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## The Crystal Structure of Tetrachloro-*p*-Benzoquinone (Chloranil)

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A three-dimensional structure analysis of chloranil,  $C_6Cl_4O_2$ , has been carried out to determine the positional parameters and the thermal motion of the molecules. A contemporary two-dimensional analysis has been reported by Ueda (1961) and the results are compared. The molecule has a quinoid structure and the quinoid ring is planar, with the oxygen and chlorine atoms displaced slightly (0.05 Å) out of the plane. The bond lengths and valence angles are normal, agreeing well with the data from 1245 tetrachlorobenzene and *p*-benzoquinone. The one unusual feature of the structure is a carbon to oxygen intermolecular separation of 2.85 Å, an observation which may be relevant to the well-known facility of chloranil to form charge transfer complexes. Because of this anomalous distance, a confirmation of the solution to the phase problem was obtained by an independent physical method. The orientation of the C-Cl bonds with respect to each other and the symmetry axis and, less precisely, the direction of the normal to the quinoid ring were measured by nuclear quadrupole resonance methods. These results completely confirmed the X-ray analysis.

Chloranil is compared with *p*-benzoquinone with respect to its molecular packing, anomalous dipole moment and infra-red spectrum.

### Introduction

This work is a continuation of a study of the structure of halogen substituted benzene derivatives by combined X-ray analysis and nuclear quadrupole resonance spectroscopy. In an earlier paper on 1245 tetrachlorobenzene by Dean, Pollak, Craven & Jeffrey (1958), the primary emphasis had been on the n.q.r. technique as a means of measuring the directions of C-Cl bonds, and thereby providing evidence pertaining to the problem of over-crowded molecules, e.g. Harnik *et al.* (1954), Coulson & Stocker (1959), by a technique independent of diffraction studies. The X-ray work was secondary in that it served to establish that, within the accuracy of the X-ray analysis, there was complete agreement between the molecular information deduced from the two techniques. Further research, employing the n.q.r. method has been reported on the planarity of 1234 tetrachlorobenzene, by Dean, Richardson & Sakurai (1961), and on the structure of tetrachloro-hydroquinone by Sakurai (1961).

In this work, the primary emphasis has been on the X-ray analysis of the crystal structure and the role of the n.q.r. technique has been to check the validity of the solution of the phase problem.

### Experimental

The C.P. grade chloranil, purchased from Matheson, Coleman and Bell Company (East Rutherford, New

Jersey), was purified by repeated recrystallization from benzene solution. The melting point of the purified material in a sealed tube is 291–293 °C. The crystals were grown from benzene solution by evaporation as thick, transparent, yellow plates elongated along *b*-axis. Twining occurred frequently on the (001) face.

The density of the crystal was determined by the floating method using a mixture of carbon tetrachloride and methyl iodide. An average density of  $1.953 \pm 0.005$  g.cm.<sup>-3</sup> was obtained from several measurements.

The unit-cell dimensions were measured from Weissenberg photographs about the principal axes, using both the Straumanis technique and an independent calibration with NaCl powder lines. The intensities were eye-estimated from multiple film equi-inclination Weissenberg photographs. The zero to fourth layers about the [*a*] and [*b*] and zero to seventh layers about the [*c*] were recorded. Of the 838 independent reflections within the Cu  $K\alpha$  sphere, 620 were observed. The range of intensities measured was approximately 1700 to 1. No absorption corrections were applied. Crystals of approximately uniform cross-section with dimensions 0.10–0.12 mm. were used. The linear absorption coefficient for Cu  $K\alpha$  radiation is 122.7 cm.<sup>-1</sup>, and the effect of ignoring absorption corrections was estimated to give rise to errors of the order of 7% in structure amplitudes.

The intensities were corrected for Lorentz-polarization and velocity factors by means of the IBM 650 Incor program of Senko, Templeton & Zalkin (1957).

The nuclear quadrupole resonance measurements were made at room temperature and about 80 °K. on a single crystal of dimensions  $14 \times 5 \times 4$  mm.<sup>3</sup>, grown from benzene solution. The n.q.r. method and equipment used have been described elsewhere (Dean, Pollak, Craven & Jeffrey, 1958; Dean & Pollack, 1958; Dean, 1960).

