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A Study of 4,4'-Dichloro Diphenyl Sulphone by Neutron Diffraction

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A Fourier and least-squares analysis of the intensities of the $h0l$ reflections from a single crystal has provided measurements of the C–H bonds and anisotropic temperature factors for the hydrogen atoms. The motion of the latter has been analysed tentatively in terms of molecular oscillation and bending and stretching vibrations, with zero-point energy, of the C–H bonds.

Introduction

4,4'-di-chloro diphenyl sulphone ($(p\text{-ClC}_6\text{H}_4)_2\text{SO}_2$) has proved to be a suitable compound for making a fairly detailed study of the thermal motions of hydrogen atoms attached to a benzene ring from two-dimensional neutron diffraction data. It is expected that the experience gained will be useful in the study of benzene itself. The study of the compound has been of particular interest because it has been carried out without the aid of the usual detailed knowledge of the parameters of the non-hydrogen atoms secured by X-rays. In fact, a three-dimensional X-ray refinement of the structure has been carried out concurrently and independently by Dr S. C. Abrahams, to whom we are grateful for supplying suitable single crystals for our own measurements.

The unit-cell dimensions of di-chloro diphenyl sulphone were first reported by Toussaint (1948) who also identified the space group as $I2/a$. As our starting point we took the later dimensions (with interchange of a, c axes), given by Abrahams (1956) as

$$a=20\cdot20,\ b=5\cdot01,\ c=12\cdot24\ \text{Å};\ \beta=90°\ 34'.$$

The monoclinic cell contains four molecules, with the sulphur atoms located in the special fourfold positions based on $(\frac{1}{4}, \frac{1}{4}, 0)$. Preliminary X-ray work by Abrahams had given estimates of 0·033 and 0·162 for the x, z parameters of the chlorine atoms. This information and estimates of the molecular dimensions, made from the results of a detailed X-ray study of the di-iodo compound by Keil & Plieth (1955), enabled us to make a first calculation of the signs of the structure factors, F_c, for the diffraction of neutrons by the $(h0l)$ planes.

Experimental details

A crystal measuring 0·3 × 0·2 × 1·5 cm. with its largest dimension along the y-axis, was used and 104 $h0l$ reflections were examined at a neutron wavelength of 1·09 Å. Corrections for secondary extinction were estimated for a few of the most intense lines by comparison of intensity ratios at this wavelength with similar measurements made at 0·81 and 1·19 Å.

Analysis of results

For the atomic co-ordinates estimated from the details of the di-iodo compound, mentioned above, and using Debye temperature factors estimated from our earlier studies of aromatic compounds (Bacon & Curry, 1956, 1957), our neutron-diffraction intensities gave a reliability index or, more correctly, discrepancy factor, of 0·51. We constructed a Fourier projection of the scattering density on the (010) plane from these data and obtained from this plot new atomic co-ordinates and temperature factors: when used for calculating new values of F_c these improved the reliability index to

