Acta Cryst. (1967). **23**, 107

Neutron Diffraction Study of the Hydrogen Bond System in Tetrachlorohydroquinone

BY S. K. SIKKA AND R. CHIDAMBARAM

Atomic Energy Establishment Trombay, Bombay, India

(*Received* 23 *June* 1966 *and in revised form* 6 *December* 1966)

The crystal structure of tetrachlorohydroquinone, $C_6Cl_4(OH)_2$, space group $P2_1/c$, has been studied by the single-crystal neutron diffraction technique. 261 independent reflexions with $(\sin\theta)/\lambda \le 0{\cdot}75$ were recorded in thrcc zones (*h*0*l*, 0*kl* and *hk*0). Starting with the heavy-atom parameters obtained in an earlier X-ray study of the crystal (*Acta Cryst.* **15**, 443), the structure has been refined by Fourier and least-squares methods. Anisotropic temperature factors have been used for all the atoms in the later stages of the refinement and a final *R* index of 0·094 has been obtained. While the heavy-atom positions agree with those given by the X-ray data, the hydrogen position postulated on the basis of a difference X-ray Fourier map has been found displaced from the correct position by more than 1 Å. Consequently, the type of $\mathrm{O{-}H}\begin{matrix}\mathrm{O}\\ ⋰ \\ \\ ⋱ \\ \mathrm{Cl}\end{matrix}$ 'bifurcated' hydrogen-bond interaction between neighbouring $C_6Cl_4(OH)_2$ molecules, proposed on the basis of the X-ray study, does not exist. There are close-packed layers of molecules parallel to the (100) plane, with sixfold coordination of each molecule. The layers are connected to one another by O–H···O hydrogen bonds of length 2·92 Å; the O–H distance is 0·97 Å (corrected for thermal motion) and the H–O···O angle is 19·2°.

Sakurai (1962) has studied the structure of tetrachlorohydroquinone by X-ray and nuclear quadrupole resonance (n.q.r.) methods and has proposed a 'bifurcated' hydrogen bond of the type $\mathrm{O{-}H}\begin{matrix}\mathrm{O}\\ ⋰ \\ \\ ⋱ \\ \mathrm{Cl}\end{matrix}$ between neighbouring $C_6Cl_4(OH)_2$ molecules. The position of the hydrogen atom was supposed to be indicated by a peak in the three-dimensional difference Fourier map of electron density. However, there was no positive evidence of O–H---Cl interaction available from the n.q.r. data.

Crystals of $C_6Cl_4(OH)_2$ were grown from an alcoholic solution. The crystals were brown and many of them exhibited regions which were lighter in shade and more transparent than the rest of the crystal. The crystals also seemed to twin easily across the $(10\bar{2})$ plane, as observed under a polarizing microscope. The single crystal used for the neutron diffraction study was of a uniform darker shade. All the measurements were carried out at the Cirus Reactor in Trombay.

The sample used for collecting the *h*0*l* data was of dimensions 4·6 mm × 2·5 mm × 1·4 mm (weight = 0·026 g), the longest dimension being the *b* axis. The intensities of 132 *h*0*l* reflexions were recorded at a wavelength of 1·031 Å on the double crystal neutron diffractometer 'DCD' described by Chidambaram, Sequeira & Sikka (1964*a*). The same crystal specimen was reduced to the size 3·2 mm × 2·5 mm × 1·4 mm (weight = 0·019 g) and intensities of 79 0*kl* and 50 *hk*0 reflexions were measured at a wavelength of 0·953 Å by remounting it suitably on the semi-automatic diffractometer 'SAND' (Chidambaram, Sequeira & Momin, 1967). The latter has an electro-mechanical system of automation to record up to twenty reflexions in the zero-layer in one setting. The data were collected for all three zones up to $(\sin\theta)/\lambda \le 0{\cdot}75$. Complete diffraction profiles were recorded for 200 out of the total of 261 independent reflexions. For the rest, which were weak, the integrated intensities I were estimated by measuring only the peak intensities I_p and using the (I/I_p) *vs.* 2θ correlation curves developed for each zone (Chidambaram, Sequeira & Sikka, 1964*b*).

The systematic absences were found to be consistent with the space group $P2_1/c$. The cell parameters used in the analysis are those reported by Sakurai (1962) and are $a = 8{\cdot}214$, $b = 4{\cdot}843$, $c = 12{\cdot}441$ Å and $\beta = 123°49'$. There are two formula units per unit cell. The linear absorption co-efficient μ was measured on 'DCD' and found to be $1{\cdot}27\ \mathrm{cm}^{-1}$.

