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A Nuclear Quadrupole Resonance and X-ray Study of the Crystal Structure of Tetrachloro-Hydroquinone

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The crystal structure of the tetrachloro-hydroquinone $C_6Cl_4(OH)_2$ was solved directly, by the application of the nuclear quadrupole resonance methods and the parameters were refined by X-ray diffraction data. The crystal is monoclinic $P2_1/c$ with two centro-symmetrical molecules in a unit cell. The molecules is almost planar except for the hydrogen atoms and the angular distortions of the C–Cl bonds out of the plane of the benzene ring are less than 1°. The carbon ring is intermediate in dimensions between benzenoid and quinoid.

The two shortest intermolecular distances are $O\text{–}H \cdots O = 2{\cdot}92$ Å, and $O \cdots Cl = 3{\cdot}29$ Å. The former corresponds to an unusually long hydrogen bond and the latter to a shorter than normal van der Waals approach. The position of the hydrogen atom suggests that this may be due to the formation of a bifurcated hydrogen bond system in the crystal structure.

Introduction

This paper is a part of the series of investigations making use of both nuclear quadrupole resonance (n.q.r.) and X-ray diffraction for the crystal structure determination. The principle of the n.q.r. method was explained in the first paper on the crystal structure of 1,2,4,5-tetrachlorobenzene by Dean, Pollak, Craven & Jeffrey (1958).

In the present paper, the combined techniques have been applied systematically for a direct solution of the structure analysis, from the n.q.r. data followed by three-dimensional isotropic Fourier refinement.

Crystal data

Fisher's highest purity grade $C_6Cl_4(OH)_2$ was purified by recrystallization from alcoholic solution. The crystals are monoclinic, with space group $P2_1/c$ and cell dimensions,

$$\begin{aligned} a &= 8{\cdot}214 \pm 0{\cdot}017 \text{ Å} \\ b &= 4{\cdot}843 \pm 0{\cdot}010 \text{ Å} \\ c &= 12{\cdot}441 \pm 0{\cdot}025 \text{ Å} \\ \beta &= 123^\circ\, 49' \pm 10',\ V = 411{\cdot}2 \pm 3{\cdot}0 \text{ Å}^3 \\ D_m &= 1{\cdot}996 \text{ g.cm.}^{-3},\ D_x = 2{\cdot}001 \pm 0{\cdot}015 \text{ g.cm.}^{-3} \\ Z &= 2;\ \text{molecular symmetry } \bar{1}. \end{aligned}$$

The molecular symmetry was confirmed by the observation of a pure quadrupole resonance of Cl^{35} consisting of two lines of frequencies 36·74 and 36·96 mc.sec.$^{-1}$ at room temperature.

Experimental

For the n.q.r. analysis a single crystal was carefully grown by slow evaporation of alcoholic solution. The crystal was a light brown color of parallelepiped shape elongated along the *b* axis. The clear cleavage faces were $\{100\}$ and $\{10\bar{2}\}$. The crystal dimensions were $15 \times 6 \times 6$ mm.^{3} and the oscillator coil was wound directly around it. The diameter of the wire used was about 0·3 mm. and number of turns was 8. The n.q.r. spectrometer was almost the same as that described by Dean (1960). The crystal is suspended by two circular plates, by means of which its orientation could be varied in any direction. The experimental observations were concerned with locating the magnetic zero splitting loci in the presence of a weak magnetic field.

The intensity data for the X-ray analysis were obtained from multiple Weissenberg photographs with Cu $K\alpha$ radiation of the zero to the 3rd layer of the *b* axis. The linear absorption coefficient for this crystal is 120 cm.$^{-1}$ for Cu $K\alpha$. Therefore in order to reduce the absorption errors, a thin well shaped crystal was selected with an approximately rectangular cross section, 0·08 mm. × 0·05 mm. A cylindrical shape absorption correction with the mean crystal diameter of 0·065 mm. was applied. For many higher angle reflections, the $K\alpha_1$ and the $K\alpha_2$ spectra were completely resolved. For these reflections, the intensity for $K\alpha_1$ was measured and a correction factor of 1·5 was applied. For intermediate reflections, where the separation was incomplete and a line broadening was observed, the correction factor was assumed to have the value $1 + 0{\cdot}5(\theta_B - \theta_0)/(\theta_S - \theta_0)$ where θ_B is the Bragg angle of the reflection, θ_S is the lowest angle at which complete $\alpha_1\alpha_2$ resolution was observed and θ_0 is the highest angle at which the resolution was not observed. After these corrections the intensities were reduced to structure amplitudes by the ordinary Lorentz and polarization corrections. The scale factor for each layer was obtained at a later stage in the analysis by comparing with the calculated structure factors.

Determination of the structure

In order to analyze the n.q.r. data, three coordinate systems were defined.

1. The spectrometer coordinates which are associated with the n.q.r. spectrometer.
2. The bond coordinates, X_b, Y_b and Z_b which coincide with the principal axis of the field gradient tensor around each nucleus.
3. The molecular coordinates, L, M and N which are characteristic of the molecule and are defined as in Fig. 1.