### Crystal data

We found the following

$$\begin{aligned} a &= 8.708 \pm 0.008, \quad b = 5.755 \pm 0.005, \\ c &= 8.603 \pm 0.008 \text{ \AA}; \quad \beta = 105^\circ 51' \pm 8'; \\ V &= 414.8 \text{ \AA}^3; \quad D_m = 1.953 \text{ g.cm.}^{-3}; \quad Z = 2; \\ D_x &= 1.969 \text{ g.cm.}^{-3}; \end{aligned}$$

space group  $P2_1/a$ , from the systematic extinctions ( $0k0$ ) absent  $k$  odd, ( $h0l$ ) absent  $h$  odd. The molecular symmetry is therefore  $\bar{1}$ , with two chlorine atoms, three carbon atoms and one oxygen atom, in the asymmetric unit.

These data are in general agreement with the observations of Ueda (1961) who reported cell dimensions consistently 2% greater, i.e.

$$a = 8.86, \quad b = 5.84, \quad c = 8.76 \text{ \AA}; \quad \beta = 107.2^\circ.$$

His value of  $1.67 \text{ g.cm.}^{-3}$  for the observed density would appear to be an error in reporting.

Chorghade (1939) in his earlier investigation reported

$$\begin{aligned} a &= 8.77, \quad b = 5.78, \quad c = 17.05 \text{ \AA}; \quad \beta = 103^\circ 31'; \\ D_m &= 1.933 \text{ g.cm.}^{-3}; \quad Z = 4, \end{aligned}$$

space group  $P2_1/a$ . Similar results were reported by Gafner & Herbstein (1960), but these have since been shown to be incorrect and the remeasurement is in agreement with our value for the  $c$  axis (Herbstein, 1961). Many efforts by us to obtain crystals with the  $17 \text{ \AA}$   $c$  axis by varying both source of material and

means of crystallization were unsuccessful, and we have concluded that Chorghade's original observation was erroneous.

The nuclear quadrupole resonance frequencies of chloranil were studied by Douglass (1960). He found two resonance lines at room temperature and four at 77 °K. These data are given in Table 1.

Table 1. *Quadrupole frequencies of chloranil*

Frequency at 77 °K. (Mc./sec.)	Width (Kc./sec.)	Frequency at room temp. (Mc./sec.)	Width (Kc./sec.)
37.5851	2.7	—	—
37.5148	2.0	—	—
37.4698	0.94	36.7885	1.1
37.4417	1.5	36.8596	1.2

We have confirmed this observation. The room temperature observation is consistent with our unit cell containing two centro-symmetrical molecules, while the low temperature observation is consistent with the larger cell containing four molecules. We were unable to detect a phase change by X-ray photographs down to  $-80^\circ\text{C}$ . and presumably the transition is below this temperature.

### The structure analysis

The structure was solved very simply by two-dimensional methods commencing with a Patterson projection down the  $[b]$  and proceeding through Fourier projections and difference syntheses. The three sets of principal projection data, about the  $[b]$ ,  $[c]$  and  $[a]$  axes, were refined to  $R$ -factors of 0.23, 0.28 and 0.19 respectively, using an uniform isotropic temperature factor of  $B = 5.0 \text{ \AA}^2$ . There were no significant discrepancies between the atomic parameters obtained from the three projections.

The three-dimensional refinement proceeding through a three-dimensional Fourier synthesis followed by three cycles of differential synthesis and structure factor calculations. At this stage, different isotropic temperature factors were used and the overall  $R$ -factor

Table 2. *Fractional atomic coordinates and atomic anisotropic thermal parameters from anisotropic refinement by least-squares method*

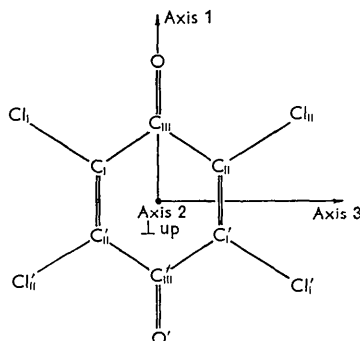
Atom	$x$	$y$	$z$
Cl <sub>I</sub>	0.0244	0.2282	-0.3218
Cl <sub>II</sub>	0.1904	0.2177	0.3295
O	0.1640	0.3843	0.0071
C <sub>I</sub>	0.0058	0.0981	-0.1501
C <sub>II</sub>	0.0824	0.0923	0.1528
C <sub>III</sub>	0.0912	0.2080	0.0020

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl <sub>I</sub>	0.0199	0.0441	0.0159	0.0021	0.0067	0.0094
Cl <sub>II</sub>	0.0158	0.0450	0.0154	-0.0030	-0.0005	-0.0115
O	0.0118	0.0272	0.0271	-0.0058	0.0056	-0.0037
C <sub>I</sub>	0.0096	0.0257	0.0118	0.0021	0.0029	0.0022
C <sub>II</sub>	0.0085	0.0296	0.0109	0.0028	0.0009	-0.0031
C <sub>III</sub>	0.0066	0.0214	0.0180	0.0027	0.0031	-0.0019





Fig. 1. The molecular axes of tetrachloro *p*-benzoquinone.