The analysis of the *h*0*l* data was carried out first. The scale factor for this zone was calculated by the method of Wilson (1949). It was noticed that the signs for 95 of the *h*0*l* reflexions were determined entirely by the heavy atoms (at the positions determined in the X-ray investigation). Using these 95 reflexions, a Fourier plot of the projection of the nuclear scattering density on the (010) plane was made. The hydrogen atom was clearly seen in this projection. The discrepancy index $R\ (=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|)$, which was 0·258 for the structure given by Sakurai (1962) (including the hydrogen atom in the position given by him) fell to 0·229 for the parameters derived from the first

Fourier synthesis. The x and z coordinates of the hydrogen atom were 0·433 and 0·239 compared with the values 0·47 and 0·22 found in the X-ray work. Full-matrix least-squares refinement with isotropic temperature factors for all the atoms, using the program written by Srikanta (1965), reduced the value of R to 0·125. The function minimized was $\Sigma\, w||F_o|-|F_c||^2$ with $w=1$ for each reflexion. The electron density projection of the nuclear scattering density normal to [010] is shown in Fig. 1.

The scale factor for the $0kl$ data was obtained by comparing the intensities of the common $00l$ reflexions in the $0kl$ and $h0l$ zones. The $0kl$ data were directly refined by the full-matrix least-squares method using isotropic temperature factors, starting with the y and z parameters (including those for the hydrogen atom) obtained in the X-ray study. The initial R index for this zone was 0·285. While all the heavy atoms showed relatively small shifts from their starting positions in the course of the refinement, the hydrogen atom really broke loose. It moved out slowly at first but soon quite rapidly with a large accompanying rise in its temparature factor. After 12 cycles, the hydrogen atom seemed to stabilize in a new position. The R value at this stage was 0·128. The position of the hydrogen atom obtained by this refinement was confirmed in the

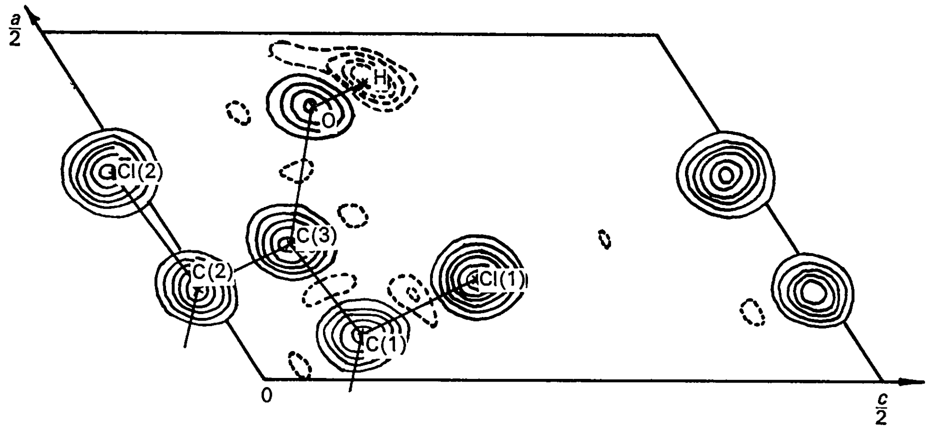


Fig. 1. Projection of the nuclear scattering density of $C_6Cl_4(OH)_2$ along [010]. The positive contours are at intervals of $0{\cdot}5\times 10^{-12}$ cm.Å^{-2} while for the negative contours, shown by broken lines, the interval is $0{\cdot}25\times 10^{-12}$ cm.Å^{-2}. The zero contour has been omitted.