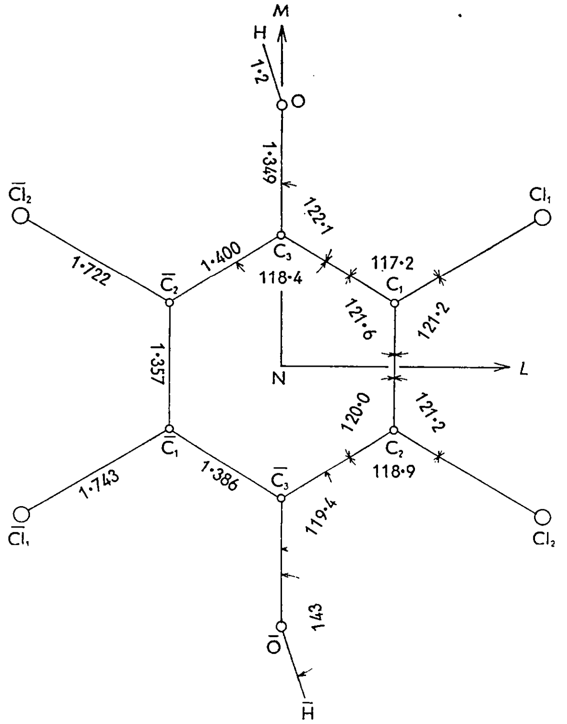

Fig. 1. The molecular structure.
N axis is perpendicular to the plane of the molecule.

The magnetic zero splitting loci was observed with respect to the spectrometer coordinate, and plotted on the surface of a unit sphere. In the presence of the weak magnetic field, the loci have an elliptic shape. For the nucleus with spin 3/2 these will be expressed by the formula $\sin^2\theta_b = 2/(3-\eta\cos 2\varphi_b)$ where θ_b and φ_b are the polar and the aximuthal angle of the bond coordinate, and η is an asymmetry parameter of the field gradient (Das & Hahn, 1958). The transformation matrices between the spectrometer coordinate and bond coordinates must be such that the observed points along the loci agree with the above formula. The actual calculation was done in the following steps. First, the best fit plane through the observed points on the unit circle was obtained and the approximate z_b axis was taken as the normal to this plane. The x, y coordinates of the locus in the bond coordinate system become an ellipse and the X_b and Y_b axes were taken as the principal axes of this ellipse. Finally, the directions of the bond coordinates and η were refined by least-square method to get the best fit with the above formula. Z_b was assigned to the σ bond and X_b was assumed to be the π bond directions. For each frequency, two different loci were observed. These loci were related by mirror symmetry. Therefore, the b axis of the crystal was obtained with respect to the spectrometer axis. Cl_1 corresponds to the low frequency and Cl_2 corresponds to the high frequency. The bond orientation data is given in Table 1. The standard deviation for the σ bonds is 1° and for the π bonds it is 1·4°.

Table 1. *Comparison between n.q.r. and X-ray bond orientation data*

Angle between	n.q.r.	X-ray
b axis and $Cl_1\,\sigma$ bond	48·2°	50·3°
b axis and $Cl_2\,\sigma$ bond	56·6°	56·6°
$Cl_1\,\sigma$ bond and $Cl_2\,\sigma$ bond	61·2°	62·4°
$Cl_1\pi$ bond and $Cl_2\pi$ bond	8·0°	

The non-unique crystallographic axes were not obtained directly from the n.q.r. observations. However, since the crystal had distinct cleavage planes, these axes could be determined approximately with respect to the spectrometer coordinate. There is no exact way to determine the direction of the molecular coordinates. However, a recent study of a related molecule (Dean, Richardson & Sakurai, 1961) suggests that, in spite of the existence of the ortho neighbour to the chlorine atoms, the molecule will be almost planar and that the angular distortion will be small. Therefore it was assumed that the molecular axis N is perpendicular to the two bonds and that the M and L axes bisect the obtuse and acute angles of the two bonds respectively. The coordinates of the atoms in the crystal were also obtained by the assumption that the bond angles are all 120° and the C–C, C–Cl and C–O distances are 1·38, 1·70 and 1·43 Å respectively. The resulting atomic coordinates are shown in Table 2. For convenience of calculation,

Table 2. *Parameters deduced directly from n.q.r. data*

Approximate direction cosines between molecular axes and crystal axes

	a'	b	c
L	−0·153	−0·701	0·695
M	0·988	−0·116	0·100
N	0·010	0·702	0·712

Approximate atomic coordinates

	x	y	z
Cl_1	0·162	−0·423	0·219
Cl_2	−0·280	−0·351	0·031
C_1	0·073	−0·190	0·099
C_2	−0·126	−0·157	0·014
C_3	0·198	−0·033	0·084
O	0·402	−0·066	0·170

Asymmetry parameter η is
0·09 ± 0·03 for Cl_1 and 0·13 ± 0·03 for Cl_2.

the direction cosines are taken with respect to the *a′*, *b* and *c* axes, where *a′* is in the *ac* plane and perpendicular to the *c* axis.

From these coordinates the crystal structure factors were calculated to give a first reliability factor of $R=0{\cdot}36$. Successive refinement of the coordinates and isotropic temperature factor by differential Fourier synthesis reduced the *R* factor to 0·17, and established that the correct solution to the phase problem had been obtained from the n.q.r. measurements. The hydrogen position was deduced from a difference Fourier synthesis which showed one peak near the oxygen which was assigned to the hydrogen atom. The atomic parameters are given in Table 3. The standard deviations of the atomic coordinates were calculated by Cruickshank's formula (1954). The larger standard deviations along the *b* axis are due to the limitation of the observed data in that direction. Comparison of these coordinates with those in Table 2 shows that the n.q.r. technique gave a very good first approximation to the structure.