The mean standard deviations of the atomic coordinates, in Å, calculated using the formula given by Busing & Levy (1959*a*), are as follows:

Cl	$\sigma(x)$	0.003	$\sigma(y)$	0.003	$\sigma(z)$	0.003
O	$\sigma(x)$	0.007	$\sigma(y)$	0.007	$\sigma(z)$	0.008
C	$\sigma(x)$	0.007	$\sigma(y)$	0.008	$\sigma(z)$	0.008

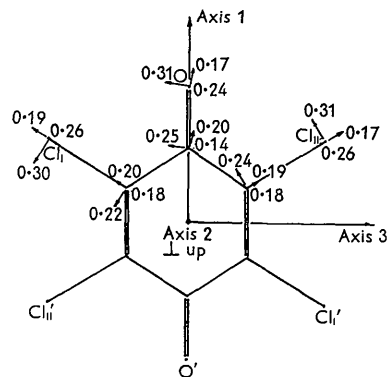
The observed and calculated structure factors are given in Table 3.

A final three-dimensional Fourier and difference synthesis was computed on the IBM 704 using Shoemaker & Sly's (1960) program, from the output of the least squares calculations. There were no significant electron densities in the difference synthesis and no features in either syntheses that were inconsistent with a completely refined analysis of the experimental data.

### The analysis of the thermal motion

The computation of the principal axes of the ellipsoid of vibration for each atom and of the amplitude of vibration along the principal axes of the molecule, from the anisotropic thermal parameters given in Table 2, were made using Busing & Levy's programs (1959*b*).

The principal axes root mean square displacements and their orientations are given in Fig. 2. These individual atomic anisotropic components were analyzed in terms of the rigid-body vibrations about the molecular axes using the procedure of Cruickshank (1956*a*). These molecular axes were defined as follows:

Fig. 2. Root mean square thermal displacements in Å of the atoms in tetrachloro *p*-benzoquinone.

- Axis 1, vector C<sub>III</sub> to O;  
 Axis 2, (axis 1) × (vector C<sub>II</sub> to C<sub>I</sub>);  
 Axis 3, (axis 1) × (axis 2)

and their direction cosines referred to the orthogonal crystal axes are given in Table 8. The twelfth order normal equations can be reduced to two third order equations, two second order equations and two first order equations, by assuming that the molecule is planar and symmetrical about the axes 1 and 3. The  $\tau$  and  $\omega$  tensors thereby obtained are shown in Table 4, together with their standard deviations which were calculated by the least squares formula, from the standard deviations of the  $\beta$ 's (Cruickshank, 1956*a*).

Table 4. Values of  $\tau_{ij}$  (in  $10^{-2}$  Å<sup>2</sup>) and  $\omega_{ij}$  (in deg.<sup>2</sup>) and their standard deviations

$$\tau = \begin{pmatrix} 3.74 & 0.22 & -0.72 \\ & 2.37 & 0.78 \\ & & 4.50 \end{pmatrix}, \quad \omega = \begin{pmatrix} 17.39 & -0.67 & 1.16 \\ & 16.79 & 0.60 \\ & & 12.71 \end{pmatrix}$$

$$\sigma\tau = \begin{pmatrix} 0.26 & 0.27 & 0.22 \\ & 0.32 & 0.27 \\ & & 0.25 \end{pmatrix}, \quad \sigma\omega = \begin{pmatrix} 1.84 & 1.77 & 1.41 \\ & 1.58 & 2.17 \\ & & 2.63 \end{pmatrix}$$

The root mean square amplitude of translational oscillation in the direction of the molecular axes 1, 2 and 3 obtained from the square roots of the diagonal elements of  $\tau$  are 0.19, 0.15 and 0.21 Å respectively. The corresponding root mean square amplitudes of angular oscillation obtained from  $\omega$  are 4.2°, 4.1°