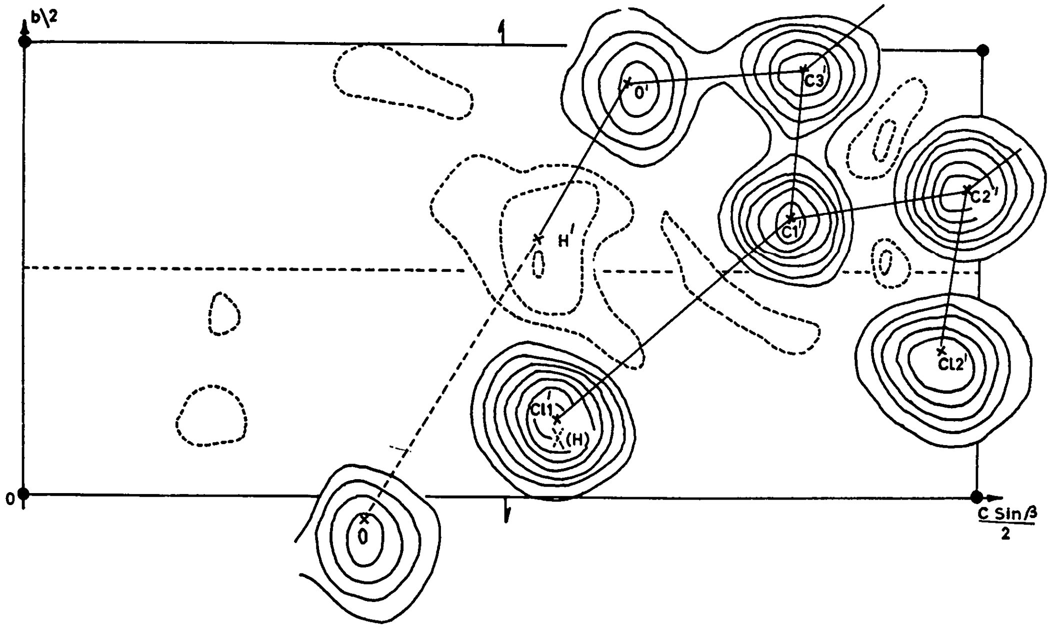


Fig. 2. Projection of the nuclear scattering density of $C_6Cl_4(OH)_2$ along [100]. The positive contours are at intervals of $0{\cdot}5\times 10^{-12}$ cm.Å^{-2} while for the negative contours, shown by broken lines, the interval is $0{\cdot}25\times 10^{-12}$ cm.Å^{-2}. The zero contour has been omitted. The primed atoms are at $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$. (H) shows the position of the hydrogen atom postulated in the X-ray work.

Table 1. *Positional and thermal parameters in* $C_6Cl_4(OH)_2$

The expression for the Debye–Waller factor is $\exp\,[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$. The least-squares standard errors are given in parentheses).

	Fractional coordinate × 10^4			Thermal parameter × 10^4					
	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl(1)	1523 (4)	−4140 (12)	2259 (3)	134 (6)	234 (23)	56 (2)	69 (22)	40 (3)	11 (12)
Cl(2)	−2992 (4)	−3519 (13)	180 (3)	112 (5)	410 (30)	75 (3)	36 (28)	47 (3)	−17 (14)
C(1)	656 (5)	−1882 (14)	1004 (3)	76 (6)	153 (27)	39 (3)	56 (23)	22 (3)	7 (13)
C(2)	−1334 (5)	−1562 (13)	80 (3)	70 (6)	111 (22)	41 (3)	−78 (21)	23 (3)	−26 (12)
C(3)	2014 (5)	−308 (17)	924 (4)	61 (6)	215 (29)	49 (3)	27 (32)	21 (3)	6 (15)
O	3945 (11)	−426 (19)	1807 (5)	50 (10)	214 (32)	59 (5)	−77 (28)	2 (7)	11 (19)
H	4299 (20)	−2081 (45)	2317 (12)	153 (27)	491 (111)	118 (14)	14 (91)	56 (22)	121 (44)

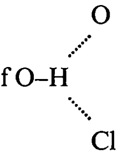
Table 2. $C_6Cl_4(OH)_2$:
observed and calculated structure factors

The nuclear scattering lengths used are (in units of 10^{-12} cm): chlorine 0·98, carbon 0·66, oxygen 0·58, hydrogen −0·378.