Table 3. *Atomic coordinates and isotropic temperature factors*

	x	*y*	*z*	*B*
Cl_1	0·1520	−0·4172	0·2264	3·70
Cl_2	−0·3009	−0·3516	0·0176	3·70
C_1	0·0624	−0·187	0·0975	3·04
C_2	−0·1329	−0·156	0·0096	3·04
C_3	0·2001	−0·030	0·0915	3·04
O	0·3944	−0·0539	0·1803	4·00
H	0·53	0·06	0·28	—

Standard deviations of the atomic coordinates

	a	*b*	*c*
Cl	0·004 Å	0·006 Å	0·004 Å
C	0·013	0·019	0·014
O	0·010	0·014	0·012

For this type of molecule, the temperature factor will be mainly due to the rigid body vibrations (Cruickshank, 1956*a*). At the isotropic stage of an analysis, rotational vibration cannot be considered correctly. However, their magnitude can be estimated in the following way. The mean square displacement (m.s.d.) of atom $\overline{u^2}$ is approximately written in the form

$$\overline{u^2}=\overline{u_t^2}+\overline{u_t^2}=\overline{u_t^2}+\overline{2k^2}r^2$$

where $\overline{u_t^2}$ is the m.s.d. due to the translational vibration, $\overline{u_r^2}$ is that due to the rotational vibration, *r* is the distance of the atom from the center of gravity of the molecule and *k* is the angle of rotational vibration. From temperature factors shown in Table 3, these values could be obtained and it was found that $(\overline{u_t^2})^{\frac{1}{2}}=0{\cdot}191$ Å, $(\overline{k^2})^{\frac{1}{2}}=1{\cdot}4°$. The bond length corrections due to this rotational motion (Cruickshank, 1956*b*) are 0·0009 and 0·0011 Å for C–C and C–Cl bond respectively. They are not included in the bond length calculations since they are negligible compared with the standard deviations.

Table 4. *Interatomic distances and valency angles**

Intramolecular distances

C_1–$\underline{C_2}$	1·357 Å
C_2–C_3	1·400
C_3–C_1	1·386
C_1–Cl_1	1·743
C_2–Cl_2	1·722
C_3–O	1·349
O–H	1·2

Bond angles

C_2–C_1–$\underline{C_3}$	121·6°
$\underline{C_1}$–C_2–C_3	120·0
C_2–C_3–C_1	118·4
C_2–C_1–Cl_1	121·2
C_3–C_1–Cl_1	117·2
$\underline{C_1}$–C_2–Cl_2	121·2
C_3–C_2–Cl_2	118·9
$\underline{C_1}$–C_3–O	122·1
C_2–C_3–O	119·4
C_3–O–H	143

Intermolecular distances

O–O′	2·921 Å
O–$\underline{Cl_1{}'}$	3·294
$O_+{}'$–Cl_2	3·520
$O_+{}'$–H	1·9
$\underline{Cl_1}{}'$–H	2·6
Cl_2–H′	2·7
Cl_1–$Cl_{2-}{}''$	3·425
Cl_1–$Cl_{2+}{}''$	3·848
Cl_1–$\underline{Cl_1{}''}$	3·752
$\underline{Cl_1}{}'$–Cl_2	4·110
Cl_2–$Cl_2{}'''$	3·371

Intermolecular angles

C_3–O · · · $O_+{}'$	117·1°
C_3–O · · · $O_-{}'$	126·8
$O_+{}'$ · · · O · · · $O_-{}'$	111·8
C_3–O · · · $Cl_1{}'$	162·4

Standard deviations

C–C	0·021 Å
C–Cl	0·016
C–O	0·019
C–C–C angle	1·4°
C–C–Cl	1·1
C–C–O	1·4

* The subscript of the atom corresponds to that in Figs. 2 and 3.
+, − mean $+\frac{1}{2}$ and $-\frac{1}{2}$ of *y* coordinates.

The interatomic distances and valency angles are listed in Table 4. The calculated and observed structure factors are shown in Table 5. The hydrogen atoms are not included in this calculation. The IBM 650 programs of Shiono (1957, 1959, 1960) were used for the computations.

Discussion of the structure

The arrangement of the molecule in the crystal is shown in Fig. 2 and 3. The direction cosines of the molecular axes are shown in Table 6.

The molecular plane makes an angle of 44·8° with *ac* plane. The distance between the two oxygen atoms of adjacent molecules related by the two-fold screw axis is 2·92 Å. Therefore if a hydrogen bond exists between these oxygen atoms, the hydrogen bond system makes a zigzag chain about two-fold axis. However, this distance is considerably longer than the averaged hydrogen bond length of 2·67 Å for many phenols (Pimentel & McClellan, 1960). On the other hand, the shortest intermolecular oxygen chlorine distance is 3·29 Å between O and Cl_1', which is shorter than the 3·6 Å which would be expected from a van der Waals O–H · · · Cl contact distance. Since the hydrogen atom lies between the lines O · · · O′