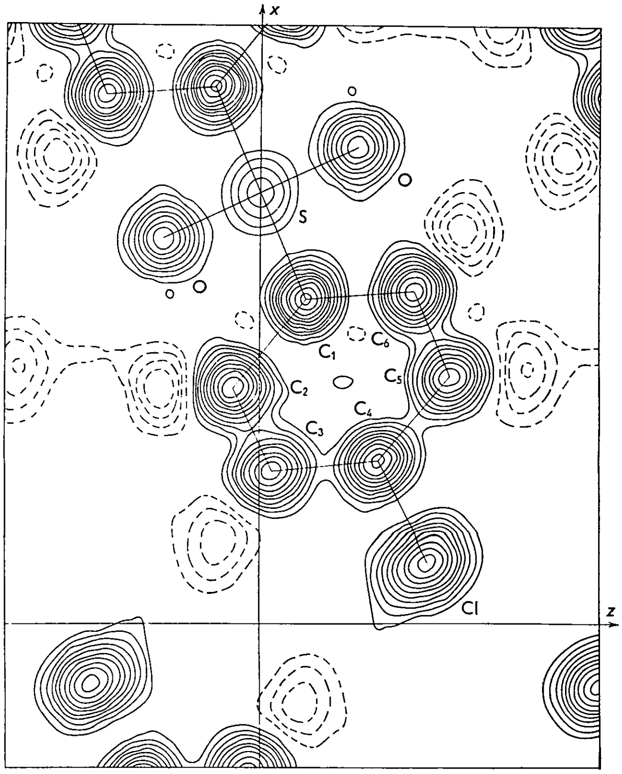

Fig. 1. A projection of the neutron scattering density on the (010) plane. Full lines are positive contours: broken lines are the negative contours of the hydrogen atoms.

0·25. A 'difference' synthesis of $(F_o - F_{nH})$, where F_o is the observed structure amplitude and F_{nH} is the calculated contribution from all the atoms *except* hydrogen, was constructed at this stage and gave us fairly accurate values of the co-ordinates and temperature factors of the hydrogen atoms. These values improved the reliability index to 0·16.

The further stages of refinement will be appreciated more readily after an examination of the Fourier projection. Fig. 1 shows the projection of neutron-scattering density obtained by direct synthesis of F_o from the experimentally measured intensities, using the signs computed from our final parameters. The sulphur atom is situated on a diad axis and is tetrahedrally co-ordinated: two of its bonds go to the sulphone oxygen atoms and the other two to the benzene rings which form the two halves of the molecule. The planes of the two benzene rings are inclined at 40° to the plane of the projection, giving quite favourable conditions for observation of the hydrogen atoms. Fig. 2 shows a 'difference' projection of hydrogen atoms only, constructed at the stage in the refinement at which the reliability index was 0·16 and in which all the subtracted atoms were assumed to be isotropic. From this figure we deduce, in particular, that the thermal vibrations of the chlorine atom and of C_4, the extreme carbon atom in the ring, are anisotropic, with their maximum vibrations at right-angles to the length of the molecule, thus giving the marked subsidiary peaks of positive scattering density at each side of their assumed positions in Fig. 2. It should be noted that the interval between contours in Fig. 2 has been reduced to a half of the value used for Fig. 1.

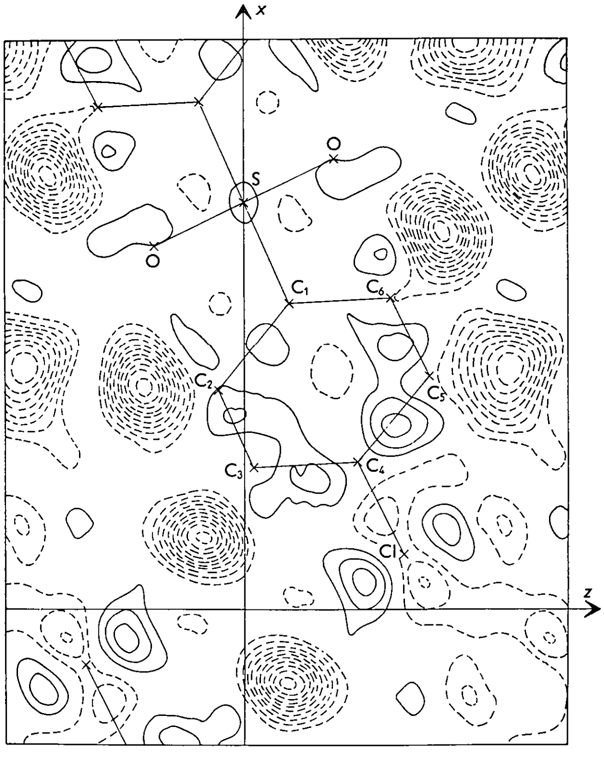

Fig. 2. An early projection on the (010) plane, by synthesis of the quantity $(F_o - F_{nH})$. The scattering density shown is primarily that due to hydrogen atoms together with 'error's, at other atomic positions caused by the assumption of isotropic motion. The interval between contours is only half as great as in Fig. 1.