H	K	L	$\|F_o\|$	F_c	H	K	L	$\|F_o\|$	F_c	H	K	L	$\|F_o\|$	F_c	H	K	L	$\|F_o\|$	F_c
0	0	2	4.34	4.40	-3	0	4	2.51	-2.32	0	1	1	2.61	2.54	0	6	0	2.24	2.14
0	0	4	3.26	3.33	-3	0	6	4.43	4.48	0	1	2	4.10	4.27	0	6	1	1.83	2.25
0	0	6	0.96	0.99	-3	0	8	0.97	-0.88	0	1	3	1.83	1.90	0	6	2	3.92	4.32
0	0	8	3.03	2.95	-3	0	10	0.69	-0.60	0	1	4	2.34	2.23	0	6	3	2.28	2.14
0	0	10	6.10	6.06	-3	0	12	1.08	1.13	0	1	5	3.38	-3.81	0	6	4	0.43	-0.35
0	0	12	2.83	2.92	-3	0	14	1.81	-1.75	0	1	6	1.54	1.05	0	6	5	0.00	0.09
1	0	0	5.27	5.52	-3	0	16	0.00	-0.45	0	1	7	1.04	0.75	0	6	6	0.88	1.60
1	0	2	4.72	-4.56	-4	0	2	0.99	0.83	0	1	8	1.34	0.56	0	6	7	1.01	-0.35
1	0	4	3.47	3.39	-4	0	4	3.41	-3.27	0	1	9	1.31	-1.26	0	6	8	1.38	1.36
1	0	6	3.58	-3.36	-4	0	6	5.69	-5.60	0	1	10	2.43	2.28	0	7	1	0.70	0.58
1	0	8	9.41	9.52	-4	0	8	2.22	-2.01	0	1	11	5.07	5.22	0	7	2	2.46	2.48
1	0	10	4.20	4.06	-4	0	10	2.65	-2.69	0	1	12	3.02	2.78	0	7	3	0.00	0.59
1	0	12	1.79	1.78	-4	0	12	0.93	-1.00	0	1	13	0.98	-0.97	0	7	4	1.06	1.15
2	0	0	5.31	-5.30	-4	0	14	2.79	-3.02	0	1	14	2.73	2.60					
2	0	2	4.72	-4.57	-4	0	16	1.52	-1.55	0	2	0	2.99	3.14	1	1	0	1.62	-1.65
2	0	4	6.33	-6.25	-5	0	2	3.77	-3.64	0	2	1	1.61	-1.48	1	2	0	2.94	-2.76
2	0	6	0.00	-0.58	-5	0	4	1.46	-1.37	0	2	2	5.17	-5.23	1	3	0	3.28	3.19
2	0	8	3.04	3.45	-5	0	6	6.45	-6.45	0	2	3	4.64	4.79	1	4	0	1.72	-1.00
2	0	10	3.13	-3.17	-5	0	8	2.97	-2.77	0	2	4	0.00	0.00	1	5	0	4.70	5.07
2	0	12	0.44	0.46	-5	0	10	2.34	-2.46	0	2	5	4.06	-3.88	1	6	0	0.55	1.12
3	0	0	2.65	-2.46	-5	0	12	4.63	4.52	0	2	6	2.20	-1.93	1	7	0	0.00	0.51
3	0	2	0.50	-0.37	-5	0	14	1.07	-0.96	0	2	7	1.07	-0.50	2	1	0	3.26	3.73
3	0	4	0.25	-0.21	-5	0	16	0.58	0.71	0	2	8	2.27	-2.22	2	2	0	1.91	-1.65
3	0	6	2.31	2.08	-6	0	2	4.05	3.81	0	2	9	3.57	-3.28	2	3	0	1.58	1.38
3	0	8	1.58	-1.54	-6	0	4	8.28	8.38	0	2	10	0.00	-0.41	2	4	0	1.40	1.22
3	0	10	0.74	-0.64	-6	0	6	0.39	-0.25	0	2	11	0.79	0.17	2	5	0	1.89	1.05
4	0	0	4.85	-4.71	-6	0	8	3.67	3.41	0	2	12	0.00	0.11	2	6	0	0.82	-0.14
4	0	2	3.72	3.65	-6	0	10	0.45	-0.53	0	2	13	2.27	1.66	2	7	0	1.35	-0.82
4	0	4	3.12	-3.05	-6	0	12	5.38	5.47	0	3	1	0.79	0.58	3	1	0	2.18	2.02
4	0	6	0.59	0.67	-6	0	14	5.29	5.20	0	3	2	2.97	2.66	3	2	0	3.08	-3.11
4	0	8	0.00	0.16	-6	0	16	1.09	1.05	0	3	3	1.28	-0.94	3	3	0	1.81	1.66
4	0	10	0.73	-0.69	-7	0	2	1.42	1.44	0	3	4	2.94	-2.60	3	4	0	0.70	1.38
5	0	0	1.40	-1.23	-7	0	4	9.21	9.18	0	3	5	1.37	1.24	3	5	0	0.81	0.61