Table 5. *Observed and calculated structure factors*

h0l		$\lvert F_o\rvert$	F_c
0	2	17.9	+18.5
0	4	30.9	+63.8
0	6	6.7	+ 8.0
0	8	16.7	+17.7
0	10	13.8	+14.8
0	12	4.4	+ 5.9
1	0	35.6	+35.4
1	2	60.2	-44.4
1	4	42.7	+37.7
1	6	24.8	-22.8
1	8	40.1	+36.6
1	10	5.2	+ 7.0
1	12	7.2	+ 9.3
-1	2	30.6	+23.4
-1	4	43.0	-34.2
-1	6	38.5	-35.2
-1	8	28.7	-30.0
-1	10	0.0	- 4.2
-1	12	0.0	-13.4
2	0	59.4	-55.5
2	2	48.6	-38.4
2	4	45.2	-36.9
2	6	18.3	-19.0
2	8	6.2	+ 4.0
2	10	12.6	-13.8
-2	2	12.7	-10.5
-2	4	32.9	-32.1
-2	6	[illegible]	+10.9
-2	8	48.2	-41.7
-2	10	20.2	+19.7
-2	12	5.7	- 7.6
3	0	15.0	-12.7
3	2	21.4	+21.3
3	4	0.0	+ 0.3
3	6	10.0	+10.0
3	8	2.5	- 2.0
3	10	0.0	- 1.8
-3	2	111.3	+84.0
-3	4	22.1	-24.4
-3	6	71.5	+65.3
-3	8	0.0	+ 0.4
-3	10	11.1	+11.7
-3	12	5.1	+ 8.5
4	0	36.2	-29.3
4	2	42.3	+32.9
4	4	11.3	-11.5
4	6	15.6	+14.5
4	8	4.8	+ 0.1
-4	2	17.8	+16.5
-4	4	14.4	-17.1
-4	6	30.5	-35.6
-4	8	4.3	- 5.8
-4	10	21.5	-22.2
-4	12	0.0	- 4.3
-4	14	10.2	-15.1
5	0	11.2	-11.1
5	2	23.0	-19.9
5	4	27.5	-22.8
5	6	0.0	- 0.6
-5	2	43.5	-35.1
-5	4	9.0	- 8.4
-5	6	37.6	-41.3
-5	8	5.7	- 7.7
-5	10	12.6	-19.7
-5	12	10.7	+16.2
-5	14	4.7	- 6.8
6	0	13.8	+14.1
6	2	14.3	-11.3
6	4	8.4	+ 2.5
6	6	0.0	- 2.1
-6	2	8.9	+ 7.7
-6	4	40.6	+41.8
-6	6	0.0	- 2.3
-6	8	25.6	+33.1
-6	10	0.0	+ 0.4
-6	12	13.7	+22.9
-6	14	8.6	+15.5
7	0	19.1	+16.4
7	2	4.5	- 0.8
7	4	13.7	+11.6
-7	2	3.4	- 0.7
-7	4	34.0	+32.4
-7	6	5.8	+ 6.9
-7	8	0.0	- 2.3
-7	10	0.0	+ 2.0
-7	12	7.9	-11.2
-7	14	5.6	+ 7.4
8	0	5.6	- 5.5
8	2	7.9	- 6.3
-8	2	9.0	- 8.1
-8	4	14.2	-13.3
-8	6	4.7	+ 7.2
-8	8	15.1	-18.5
-8	10	3.2	- 3.6
-8	12	9.8	-16.0
-8	14	2.4	+ 2.6
-9	2	1.8	+ 3.5
-9	4	6.3	- 6.0
-9	6	9.7	+12.3
-9	8	1.7	+ 1.1
-9	10	9.6	+12.4
-9	12	2.5	- 2.5
-9	14	4.2	+ 6.9
-10	6	9.2	+ 7.7
-10	8	0.0	- 0.2
-10	10	5.3	+ 2.1