Table 5. Observed and calculated  $U_{ij}$  referred to the molecular axes  
 (In  $10^{-2}$  Å<sup>2</sup>)

	$U_{11}$		$U_{22}$		$U_{33}$		$U_{12}$		$U_{13}$		$U_{23}$	
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Cl <sub>I</sub>	7.36	7.42	7.43	7.48	5.50	5.80	0.03	0.33	0.75	1.47	0.93	0.74
Cl <sub>II</sub>	7.20	7.49	6.85	6.91	5.42	5.75	0.48	0.48	-2.06	-2.88	0.58	0.73
O	4.01	3.74	5.21	5.03	9.45	8.03	0.19	0.16	-1.21	-0.75	0.85	0.66
C <sub>I</sub>	4.30	4.54	3.73	3.44	4.12	4.74	0.20	0.24	-0.12	-0.28	0.68	0.79
C <sub>II</sub>	4.91	4.54	3.52	3.32	3.82	4.72	0.52	0.27	-0.82	-1.14	0.54	0.77
C <sub>III</sub>	3.68	3.74	2.62	3.17	6.28	5.55	0.26	0.21	-0.82	-0.71	0.85	0.75

and 3.6°. Within the experimental errors, the principal axes of  $\tau$  and  $\omega$  coincide with the molecular axes. The amplitudes of translational vibration are greater in the plane of the molecule than normal to it. There are no pronounced differences in the angular oscillations about the three axes.

The calculated  $U$  tensors for each atom are compared with observed values in Table 5. The agreement supports the assumption of rigid-body motion about the molecular axes.

The thermal motion of this molecule at room temperature is less than that of *p*-benzoquinone, which melts at 180 °C. lower, although the observed difference is not as great as might be expected. With respect to the same axes, the translation amplitudes reported by Trotter (1960) for benzoquinone are 0.24, 0.24, and 0.22 Å and the angular amplitudes are 7.3°, 3.7° and 5.8°.

### Comparison with Ueda's two-dimensional analysis

An independent X-ray analysis has been made by Ueda (1961) using principal projection data obtained with Mo  $K\alpha$  radiation. 134 independent reflexions were observed, of which only 4 were additional to what we recorded with the Cu  $K\alpha$  radiation. The only completely resolved atoms were the chlorines in one of the projections and the remaining parameters were deduced from the overlapping atomic peaks by the difference synthesis method. The mean and maximum differences in the atomic coordinates compared with our values are respectively:

$$\begin{aligned} \text{Cl, } & 0.005, 0.010 \text{ \AA}; \text{ O, } 0.032, 0.056 \text{ \AA}; \\ \text{C, } & 0.014, 0.027 \text{ \AA}. \end{aligned}$$

With the exception of the oxygen atoms these differences do not exceed the 1% significance level calculated from the r.m.s. of the standard deviations, only the oxygen  $y$  parameters exceeds the 0.1% significance level. With the exception of this parameter, therefore, it would appear that the estimates of the accuracy of the respective analyses are consistent with the comparison of the results. Because of the overlapping in the projections, the oxygen  $y$  coordinate would, in fact, be the most difficult to determine from the difference syntheses.

An attempt was also made by Ueda to carry out an analysis of the thermal motion, based on the anisotropy of the chlorine temperature factors in projection. The translational oscillation amplitudes agree surprisingly well, i.e. Ueda's values of 0.19, 0.22 and 0.22 Å, being slightly larger than we obtained. The amplitudes of angular oscillation differ most markedly about axis 3 (see Fig. 2); they are 3.0°, 4.3° and 1.1° as compared with our 4.2°, 4.1° and 3.6°. We believe that this is an inaccuracy due to the incomplete nature of a thermal analysis based on projection data.

