdot 241 \pm 0 \cdot 006$	$41 \cdot 1 \pm 5 \cdot 14$	$128 \cdot 5 \pm 4 \cdot 68$	$78 \cdot 4 \pm 10 \cdot 85$
	3	$0 \cdot 266 \pm 0 \cdot 006$	$80 \cdot 9 \pm 10 \cdot 11$	$97 \cdot 8 \pm 8 \cdot 80$	$168 \cdot 4 \pm 10 \cdot 81$
C_6	1	$0 \cdot 272 \pm 0 \cdot 006$	$149 \cdot 9 \pm 5 \cdot 76$	$120 \cdot 1 \pm 5 \cdot 77$	$89 \cdot 5 \pm 8 \cdot 58$
	2	$0 \cdot 225 \pm 0 \cdot 006$	$61 \cdot 6 \pm 5 \cdot 87$	$145 \cdot 2 \pm 7 \cdot 85$	$71 \cdot 9 \pm 13 \cdot 59$
	3	$0 \cdot 244 \pm 0 \cdot 006$	$80 \cdot 9 \pm 10 \cdot 22$	$105 \cdot 8 \pm 12 \cdot 32$	$161 \cdot 9 \pm 13 \cdot 57$

clearly demonstrates the ineptness of the isotropic assumption in the case of 4,4'-dichlorodiphenyl sulfone.

Table 14. *Comparison of NY XR2 B_i and corresponding ORACLE B_{ii}*

	B_i	B_{11}	B_{22}	B_{33}
C_6	4·38	5·41	4·52	4·63
C_5	5·09	5·66	6·14	5·52
C_4	5·50	4·84	5·69	6·98
C_3	5·39	4·83	7·29	6·11
C_2	4·73	4·44	5·99	4·84
C_1	3·69	4·58	3·58	4·56
O	4·95	6·58	4·33	5·55
Cl	6·96	7·41	7·89	10·19
S	3·94	5·09	3·70	4·53

12. The thermal vibrations along the molecular axes

It is easier to visualize the thermal motions of the individual atoms with respect to a set of molecular axes than to their principal axes. A natural choice of molecular axes is that given by

$$X_1 \propto V, \quad X_2 \propto V \times W, \quad X_3 \propto X_1 \times X_2$$

where V is S,Cl and W is $C_5,C_3 + C_6,C_2$. The amplitudes of thermal vibration along X_1, X_2, X_3 (corresponding to $U_{ii}^{\frac{1}{2}}$ in Cruickshank's (1956) notation) are readily obtainable from $\mu(r)$, using the known angles between the principal axes and the molecular axes (not given here to conserve space). These amplitudes, $u(m)$ where $m = 1, 2, 3$, are given in Table 15.

Table 15. *R.m.s. displacements, with standard deviations, along the molecular axes*

Atom	$u(1)$	$u(2)$	$u(3)$
Cl	0·239 ± 0·002 Å	0·330 ± 0·002 Å	0·395 ± 0·002 Å
S	0·242 ± 0·001	0·233 ± 0·001	0·236 ± 0·002
O	0·281 ± 0·004	0·254 ± 0·004	0·255 ± 0·004
C_1	0·253 ± 0·005	0·209 ± 0·005	0·232 ± 0·005
C_2	0·273 ± 0·006	0·252 ± 0·006	0·237 ± 0·006
C_3	0·274 ± 0·007	0·283 ± 0·007	0·275 ± 0·006
C_4	0·249 ± 0·006	0·244 ± 0·006	0·316 ± 0·007
C_5	0·247 ± 0·006	0·297 ± 0·007	0·264 ± 0·006
C_6	0·236 ± 0·006	0·261 ± 0·006	0·246 ± 0·005

13. Rigid body vibrations

An alternative description of the thermal atomic motions in 4,4'-dichlorodiphenyl sulfone is possible in terms of the molecular rigid body vibrations. The method of Cruickshank (1956) was used to reduce the atomic transformed-β_{ij} values to the two symmetric tensors τ_{ij} and ω_{ij}. This complete calculation, based on the resulting U_{ij} values for all 17 'heavy' atoms in this non-planar molecule, was performed on the DEUCE computer in the University of Glasgow.