h1l		$\lvert F_o\rvert$	F_c
0	2	40.5	+42.2
0	3	22.5	-23.4
0	4	7.0	+ 7.4
0	5	30.2	-31.2
0	6	21.8	+23.2
0	7	7.2	+ 4.8
0	8	0.0	+ 0.1
0	9	15.4	-15.6
0	10	13.9	+14.1
0	11	15.7	+13.4
0	12	3.1	+ 5.8
0	13	6.2	- 4.5
1	0	15.8	-16.2
1	1	24.0	+23.7
1	2	50.5	-48.7
1	3	9.3	- 9.8
1	4	17.2	-19.1
1	5	7.9	- 4.9
1	6	24.7	-24.8
1	7	0.0	- 1.6
1	8	15.7	-17.7
1	9	0.0	+ 1.2
1	10	4.3	- 1.7
1	11	5.5	+ 1.6
-1	1	3.9	+ 3.1
-1	2	55.7	+54.7
-1	3	57.6	+91.6
-1	4	23.3	+31.7
-1	5	28.6	-31.5
-1	6	25.0	+30.7
-1	7	24.0	+32.2
-1	8	5.2	- 2.6
-1	9	4.0	- 2.6
-1	10	8.8	+ 7.5
-1	11	9.9	+11.5
-1	13	7.2	+ 6.3
2	0	35.9	+34.9
2	1	55.8	+60.7
2	2	3.7	+ 2.7
2	3	23.0	-21.2
2	4	8.1	+ 8.2
2	5	29.5	+29.3
2	6	17.0	-17.6
2	7	8.7	+ 8.1
2	8	1.2	- 1.0
2	9	8.4	+ 9.7
2	10	5.5	- 4.6
2	11	0.0	+ 1.0
-2	1	29.3	-33.2
-2	2	2.6	+ 2.6
-2	3	43.8	+54.9
-2	4	21.3	-23.3
-2	5	9.6	+10.5
-2	6	2.8	- 4.5
-2	7	6.4	- 7.9
-2	8	17.0	-20.5
-2	9	3.8	- 2.0
-2	10	11.5	-14.8
-2	11	8.8	- 7.9
-2	14	4.0	- 4.6
3	0	28.4	+28.0
3	1	18.3	-18.8
3	2	6.4	+ 6.7
3	3	23.0	-23.0
3	4	14.7	+14.1
3	5	19.4	+14.7
3	6	1.3	+ 0.2
3	7	15.9	-13.4
3	8	11.6	+ 9.1
3	9	8.3	+ 5.4
3	10	0.0	+ 1.6
-3	1	18.7	-20.4
-3	2	1.0	- 2.8
-3	3	41.1	-46.6
-3	4	10.4	+11.0
-3	5	9.2	-10.6
-3	6	1.5	- 3.7
-3	7	20.9	-22.5
-3	8	12.8	+15.6
-3	9	2.0	- 5.2
-3	10	8.0	- 5.8
-3	11	18.8	-21.4
-3	12	10.7	+10.9
-3	15	9.1	- 8.3
4	0	25.5	-23.3
4	1	16.8	-15.1
4	2	10.6	- 9.4
4	3	1.2	+ 1.2
4	4	13.0	-10.3
4	5	14.3	-10.6
4	6	8.7	- 8.9
4	7	10.1	- 8.3
4	8	0.0	- 0.6
-4	1	3.0	+ 0.9
-4	2	2.9	+ 3.7
-4	3	21.2	-21.5
-4	4	42.2	+46.0
-4	5	12.2	+16.4
-4	6	6.9	+ 8.4
-4	7	18.2	-20.9
-4	8	17.1	+18.8
-4	9	23.9	+31.0
-4	10	2.2	- 2.0
-4	11	4.3	- 5.7
-4	12	5.5	+ 5.0
-4	13	7.1	+ 7.9
5	0	1.2	- 1.3
5	1	1.2	- 0.7
5	2	10.5	+ 9.4
5	3	12.1	+11.1
5	4	13.0	- 9.8
5	5	0.0	- 2.9
5	6	0.0	- 1.0
5	7	4.8	+ 4.2
-5	1	37.7	+37.0
-5	2	20.4	-21.1
-5	3	12.5	-13.2
-5	4	5.3	- 4.0
-5	5	26.7	+29.3
-5	6	16.5	-16.8
-5	7	6.2	- 7.2
-5	8	12.4	-13.7
-5	9	5.5	+ 5.1
-5	10	19.5	-20.9
-5	11	11.7	+12.4
-5	12	12.6	-14.4
-5	13	1.2	- 2.1
-5	14	4.9	- 5.3
-5	15	4.1	+ 2.5
6	0	16.5	+14.6
6	1	17.0	-14.1
6	2	16.1	+13.5
6	3	10.6	+ 5.9
6	4	4.0	+ 2.6
6	5	7.2	- 5.2
-6	1	9.9	+ 7.1
-6	2	23.2	-21.8
-6	3	4.7	+ 1.7
-6	4	12.7	-11.9
-6	5	15.7	-15.9
-6	6	6.6	- 5.4
-6	7	1.2	- 0.9
-6	8	8.8	- 9.6
-6	9	19.0	-22.2
-6	10	1.3	+ 0.1
-6	11	1.3	+ 1.6
-6	12	9.0	- 9.8
-6	13	8.0	- 6.3
-6	14	7.5	+ 5.8
-6	15	5.7	+ 3.8
7	0	1.2	- 1.6
7	1	2.3	- 2.8
7	2	4.9	- 3.2
7	3	6.5	- 4.0
-7	1	17.3	-13.1
-7	2	9.2	+ 6.6
-7	3	8.8	+10.7
-7	4	1.3	+ 2.1
-7	5	5.8	- 4.4
-7	6	23.6	+24.1
-7	7	7.7	+ 9.7
-7	8	7.7	+ 6.8
-7	9	11.3	-10.9
-7	10	15.7	+15.9
-7	11	9.0	+10.0
-7	13	2.2	- 2.5
-7	14	6.7	+ 5.9
-7	15	9.8	+10.0
8	1	7.4	+ 6.6
-8	1	0.0	- 2.5
-8	2	8.6	+ 6.5
-8	3	13.1	+12.6
-8	4	5.6	- 4.8
-8	5	4.4	+ 2.4
-8	6	7.0	+ 6.4
-8	7	21.4	+21.1
-8	11	6.5	+ 4.5
-8	12	7.1	- 4.8
-8	13	3.9	+ 3.4
-8	14	5.4	- 5.0
-9	1	5.2	- 4.2
-9	2	6.3	- 3.5
-9	3	3.5	+ 1.8
-9	4	8.8	- 6.4
-9	5	3.4	- 3.5
-9	6	7.0	- 4.7
-9	8	1.1	- 0.6
-9	9	5.0	+ 3.9
-9	10	3.0	- 2.8
-9	11	12.0	-10.9
-9	14	4.3	- 4.2
-10	6	1.6	+ 1.4
-10	7	13.6	- 9.3
-10	8	13.0	+ 9.1
-10	10	5.0	+ 2.9
-10	11	5.6	- 4.4
-10	12	8.6	+ 7.6