5	0	2	4.85	-4.77	-7	0	6	4.51	4.00	0	3	6	3.46	3.67	3	6	0	0.73	0.82
5	0	4	7.23	-7.14	-7	0	8	0.76	-0.82	0	3	7	1.09	-1.25	4	1	0	0.74	-0.77
5	0	6	0.80	0.78	-7	0	10	0.24	0.04	0	3	8	1.94	-1.86	4	2	0	1.51	-1.75
5	0	8	3.78	-3.75	-7	0	12	1.35	-1.41	0	3	9	1.46	-1.68	4	3	0	5.32	-5.16
6	0	0	1.89	1.88	-7	0	14	3.71	3.88	0	3	10	1.54	1.46	4	4	0	1.34	1.77
6	0	2	5.14	-4.94	-7	0	16	0.96	0.98	0	3	11	0.39	-0.47	4	5	0	1.67	-1.80
6	0	4	1.62	1.58	-8	0	2	2.90	-2.85	0	3	12	0.80	-0.95	4	6	0	0.00	-0.39
6	0	6	1.00	-0.93	-8	0	4	0.94	-0.91	0	3	13	0.66	-0.29	5	1	0	1.26	1.06
7	0	0	1.38	1.46	-8	0	6	4.28	4.27	0	3	14	1.78	1.32	5	2	0	5.83	5.67
7	0	2	0.91	0.97	-8	0	8	1.62	-1.49	0	4	0	3.14	-2.95	5	3	0	0.88	-2.02
7	0	4	3.24	3.50	-8	0	10	2.11	-2.00	0	4	1	1.18	-0.82	5	4	0	3.22	3.07
7	0	6	4.55	4.73	-8	0	12	3.29	-3.09	0	4	2	1.61	-1.40	5	5	0	2.55	-2.83
8	0	0	1.24	-1.14	-8	0	14	1.02	1.07	0	4	3	0.38	0.31	5	6	0	1.86	-1.97
8	0	2	1.95	-1.98	-8	0	16	0.38	0.57	0	4	4	5.16	-5.10	6	1	0	5.51	5.30
8	0	4	5.40	5.56	-9	0	2	0.00	0.04	0	4	5	1.15	-1.38	6	2	0	0.49	0.73
9	0	0	3.09	-3.36	-9	0	4	2.01	-2.09	0	4	6	2.10	-2.02	6	3	0	1.33	0.38
9	0	2	3.53	3.55	-9	0	6	3.13	3.06	0	4	7	2.29	2.17	6	4	0	1.26	-1.94
-1	0	2	3.56	3.49	-9	0	8	1.32	1.52	0	4	8	2.83	-2.82	6	5	0	1.41	-1.44
-1	0	4	1.08	-0.94	-9	0	10	2.37	2.30	0	4	9	0.00	-0.72	7	1	0	1.44	0.61
-1	0	6	5.83	-6.02	-9	0	12	2.16	-2.00	0	4	10	0.00	-0.28	7	2	0	1.39	0.02
-1	0	8	3.44	-3.26	-9	0	14	1.01	1.04	0	4	11	1.35	-1.49	7	3	0	0.55	-1.18
-1	0	10	0.22	0.25	-9	0	16	0.73	0.75	0	4	12	0.77	-0.05	7	4	0	4.06	-4.11
-1	0	12	0.52	-0.56	-10	0	2	0.00	-0.24	0	5	1	2.95	2.91	7	5	0	0.79	-0.51
-1	0	14	1.12	1.14	-10	0	4	1.08	-0.89	0	5	2	1.51	1.23	8	1	0	1.40	-0.64
-2	0	2	1.28	1.19	-10	0	6	1.36	1.18	0	5	3	1.63	-1.23	8	2	0	1.06	0.51
-2	0	4	2.63	-2.59	-10	0	8	0.53	-0.41	0	5	4	2.29	-1.05	8	3	0	0.92	1.15
-2	0	6	1.02	0.92	-10	0	10	0.00	0.03	0	5	5	1.28	-0.75	8	4	0	0.72	0.43
-2	0	8	7.74	-7.83	-10	0	12	0.45	-0.18	0	5	6	0.00	-0.11	9	1	0	0.42	-0.62
-2	0	10	3.01	3.14	-10	0	14	2.29	-2.42	0	5	7	1.61	-1.84	9	2	0	0.87	0.00
-2	0	12	2.15	-2.03	-10	0	16	0.21	0.15	0	5	8	2.19	-1.83	9	3	0	0.65	-0.76
-2	0	14	1.65	1.46	-11	0	4	2.83	-2.74	0	5	9	2.59	2.31	10	1	0	3.03	-2.28
-2	0	16	0.66	-0.66	-11	0	10	4.12	-4.49	0	5	10	1.83	-1.96					
-3	0	2	5.35	5.34	-11	0	12	1.29	-1.40	0	5	11	0.95	0.60					