The choice of molecular axes was $X_1' \propto Cl$, Cl', $X_2' \propto \mathbf{b}$, $X_3' \propto X_1' \times X_2'$, and the results are:

$$\tau_{ij} = \begin{pmatrix} 6\cdot013 \pm 0\cdot216 & 0 & -0\cdot470 \pm 0\cdot219 \\ & 4\cdot796 \pm 0\cdot295 & 0 \\ & & 4\cdot076 \pm 0\cdot329 \end{pmatrix} \times 10^{-2} \ \text{Å}^2$$

$$\omega_{ij} = \begin{pmatrix} 16\cdot244 \pm 2\cdot570 & 0 & -8\cdot317 \pm 1\cdot133 \\ & 12\cdot167 \pm 0\cdot932 & 0 \\ & & 7\cdot952 \pm 0\cdot839 \end{pmatrix} \ \text{deg.}^2$$

These tensors correspond to librations of the center of mass of $0\cdot245 \pm 0\cdot047$, $0\cdot219 \pm 0\cdot054$ and $0\cdot202 \pm 0\cdot057$ Å, and oscillations of $4\cdot03 \pm 1\cdot62$, $3\cdot49 \pm 0\cdot97$ and $2\cdot82 \pm 0\cdot92°$ respectively about X_1', X_2', and X_3'.

14. Discussion

The bond arrangement within the sulfone group of 4,4'-dichlorodiphenyl sulfone, Table 10, as in all other sulfone groups that have been measured, (for a review, see Abrahams, 1956) is not that of a regular tetrahedron. The O–S–O bond angle is consistently and very significantly greater than 109·5°, whereas the C–S–O and the C–S–C angles in the present molecule, as in the other cases measured, are significantly less than tetrahedral. The S–O bond length in this, as in most sulfones, appears to be very close to 1·43 Å, the standard double S–O bond distance. The C–S bond length of $1\cdot765 \pm 0\cdot006$ Å is significantly less than the standard single C–S bond length of 1·82 Å, in agreement with the measurements in other comparable sulfones. Indeed, this C–S bond length in an Ar–S'–Ar molecule (Ar = aromatic group) appears remarkably constant, whether S' is a sulfide, sulfoxide or sulfone group. The dihedral angle made by the plane of the benzene ring with the C_1–S–C_1' plane is $84\cdot7 \pm 0\cdot3°$, in good agreement with Koch & Moffitt's (1951) prediction of 90°, assuming overlap of the sulfur atom $3d$ with the C_1 atom $2p$ orbitals. It is also very close to the corresponding dihedral angle of 82° found in diphenyl sulfoxide (Abrahams, 1957), as was considered likely in the study of the diphenyl sulfoxide–diphenyl sulfone system (Abrahams & Silverton, 1956). The slight but highly significant displacement of the chlorine and sulfur atoms out of the plane of the benzene ring is interesting although the only close contacts between these atoms and adjacent molecules is the Cl · · · Cl distance of 3·56 Å and a Cl · · · C_4 distance of 3·98 Å.

The three intermolecular C · · · O distances of 3·21, 3·24 and 3·27 Å are most probably purely van der Waal's contacts: there are no angular relations involving these distances to indicate otherwise. Many cases of C · · · O contacts, in the length range 3·14–3·25 Å,

are given in the literature.* The usual van der Waal's C $\cdots$ O distance of about 3·3 Å should hence presumably be revised to about 3·2 Å.

An examination of the r.m.s. displacement of the atoms along the direction of the molecular axes (Table 15) shows that the atomic vibration along the length of the molecule is very constant, at about 0·25 Å. The excursions in the direction normal to the benzene ring plane tend to increase from 0·23 Å at the center to 0·33 Å at the periphery of the molecule. Those normal to the length of the molecule in the plane of the benzene ring increase even more rapidly. No attempt has been made in this paper to extract the characteristic lattice frequencies, because of the possible accumulation of systematic $F_{meas.}$ errors in the anisotropic temperature factors.

A comparison of the coordinates obtained in the present study with those reported by Bacon & Curry (1960) shows no disagreement,† within the limit of 3 standard deviations of each measurement. This observation is of importance in demonstrating that X-ray and neutron diffraction studies produce essentially identical results.

* For example, 3·14 Å in furoic acid (Goodwin & Thomson, 1954); 3·24 Å in N,N′ diglycyl-L-cystine dihydrate (Yakel & Hughes, 1954); 3·24 Å in nicotinamide (Wright & King, 1954); etc.

† Except for the thermal parameter μ_3 for sulfur (see Bacon & Curry's (1960) paper).

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