We continued the refinement in two ways. First, we carried out four cycles of 'least squares' starting from the stage above at which $R = 0{\cdot}25$ and using isotropic temperature factors. The atomic co-ordinates obtained as a result are included in Tables 1 and 2. These co-ordinates were then regarded as fixed and four further cycles of least squares were carried out to refine anisotropic temperature factors for the atoms S, Cl, and all the hydrogen atoms. This was done with a programme written by A. R. Curtis and it was considered that our limited two-dimensional data did not justify the introduction of anisotropic parameters for any of the other atoms (our 'difference' projections had suggested that the anisotropies of motion of the remaining atoms, except probably C_4 and to a less extent C_3, C_5, were much smaller). The anisotropic temperature factors were expressed in the form

$$\exp\,(R_{11}h^2 + R_{13}hl + R_{33}l^2)\ .$$

From the values obtained for R_{11}, R_{13}, R_{33} can be calculated u_x, u_z, the root mean-square displacements along the x, z axes. We can also compute $u_{\text{max.}}$ and $u_{\text{min.}}$, the maximum and minimum displacements, u_1 and u_3 the displacements along and perpendicular to the length of the molecule, and the value of φ_o, which is the angle between the axis Ox and the determined direction of maximum motion. Table 2 for the hydrogen atoms also shows the values of φ_c which would correspond to maximum thermal motion at right-angles to the C–H bonds and the values of $B_{\text{max.}}$, $B_{\text{min.}}$ which are the effective Debye factors for the directions of the maximum and minimum motion respectively. As a result of the introduction of these anisotropic temperature factors, the reliability index was improved to 0·08. As a second independent process of refinement we have introduced anisotropic temperature factors for S, Cl, and C_4 from a detailed examination of the residual peaks in the difference projection of Fig. 2 and its later improvements. This process has yielded values of $B_{\text{max.}}$, $B_{\text{min.}}$, and φ_o for C_4 but has also produced a shift of the atomic co-ordinates of C_4 away from the position deduced by the least-squares analysis. This anomaly may be due to experimental errors in the intensity measurements which have built up false detail in the projection near the position of C_4. The same procedure has not called for any positional changes of the chlorine atom and has yielded values of $B_{\text{max.}}$, $B_{\text{min.}}$, and φ_o which are in reasonable, but not particularly good, agreement with those found from the least-squares analysis.

Fig. 3 shows our final 'difference' projection, synthesising $(F_o - F_{nH})$. In calculating F_{nH} we have used our final values of the atomic co-ordinates and anisotropic thermal parameters. The anisotropy of the hydrogen motion is clearly visible in the projection and this will be analysed further in the subsequent discussion.

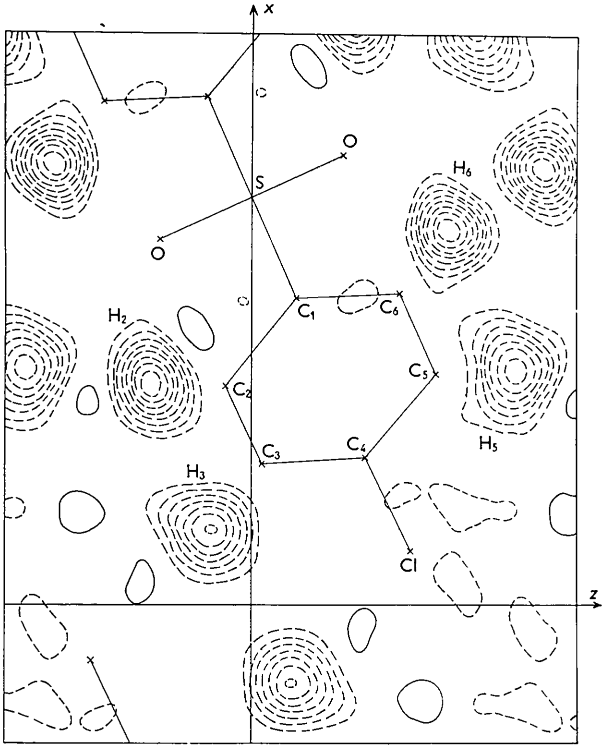

Fig. 3. The final projection of the neutron scattering density on the (010) plane due to hydrogen atoms alone.