h2l		$\lvert F_o\rvert$	F_c
0	1	23.5	-19.4
0	2	48.2	-38.9
0	3	29.9	+25.2
0	4	2.0	- 0.9
0	5	30.6	-29.5
0	6	5.9	- 9.9
0	7	2.8	- 2.9
0	8	6.8	- 6.0
0	9	12.8	-15.4
1	0	4.6	- 3.4
1	1	14.3	+10.7
1	2	24.6	-20.9
1	3	51.6	+47.2
1	4	16.6	+13.5
1	5	2.6	+ 0.9
1	6	18.2	-15.7
1	7	19.4	+18.1
1	8	3.1	+ 6.2
1	9	2.9	- 1.7
1	10	2.6	- 5.5
1	11	11.4	+10.4
-1	1	63.8	-51.9
-1	2	17.6	+15.6
-1	3	3.1	+ 5.5
-1	4	4.1	+ 7.4
-1	5	2.1	- 2.4
-1	6	4.2	+ 6.3
-1	7	12.1	-17.0
-1	8	2.9	+ 0.4
-1	9	5.3	+ 7.6
-1	10	3.1	+ 2.8
-1	11	5.8	- 6.6
-1	12	2.5	- 0.7
-1	13	10.1	+ 8.6
2	0	7.7	- 6.8
2	1	13.7	-13.1
2	2	9.7	+ 9.0
2	3	4.8	- 5.3
2	4	6.0	+ 6.7
2	5	18.5	-19.0
2	6	4.3	+ 6.9
2	7	4.4	+ 4.4
2	8	0.0	+ 6.7
2	9	0.0	- 3.6
2	10	0.0	- 4.5
-2	1	50.6	+47.4
-2	2	1.5	+ 2.2
-2	3	10.6	+ 9.1
-2	4	10.2	+11.5
-2	5	47.3	+64.5
-2	6	18.1	+21.8
-2	7	2.6	+ 8.5
-2	8	11.0	-11.5
-2	9	21.5	+27.0
-2	10	3.1	+ 5.1
-2	11	3.0	+ 3.9
-2	12	5.5	- 7.9
-2	13	11.0	+11.8
3	0	23.1	-21.6
3	1	6.3	+ 6.6
3	2	3.6	+ 4.5
3	3	37.8	-38.2
3	4	3.0	+ 3.8
3	5	6.2	- 9.3
3	6	3.0	+ 3.2
3	7	14.5	-13.2
3	8	0.0	- 3.9
3	9	0.0	- 7.8
-3	1	42.3	+39.1
-3	2	1.9	+ 1.4
-3	3	6.2	- 6.6
-3	4	25.6	-29.7
-3	5	21.4	+21.1
-3	6	16.8	+21.7
-3	7	11.6	-12.7
-3	8	2.8	- 3.2
-3	9	2.9	+ 1.6
-3	10	3.1	- 4.3
-3	11	10.7	-11.7
4	0	11.8	-11.9
4	1	32.1	+29.6
4	2	21.0	+18.9
4	3	3.0	+ 1.0
4	4	4.4	- 5.4
4	5	14.8	+14.9
4	6	0.0	- 0.0
4	7	0.0	- 4.2
4	8	0.0	- 5.0
-4	1	15.9	-14.5
-4	2	2.4	+ 1.0
-4	3	34.2	-35.6
-4	4	2.3	- 4.2
-4	5	13.3	-14.0
-4	6	2.5	- 0.3
-4	7	19.0	-22.7
-4	8	16.9	+18.5
-4	9	19.0	-22.2
-4	13	8.4	-12.1
5	0	19.0	+15.8
5	1	11.9	+10.2
5	2	8.8	+ 8.2
5	3	4.3	+ 1.3
5	4	2.8	- 0.9
5	5	4.3	+ 7.2
5	6	0.0	+ 2.8
-5	1	2.9	- 3.5
-5	2	2.8	- 1.9
-5	3	6.1	+ 9.9
-5	4	2.8	+ 5.2
-5	5	2.7	- 5.1
-5	6	2.7	- 3.0
-5	7	24.0	+27.7
-5	8	4.2	+ 9.5
-5	9	5.3	- 9.5
-5	10	3.1	+ 0.6
-5	11	13.1	+15.8
-5	12	4.2	+ 7.1
-5	13	2.7	+ 0.8
-5	14	5.0	- 6.3
-5	15	7.5	+ 8.0
6	1	0.0	-13.8
6	2	0.0	- 4.0
6	3	0.0	- 3.8
6	4	0.0	+ 0.8
6	5	0.0	- 5.4
-6	1	5.4	- 8.2
-6	2	4.3	- 3.8
-6	3	23.6	+23.9
-6	4	3.0	+ 0.5
-6	5	3.0	- 4.4
-6	6	15.1	-17.1
-6	7	16.7	+17.1
-6	8	3.0	+ 3.0
-6	9	4.4	- 6.0
-6	10	5.4	- 9.8
7	1	0.0	- 2.3
7	2	0.0	- 5.4
7	3	0.0	+ 6.5
-7	1	16.9	-16.8
-7	2	6.1	- 9.0
-7	3	6.2	- 8.3
-7	4	4.4	+ 4.2
-7	5	14.6	-13.6
-7	6	3.1	- 4.8
-7	7	5.4	- 7.0
-7	8	3.1	- 8.0
-7	9	7.5	- 9.5
-7	10	4.2	+ 2.8
-7	11	10.5	-12.6
-8	6	6.5	+ 8.0
-8	9	14.7	+15.7
-8	13	10.2	+11.3
-9	4	7.0	- 5.2
-9	5	19.7	+14.1
-9	9	18.6	+14.8
-9	13	4.9	+ 4.0