electron density projection of the nuclear scattering density in the plane normal to [100], which is shown in Fig. 2.

The absorption corrections for the three zones of data were now computed by the program ORABS (Wehe, Busing & Levy, 1962). The combined data were subjected to several cycles of full-matrix least-squares refinement using the program ORFLS (Busing, Martin & Levy, 1962). The weighting scheme used was the following: $w\propto(A/\sin 2\theta)\,(1+2C_B/C_N)^{-1}$, where A is the absorption correction, $1/\sin 2\theta$ the Lorentz factor, C_N the net signal count and C_B the background count (the background was recorded for the same time as the signal). At first only isotropic temperature factors were used and, in the final stages, individual anisotropic temperature factors for all the atoms. In the last cycle of refinement, the maximum parameter shifts were only one-tenth of the corresponding standard errors. The final overall discrepancy indices R and R_w (= $[\Sigma\, w||F_o|-|F_c||^2/\Sigma\, w|F_o|^2]^{\frac{1}{2}}$) are 0·094 and 0·054 respectively. The final parameters[*] and the least-squares standard errors are listed in Table 1. The observed and calculated values of F are compared in Table 2. The interatomic distances and bond angles, calculated by the program ORFFE (Busing, Martin & Levy, 1964), are given in Table 3. The molecule is very nearly planar.

Fig. 2 shows that the hydrogen atom is shifted from the site [indicated by (H)] given by Sakurai by as much as 1·2 Å. Consequently, the proposed type of  $\mathrm{O{-}H}\genfrac{}{}{0pt}{}{\cdots\mathrm{O}}{\cdots\mathrm{Cl}}$ 'bifurcated' interaction is absent;[†] the donor oxygen atom in the proposed 'bifurcated' bond is really the acceptor atom in an O–H---O hydrogen bond of length 2·92 Å. The O–H distance is 0·961 Å, which increases to 0·970 Å on correction for thermal motion

---

[*] A refinement of Sakurai's X-ray data carried out by us with anisotropic temperature factors improved the R value marginally from 0·17 to 0·16. The heavy-atom coordinates obtained in this refinement as well as those from our neutron data show no significant difference from Sakurai's.

[†] Some other structures in which bifurcated hydrogen bonds proposed on the basis of X-ray studies have been disproved by neutron investigations are sulphamic acid (Sass, 1960) and α-iodic acid (Garrett, 1954). Neutron studies have, however, revealed or confirmed the existence of bifurcated hydrogen bonds in Tutton's salts (Brown & Chidambaram, 1966), perdeuterated violuric acid (Craven & Takei, 1964), barium chloride dihydrate (Padmanabhan, Busing & Levy, 1963) and glycine (Burns & Levy, 1962).

Table 3. *Interatomic distances and bond angles in* $C_6Cl_4(OH)_2$*

In the molecule

Distances		Angles	
C(1)–C(2)	1·388 ± 0·006 Å	C(2)–C(1)–C(3)	119·9 ± 0·5°
C(1)–C(3)	1·400 ± 0·009	Cl(1)–C(1)–C(2)	122·0 ± 0·5
C(2)–C($\bar{3}$)	1·384 ± 0·008	Cl(1)–C(1)–C(3)	118·1 ± 0·3
C(1)–Cl(1)	1·704 ± 0·007	C(1)–C(2)–C($\bar{3}$)	121·2 ± 0·5
C(2)–Cl(2)	1·720 ± 0·008	Cl(2)–C(2)–C(1)	119·6 ± 0·5
C(3)–O	1·337 ± 0·009	Cl(2)–C(2)–C($\bar{3}$)	119·2 ± 0·3
H---Cl(1)	2·453 ± 0·020	C(1)–C(3)–C($\bar{2}$)	117·9 ± 0·6
O---Cl(1)	2·959 ± 0·011	O——C(3)–C(1)	123·1 ± 0·6
		O——C(3)–C($\bar{2}$)	118·9 ± 0·4
		O——O——H	111·3 ± 1·2
		C(3)–H---Cl(1)	112·6 ± 1·1

In the hydrogen-bond network

O---O′	2·918 ± 0·009 Å	O–H---O′	151·8 ± 1·7°
O—H	0·961 ± 0·021† 0·970 ± 0·024‡		
H---O′	2·035 ± 0·021		

* The standard errors for bond distances and bond angles have been calculated after allowing for the errors in the cell parameters. C($\bar{2}$) and C($\bar{3}$) are respectively related to C(2) and C(3) in the same molecule by a centre of symmetry. O′ is related to O by a twofold screw axis and belongs to a different molecule.