Discussion

Table 1 includes a comparison of our x, z parameters with those found in Sime & Abrahams' (1960) 3-dimensional X-ray study for the non-hydrogen atoms. The random differences between the two sets of values average at 0·02 Å for x and 0·01 Å for z. These discrepancies are to be compared with the standard deviations of the neutron co-ordinates as estimated by Cruickshank's (1949) method, which are about 0·007 Å for the non-hydrogen atoms. In the light of the latter figure the difference of 0·016 Å between the Fourier and least-squares values of x for C_4, which was mentioned above, is not significant.

Table 1 also compares the root-mean square thermal displacements of the non-hydrogen atoms. For the X-ray data the three axes of the vibration ellipsoid are measured, leading to u_{X_1} and u_{X_3} which are vibration components in the plane of the benzene ring along and perpendicular respectively to the length of the molecule, and u_{X_2} which is the component normal to the plane of the ring. With neutrons we measure simply the elliptical projection of the ellipsoid on the (010)

Table 1. *Atomic co-ordinates and thermal data for non-hydrogen atoms*

	Co-ordinates				Thermal data												
	x/a ($a=20{\cdot}2$ Å)		z/c ($c=12{\cdot}2$ Å)					Neutrons							X-rays		
Atom	Neut.	X-ray	Neut.	X-ray	R_{11}	R_{13}	R_{33}	$B_{\max.}$		$B_{\min.}$	φ_o	u_1		u_3	φ_c	u_{X_1}	u_{X_2}	u_{X_3}
S	0·25	0·25	0	0	0·003688	−0·001339	0·004695	6·2		2·7	−11°	0·28		0·18	−24°	0·24	0·23	0·24
O	0·2234	0·2244	0·9064	0·9072					5·2				0·25			0·28	0·25	0·26
Cl	0·0343	0·0327	0·1636	0·1621	0·003985	0·004691	0·015557	10·6		5·2	61°	0·25		0·36	64°	0·24	0·33	0·39
C_1	0·1883	0·1868	0·0456	0·0456					4·1				0·23			0·25	0·21	0·23
C_2	0·1345	0·1352	0·9738	0·9760					4·4				0·23			0·27	0·25	0·24
C_3	0·0867	0·0877	0·0114	0·0112					5·6				0·26			0·27	0·28	0·27
C_4	0·0923 0·0915*	0·0926	0·1164 0·1156*	0·1164	0·002929	0·002089	0·010576	6·8		4·3	64°	0·23		0·29	66°	0·25	0·24	0·32
C_5	0·1420	0·1431	0·1874	0·1867					5·0				0·25			0·25	0·30	0·26
C_6	0·1919	0·1910	0·1509	0·1503					4·3				0·23			0·24	0·26	0·25

* These are Fourier values based on the 7th Difference Synthesis: all other co-ordinates are from least-squares.

Values of B are in 10^{-16} cm.^{2}. Values of u are in 10^{-8} cm.

φ_o is the angle between Ox and the experimentally determined direction of maximum motion: a positive value indicates clockwise rotation towards Oz. φ_c gives the value of this angle which would correspond to motion along or at right-angles to the length of the molecule in projection.