h3l		$\lvert F_o\rvert$	F_c
0	1	18.3	+19.1
0	2	19.4	+16.6
0	3	12.3	+10.5
0	4	16.5	-14.1
0	5	13.5	+13.5
0	6	18.7	+18.6
0	7	5.2	+ 5.3
0	8	9.1	- 7.0
0	9	1.5	+ 0.8
0	10	8.7	+ 8.3
1	0	23.2	+19.4
1	1	25.5	-18.7
1	2	33.5	-29.7
1	3	1.2	- 1.9
1	4	1.3	+ 1.9
1	5	1.4	+ 0.9
1	6	5.2	- 5.9
1	7	4.5	+ 2.6
1	8	5.5	- 7.0
1	9	1.3	+ 3.7
1	10	4.1	+ 3.5
-1	1	17.0	-15.0
-1	2	23.8	+28.0
-1	3	8.8	- 9.5
-1	4	8.8	- 8.5
-1	5	14.2	-16.4
-1	6	19.1	+18.6
-1	7	11.6	-12.8
-1	8	8.0	- 6.9
-1	9	10.8	-13.7
-1	10	8.0	+ 7.4
-1	11	11.8	- 9.6
-1	12	4.0	- 4.4
2	0	19.3	+17.7
2	1	20.5	-18.8
2	2	21.1	-16.5
2	3	16.7	-16.1
2	4	13.9	+12.9
2	5	12.2	- 9.7
2	6	14.5	-12.1
2	7	4.0	+ 7.2
2	8	10.1	+ 7.3
2	9	0.0	- 8.7
-2	1	31.2	-27.3
-2	2	9.8	+ 6.5
-2	3	9.9	- 9.7
-2	4	22.9	-24.4
-2	5	8.4	+ 5.7
-2	6	9.0	+ 8.2
-2	7	1.4	+ 0.8
-2	8	2.7	- 4.9
-2	9	3.5	+ 1.1
-2	10	4.9	- 4.6
-2	11	1.4	+ 0.5
-2	12	1.2	+ 1.6
-2	13	3.3	+ 2.4
3	0	13.9	+10.5
3	1	17.2	+13.7
3	2	11.1	-10.3
3	3	16.8	+16.2
3	4	14.1	+11.3
3	5	11.6	+11.0
3	6	0.0	- 1.7
3	7	0.0	+ 0.0
3	8	0.0	+ 7.8
-3	1	20.2	+16.6
-3	2	1.1	+ 2.0
-3	3	15.7	+15.2
-3	4	2.0	- 0.6
-3	5	24.7	+27.0
-3	6	15.9	-15.1
-3	7	26.6	+30.1
-3	8	16.9	+19.5
-3	9	14.0	+14.5
-3	10	9.8	- 3.8
-3	11	4.6	+ 6.4
-3	12	10.7	+ 9.1
4	0	22.1	-21.1
4	1	18.0	+14.2
4	2	1.5	- 0.8
4	3	16.0	+16.1
4	4	3.4	+ 1.0
4	5	8.7	+ 7.1
4	6	2.0	- 2.6
4	7	0.0	+ 3.8
-4	1	1.4	+ 1.4
-4	2	13.5	-12.2
-4	3	1.3	- 1.4
-4	4	25.8	+25.0
-4	5	4.4	- 4.0
-4	6	13.5	-16.1
-4	7	1.5	+ 0.8
-4	8	13.2	+13.6
-4	9	1.5	+ 2.0
-4	10	3.1	- 2.2
-4	11	4.7	- 7.1
-4	12	7.5	+ 6.7
-4	13	9.3	- 7.6
5	0	16.3	-13.6
5	1	1.5	- 3.3
5	2	13.7	+13.1
5	3	8.1	- 5.9
5	4	9.5	- 7.0
5	5	3.8	- 5.1
-5	1	9.0	- 8.5
-5	2	6.9	-10.1
-5	3	17.7	-19.0
-5	4	6.7	+ 5.7
-5	5	10.7	-13.9
-5	6	8.4	-12.3
-5	7	6.0	- 9.1
-5	8	1.5	- 1.4
-5	9	2.2	- 3.0
-5	10	2.2	- 6.2
-5	11	1.4	+ 0.2
-5	12	1.3	- 2.1
-5	13	2.2	- 2.9
6	0	1.5	+ 0.8
6	1	1.4	+ 1.8
6	2	9.5	+ 7.9
6	3	0.0	- 0.0
-6	1	6.6	+ 6.4
-6	2	7.7	- 6.0
-6	3	6.5	+ 6.4
-6	4	1.5	+ 0.0
-6	5	2.2	+ 2.8
-6	6	3.1	- 1.6
-6	7	8.4	+ 8.2
-6	8	10.2	- 8.3
-6	9	6.2	+ 8.6
-6	10	3.0	+ 7.2
-6	11	4.5	+ 6.7
-6	12	9.6	- 8.6
-6	13	3.4	+ 5.3
-6	14	3.7	+ 7.2
7	0	1.2	+ 0.2
7	1	3.7	+ 4.2
-7	1	2.3	+ 2.6
-7	2	2.8	+ 6.1
-7	3	1.4	+ 2.6
-7	4	5.4	- 6.1
-7	5	1.5	+ 1.3
-7	6	13.0	+15.6
-7	7	1.5	- 2.8
-7	8	6.7	- 8.1
-7	9	1.4	- 2.2
-7	10	10.5	+11.4
-7	11	3.4	- 4.2
-7	12	1.1	- 2.7
-7	13	3.1	- 5.6
-8	1	4.2	- 5.6
-8	2	10.2	+ 8.5
-8	3	11.6	- 9.7
-8	4	3.3	- 7.3
-8	5	10.9	- 9.8
-8	6	5.4	+ 4.5
-8	7	7.0	- 6.8
-8	8	1.3	- 2.9
-8	9	5.2	- 7.0
-8	10	3.2	+ 0.9
-8	11	4.5	- 5.2
-9	9	6.7	+ 8.8
-9	10	3.0	- 2.8