† Uncorrected for thermal motion.

‡ Corrected for thermal motion, assuming that the hydrogen atom 'rides' on the oxygen atom (Busing & Levy, 1964). This correction is somewhat uncertain owing to the unreliability of the anisotropic thermal parameters derived from two-dimensional data.

assuming that the hydrogen atom 'rides' on the oxygen atom (Busing & Levy, 1964). The H---O distance is 2·04 Å and the H–O---O angle is 19·2°; the hydrogen bond is, therefore, among the more severely bent ones found in crystalline solids. The distance between H and Cl(1) atoms of the same molecule is 2·45 Å but the H–O---Cl(1) angle is 40°. While the interaction between H and Cl(1) of the same molecule undoubtedly contributes a small amount to the total potential energy of the crystal and is even perhaps partly responsible for weakening and bending the O–H---O bond, we hesitate to call this a 'bifurcated' hydrogen bond system (note that the 'bifurcated' system proposed by Sakurai, in which both the acceptor atoms O and Cl belonged to the same molecule, is different). The configuration around the hydrogen atom is shown in Fig. 3; the hydrogen atom is out of the O---O---Cl(1) plane by only 0·104 Å.

The O–H---O hydrogen bond is propagated through the structure by a twofold screw axis, linking $C_6Cl_4(OH)_2$ molecules into a zigzag chain parallel to the *b* axis. In view of the nature of the hydrogen bonding, it was considered interesting to examine the possibility of (partial) disorder in the structure involving two fractional hydrogen atoms in each hydrogen bond. So a model in which a half-hydrogen atom was placed at the position already determined and another at a distance of 0·96 Å from the acceptor oxygen atom along the O---O line was tried. The former was given the same anisotropic temperature factor as that determined above and given in Table 1; the latter was given an isotropic temperature factor $B = 4{\cdot}5$ Å^2. The positional parameters of the two fractional hydrogen atoms and their multiplicity (with the constraint that their sum was equal to unity) were now refined by the ORFLS least-squares program (Busing, Martin & Levy, 1962). In one cycle of refinement, the multiplicity corresponding to the hydrogen position given in Table 1 rose to 1·025 and that at the new position fell to −0·025, indicating that there is no hydrogen disorder in the structure. Difference nuclear scattering density maps calculated for all three projections along [010], [100] and [001] also confirmed the position of

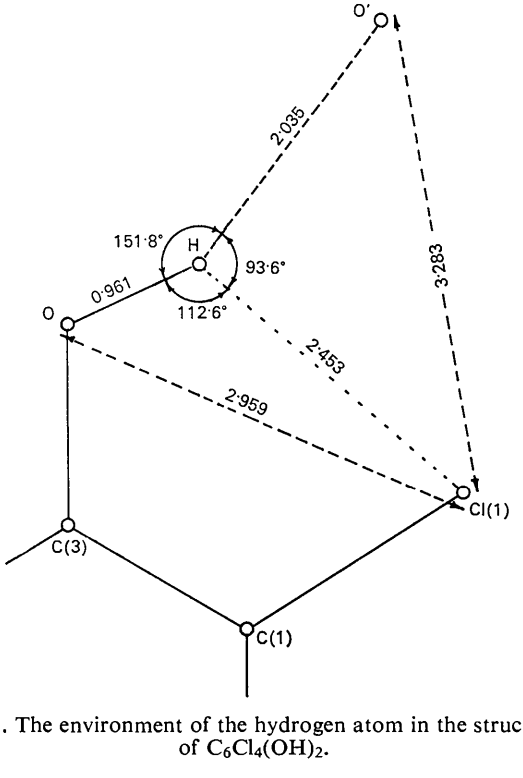


Fig. 3. The environment of the hydrogen atom in the structure of $C_6Cl_4(OH)_2$.

the hydrogen atom found by the least-squares refinement. The highest background peaks had heights of 0·12, 0·38 and 0·36 respectively of the hydrogen peak heights in the three projections. But none of the background peaks in the three projections is close to the hydrogen peak.