Table 2. *Hydrogen atom data*

	Co-ordinates			Thermal parameters									
	x/a	y/b	z/c	R_{11}	R_{13}	R_{33}	$B_{\text{max.}}$	$B_{\text{min.}}$	φ_o	φ_c	ψ	$u_{\text{max.}}$	$u_{\text{min.}}$
H_2	0·1356	0·3537	0·8979	0·005357	−0·004996	0·008233	10·0	3·7	−26°	+1°	−31°	0·36	0·22
H_3	0·0462	0·6663	0·9576	0·004808	−0·003957	0·015247	10·6	6·4	−54°	−51°	−70°	0·37	0·28
H_5	0·1465	0·7257	0·2685	0·006088	−0·000021	0·010476	9·9	6·3	0°	−5°	−18°	0·35	0·28
H_6	0·2308	0·4198	0·2020	0·004553	−0·000814	0·008885	7·5	5·2	−10°	−52°	−25°	0·31	0·26

φ_o is the inclination of $B_{\text{max.}}$ to the x-axis as deduced experimentally (a positive value of φ_o indicates clockwise rotation towards $0z$).

φ_c is the value of this angle which would correspond to $B_{\text{max.}}$ directed at right-angles to the C–H bond.

ψ is the inclination to the x-axis of the direction of tangential motion about carbon C_1.

The values of y/b are deduced from the X-ray data (Sime & Abrahams, 1960) for the carbon atoms, making the assumption that the hydrogen atoms lie in the plane of the carbon ring.

Values of B are in 10^{-16} cm.^{2}. Values of u are in 10^{-8} cm.

plane, obtaining from it a value u_3 (which is very close to u_{X_3} since the direction of X_3 is almost parallel to the plane of projection) and u_1 which depends on both u_{X_1} and u_{X_2}. The mean value of u_1, u_3 for neutrons is 0·25 Å for the non-hydrogen atoms: the mean value of u_{X_1}, u_{X_3} for X-rays is 0·26 Å. These should not be quite identical of course but it is satisfying to see that their difference is not outside experimental error. We have calculated the standard deviation of our thermal parameters using the expression given by Cruickshank (1956), obtaining values of 0·35, 0·40, 0·61, and 0·23 for the deviations of the B values of carbon, oxygen, hydrogen and chlorine respectively. These correspond to standard deviations of the displacements u of about 0·01 Å for the oxygen and hydrogen atoms and a little less for carbon and chlorine. Both neutron and X-ray data agree that the carbon atoms C_2, C_1 and C_6, which are closer to the sulphur atom at the centre of the molecule, move less than the atoms C_3, C_4 and C_5 which are nearer the end. C_4 and Cl undoubtedly have appreciably larger motions at right-angles to the bond C_4–Cl than along this bond. There is, however, one marked difference between the two sets of data. The thermal motion of the sulphur atom appears to be markedly anisotropic for neutrons (whether analysed by least-squares or Fourier projections) whereas X-rays deduce an almost isotropic motion: Dr Abrahams has calculated that his thermal displacements correspond to projected distances $u_1 = 0{\cdot}257$, $u_3 = 0{\cdot}236$. One can but speculate whether this is an authentic difference between the nuclear motion and that of the electrons, obscured perhaps by some anisotropy of the electronic distribution about the sulphur atom. It should be emphasised, however, that so far as neutrons are concerned sulphur is a 'light' atom. Its scattering length b is only $0{\cdot}31 \times 10^{-12}$ cm., which is lower numerically than that of hydrogen (for which $b = -0{\cdot}38 \times 10^{-12}$) and much smaller than the values of 0·58, 0·66 and $0{\cdot}99 \times 10^{-12}$ for O, C and Cl respectively. The small value of b for sulphur accounts for the fact that there is little evidence of its anisotropic motion in Fig. 2, in contrast to the marked pairs of positive and negative contours around the position of the 'heavy' chlorine atom. The motion of the sulphur atom along the S–C bond is in fact the only thermal displacement for which there is a significant difference between the X-ray and neutron results. The difference between the two values is about five times the sum of the two standard deviations.