Table 6. *Direction cosines of molecular axes*

	a′	*b*	*c*
L	−0·201	−0·694	0·691
M	0·982	−0·108	0·155
N	−0·035	0·710	0·703

and O $\cdots$ Cl$_1'$, it is possible that a weak bifurcated hydrogen bond might exist between O–H and O, Cl. The distances between the hydrogen and chlorine atoms of the same molecule are 3·8 and 3·4 Å respectively, and a intramolecular hydrogen bond is not possible.

The pure n.q.r. frequency difference between two nuclei is about 220 kg.cal. This separation is considerably larger than the corresponding separation in 1,2,4,5-tetrachlorobenzene. However, the non-linear response of the super-regenerative oscillator prevent the detailed study of the line width, and any positive evidence of the O–H $\cdots$ Cl hydrogen bond was not available from the present n.q.r. observations.

The intermolecular O–H $\cdots$ Cl$_2$ distance, 3·52 Å corresponds to a normal van der Waals distance. Some of the intermolecular Cl $\cdots$ Cl distances are considerably shorter than the normal van der Waals separation of 3·6 Å.

Within the experimental error, the molecule has D_{2h} symmetry except for the hydrogen atoms. The mean C–Cl bond length = 1·73 Å, mean C–C = 1·39 Å, C=C = 1·36 Å, C–O = 1·35 Å. The molecular dimen-

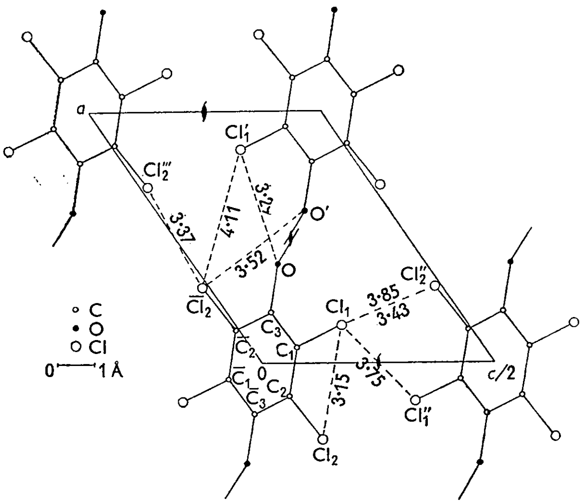

Fig. 2. The molecular arrangement in the crystal. Projection on (010).

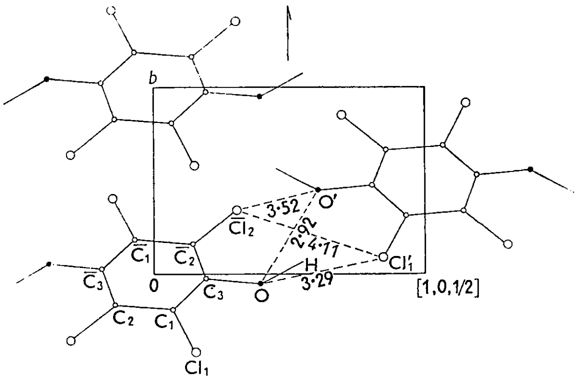

Fig. 3. The molecular arrangement in the crystal. Projection on (10$\bar{2}$) along the c axis.

sions are shown in Fig. 1. The carbon atoms form a slightly deformed hexagon, the equation to the plane of which was obtained by least-square method and is $-0{\cdot}035X+0{\cdot}710Y+0{\cdot}703Z=0$ with respect to the orthogonal a', b, c axes. The deviation of carbon atoms from this plane is 0·006 Å, which is within the standard deviations. The C–Cl bond directions deviate 0·8° from this plane, one is up and another is down. The C–O bond also makes an 0·9° from the carbon plane in the same direction as neighboring chlorine atoms. However, from the standard deviation of the angles, this out-of-plane bending is not significant and within the accuracy of this analysis the molecule is planar. This conclusion adds further support for the non-existence of overcrowding in chlorine substituted benzene and benzoquinone derivatives, as recently discussed by many authors (Gafner & Herbstein, 1958, 1960; Coulson & Stocker, 1959; Dean, Richardson & Sakurai, 1961). The C–O bond length of 1·35 Å agrees with those obtained for resorcinol (Robertson, 1936; Bacon & Curry, 1956) and hydroquinone clathrates (Palin & Powell, 1947). However, this is considerably shorter than the single bond length 1·43 Å and will have more than 40% double bond character. The C–Cl bonds also have a small degree of double bond character which is estimated to be 5% from the observed n.q.r. asymmetry parameter. The π electrons will therefore be more localized in the C–O bonds than in the C–Cl bonds, and the C_1–C_3 and C_2–C_3 bonds have more single bond character than C_1–C_2 bond. This agrees with the observed difference between these bond lengths, which indicates a carbon ring intermediate in character between benzenoid and the pure quinoid as found in tetrachloro *p*-benzoquinone.

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