There are close-packed layers of (two-dimensional black-and-white space group) symmetry $2_1t[\bar{1}]$ (notation of Kitaigorodskii, 1955) parallel to the (100) plane with a sixfold coordination of each molecule. These layers are stacked parallel to one another and neighbouring layers are connected by hydrogen bonds. There are also hydrogen-bonded layers parallel to the $(10\bar{2})$ plane. The interaction between neighbouring layers of the latter type involves only van der Waals forces, which incidentally explains the easy cleavage of the crystal along the $(10\bar{2})$ plane (as well as the twinning across this plane, referred to earlier).

We are very grateful to Dr H. A. Levy and Dr W. R. Busing for making the various Oak Ridge crystallographic programs available to us. All the calculations were carried out on the CDC 3600 computer at the Tata Institute of Fundamental Research and our thanks are due to Dr S. Srikanta for making suitable minor alterations in the Oak Ridge programs as also for help in running them. The assistance of Shri A. Sequeira and Shri S. N. Momin in operating the diffractometer 'SAND' is gratefully acknowledged. Shri S. N. Momin and Shri H. Rajagopal also helped in collecting the data.

References

Brown, G. M. & Chidambaram, R. (1967). To be published.

Burns, J. H. & Levy, H. A. (1962). *Abstracts Amer. Cryst. Assoc. Meeting.*

Busing, W. R. & Levy, H. A. (1964). *Acta Cryst.* **17**, 142.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS, A Fortran Crystallographic Least Squares Program.* Oak Ridge National Laboratory Report ORNL-TM-305. (The version is the one currently in use at Oak Ridge and incorporates modifications by W. C. Hamilton, J. A. Ibers and C. K. Johnson.)

Busing, W. R., Martin, K. O. & Levy, H. A. (1964). *ORFFE, A Fortran Crystallographic Function and Error Program.* Oak Ridge National Laboratory Report ORNL-TM-306. (The version used incorporates modifications by C. K. Johnson.)

Chidambaram, R., Sequeira, A. & Momin, S.N. (1967). To be published.

Chidambaram, R., Sequeira, A. & Sikka, S. K. (1964*a*). *J. Chem. Phys.* **41**, 3616.

Chidambaram, R., Sequeira, A. & Sikka, S. K. (1964*b*). *Nucl. Instrum. Methods,* **26**, 340.

Craven, B. M. & Takei, W. J. (1964). *Acta Cryst.* **17**, 415.

Garrett, B. S. (1954). Oak Ridge National Laboratory Report ORNL-1745.

Kitaigorodskii, A. I. (1955). *Organic Chemical Crystallography.* English Transl. New York: Consultants Bureau.

Padmanabhan, V. M., Busing, W. R. & Levy, H. A. (1963). *Acta Cryst.* **16**, A26.

Sakurai, T. (1962). *Acta Cryst.* **15**, 443.

Sass, R. L. (1960). *Acta Cryst.* **13**, 320.

Srikanta, S. (1965). *CDC-3600 Crystallographic Programs for Neutron Diffraction. Part* I. *NP-SFLS*1. Atomic Energy Establishment Trombay Report AEET-203.

Wehe, D. J., Busing, W. R. & Levy, H. A. (1962). *A Fortran Program for Calculating Single Crystal Absorption Corrections.* Oak Ridge National Laboratory Report ORNL-TM-229.

Wilson, A. J. C. (1949). *Acta Cryst.* **2**, 318.

Acta Cryst. (1967). **23**, 111

The Crystal Structure of In_6S_7

By J. H. C. Hogg and W. J. Duffin
Department of Physics, The University, Hull, England

(*Received* 1 *February* 1967)

The crystal structure of In_6S_7 has been determined from powder and single-crystal X-ray diffraction data. The unit cell is monoclinic with $a=9{\cdot}090$, $b=3{\cdot}887$, $c=17{\cdot}705$ Å, $\beta=108{\cdot}20°$ and the space group $P2_1/m$. There are 2 formula units per cell and all In and S atoms are in special positions 2(*e*). The structure consists basically of two separate sections both consisting of almost cubic close-packed arrays of S atoms with In atoms in octahedral coordination, the two sections having equivalent directions at 61·5° to each other.

Introduction

A black crystalline phase occurring in the system In–In_2S_3 has from time to time been allocated various chemical formulae, including both In_4S_5 and In_5S_6. In a recent general survey of the system, however, Duffin & Hogg (1966) presented evidence showing that the phase is in fact In_6S_7.

Direct analysis to decide between the various formulae proved quite impossible, partly because some methods were inherently incapable of achieving the necessary accuracy but mostly because specimens sufficiently free from contamination by other phases could not be prepared. However, none of the ranges of composition yielded by analysis was in conflict with the formula finally adopted and this also applies to those