The main interest, of course, in the neutron results lies in the information given about the hydrogen atoms. From our single (010) projection and the y-parameters of the other atoms as measured by X-rays we can deduce the y-parameters of the hydrogen atoms if we assume that they lie in the plane of the carbon ring. On this assumption we get the complete sets of parameters given in Table 2 and arrive at the C–H bond lengths shown in Table 3. The mean length of the four C–H bonds which we measure is 1·05 Å. The calculated standard deviation of the hydrogen atom co-ordinates by Cruickshank's method is 0·022 Å, so that the individual divergences of the C–H bonds from the mean length of 1·05 Å are not significant.

Table 3. C–H *bond lengths*

C_2–H_2	1·02 Å
C_3–H_3	1·08
C_5–H_5	1·06
C_6–H_6	1·04

The movements of the hydrogen atoms H_3, H_5 are greater than those of H_2, H_6 in conformity with the difference between the pairs of associated carbon atoms: the former pair of hydrogens have mean Debye factors B of 8·5, 8·1 whereas the second pair give 6·8, 6·4. It is tempting to analyse further the details of the hydrogen atom motion as given by the least-squares analysis, although our standard deviation of 0·61 for the B values of hydrogen is rather large and our data have not permitted an anisotropic analysis of the motion of carbons C_3, C_5. However, we can discuss some tentative conclusions.

For H_3 and H_5 the calculated direction of maximum motion is within a few degrees of the normal to the C–H bond, as shown by columns 7, 8 of Table 2. For H_2 and H_6, however, this is not the case and the directions of maximum movement are thrust outwards by thirty or forty degrees away from the oxygen atoms and more in line with the length of the molecule. This behaviour could be accounted for if there is an angular oscillation of the benzene ring about a point near to the carbon atom C_1. Such an oscillation would not disturb the central tetrahedral distribution of oxygen and carbon atoms about the sulphur atom. This type of motion is supported by the thermal parameters for both X-rays and neutrons which for C_4 and Cl, but not for C_1, show markedly greater displacements at right angles to the length of the molecule. The values of $(B_{\text{max.}} - B_{\text{min.}})$ for C_4, Cl will indicate the extent of the molecular oscillation: they are 2·5, 5·4 respectively for the two atoms, giving a ratio of 0·46 which is in rough agreement with 0·40, the ratio of the squares of their distances from C_1, and corresponds to a root mean square angular oscillation of about $3\frac{1}{2}$ degrees. If we permit an oscillation about C_1 we can understand why the axis of maximum vibration for H_2, H_6 is displaced so far away from the normal to the C–H bond, as we noted above. Alongside φ_c in Table 2 we list also the value of ψ which defines the direction corresponding to tangential motion about C_1. It will be seen that the observed values φ_o are much closer to ψ than to φ_c for H_2, H_6.

The above type of molecular oscillation, whether it be strictly about carbon C_1 or not, seems to be the main factor responsible for the larger thermal displacements of the hydrogen atoms relative to their associated carbon atoms: these relative motions will not be affected by possible anisotropic translational vibrations of the molecule as a whole. It can be shown that the *remainder* of the differential motion can be accounted for by bending and stretching vibrations of the C–H bonds. For example, we find for H_3 that a component of B perpendicular to the C–H bonds of $1\frac{1}{2}$ or 2 units, corresponding to an angular bonding of about 8 degrees, remains to be accounted for by bending of the C–H bond. Treating this motion in terms of a harmonic oscillator (see, for example, Herzberg (1950)) it is calculated that the proton is in a state of zero-point energy such as to give an infra-red vibration frequency of about 1000 cm.^{-1} which is comparable with experimental values of 1300 cm.^{-1} for the bending of the C–H bonds. A similar sort of agreement can be obtained for the residual differential movement of the hydrogen atom along the C–H bond in relation to C–H stretching frequencies. We may regard these semi-quantitative agreements as supporting our division of the hydrogen atom motion among molecular oscillation and zero-point energy oscillations. The extent of agreement is in accord with the limited accuracy of our present thermal parameters. We conclude that a study of reflections in three principal zones, providing sufficient additional data to permit allocation of anisotropic thermal parameters to *all* the atoms, might give significant chemical information about the atomic and molecular motions.

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