### Discussion of the structure

The mean intramolecular dimensions corrected for the contracting effect of the molecular oscillations (Cruickshank, 1956*b*) are given in Table 6 and Fig. 3. The standard deviations were calculated by Cruickshank & Robertson's (1953) method. The two independently measured C-Cl and C-C bond distances differed from the mean values by 0.005, 0.006, 0.008, 0.009 Å,

Table 6. Mean bond lengths and bond angles and their standard deviations

Bond or angle	Mean, without rotational correction	Mean, with rotational correction	S.D.	Ueda (1961)
C-Cl	1.708 Å	1.714 Å	0.008 Å	(1.721)
C-O	1.191	1.195	0.011	(1.241)
C-C	1.469	1.477	0.011	(1.483)
C-C	1.335	1.342	0.011	(1.307)
C-C-Cl	116° 11'	116° 15'	35'	
C-C-Cl	122 24	122 23	43	
C-C-O	121 27	121 22	46	
C-C-C	117 06	117 16	41	
C-C-C	121 25	121 22	44	

respectively, i.e. less than the estimated standard deviations. Ueda's corresponding values are given in parenthesis. The bond lengths and angles differ from those published in his paper by about 2% since we recalculated them using our more accurate cell constants. It is to be expected that the largest differences occur between the pairs of least resolved atoms in projection.

The best plane through the six carbon atoms, obtained by the IBM 650 least squares program of Stewart (1959), is

$$0.8011X' - 0.5569Y - 0.2197Z' = 0,$$

where  $X'$  and  $Z'$  refers to the orthogonal axis  $a \sin \beta$  and  $c$ . The perpendicular distances of the atoms from this plane are

Cl <sub>I</sub>	-0.054 Å (-0.060)	Cl <sub>I</sub>	-0.011 Å (0.000)
Cl <sub>II</sub>	-0.057 (-0.060)	Cl <sub>II</sub>	-0.011 (0.000)
O	+0.059 (+0.054)	Cl <sub>III</sub>	+0.011 (0.000)

Within the accuracy of the analysis, the quinoid ring is planar. The deviations of the substituents out of the plane are significant. They correspond to a bending of the C-Cl and C-O bonds out of the plane by 1.5° and 2.2° respectively, so that the substituent atoms alternate 0.05 Å, above and below the plane around the ring. In this respect there is very close agreement indeed between our results and those of Ueda (given in parenthesis).

The observed length of the C-Cl bonds, 1.714 Å, is in good agreement with values from other aromatic compounds and from the chloroethylenes, of  $1.70 \pm 0.02$  Å. It is significantly shorter than the sum of the single bond covalent radii, 1.742 Å. Following

Pauling's (1960) concepts and subtracting  $0.004 \text{ \AA}$  for partial ionic character, the remaining  $0.024 \pm 0.008 \text{ \AA}$  shortening corresponds to  $6.7 \pm 2.4\%$  double-bond character. This is in good agreement with the  $9.4\%$  estimated by Bersohn's method (1954) from the value of the asymmetric parameter,  $\eta$  of  $0.21 \pm 0.03$ , from the chlorine nuclear quadrupole coupling constant. If the partial ionic character correction is ignored, the agreement is better.

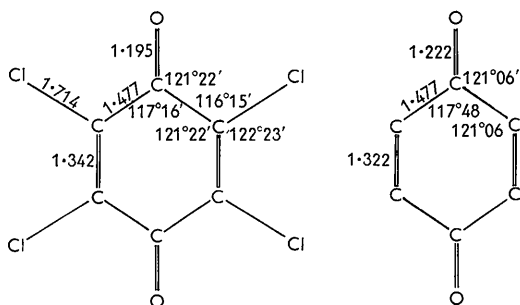


Fig. 3. Bond lengths and bond angles in tetrachloro *p*-benzoquinone and *p*-benzoquinone.

It is of interest to compare the remaining bond lengths with those observed in *p*-benzoquinone by Trotter (1960), see Fig. 3. The single C-C bond lengths are the same,  $1.477 \text{ \AA}$ . At present the theoretical ideal length of  $sp^2-sp^2$  C-C single bond is not sufficiently well defined to be able to make any deduction other than that the  $\pi$ -bond character in these bonds must be quite small (cf., Dewar & Schmeising, 1959). The C-C double bond length is  $0.02 \text{ \AA}$  longer in chloranil than *p*-benzoquinone, but neither of these distances are significantly different from the double bond C-C length of  $1.334 \text{ \AA}$ .

The C-O bonds are  $0.03 \text{ \AA}$  shorter in chloranil than in *p*-benzoquinone. Although this difference between the two results is not statistically significant there is some infra-red evidence leading to the expectation of a shorter bond length, since study of substituted benzoquinones (Yates, Ardao & Fieser, 1956) has shown that the carbonyl stretching frequency increased with the electronegativity of the substituents. The ring angles agree in both compounds and the small, but significant, differences from  $120^\circ$  can be regarded as characteristic of the quinoid ring.

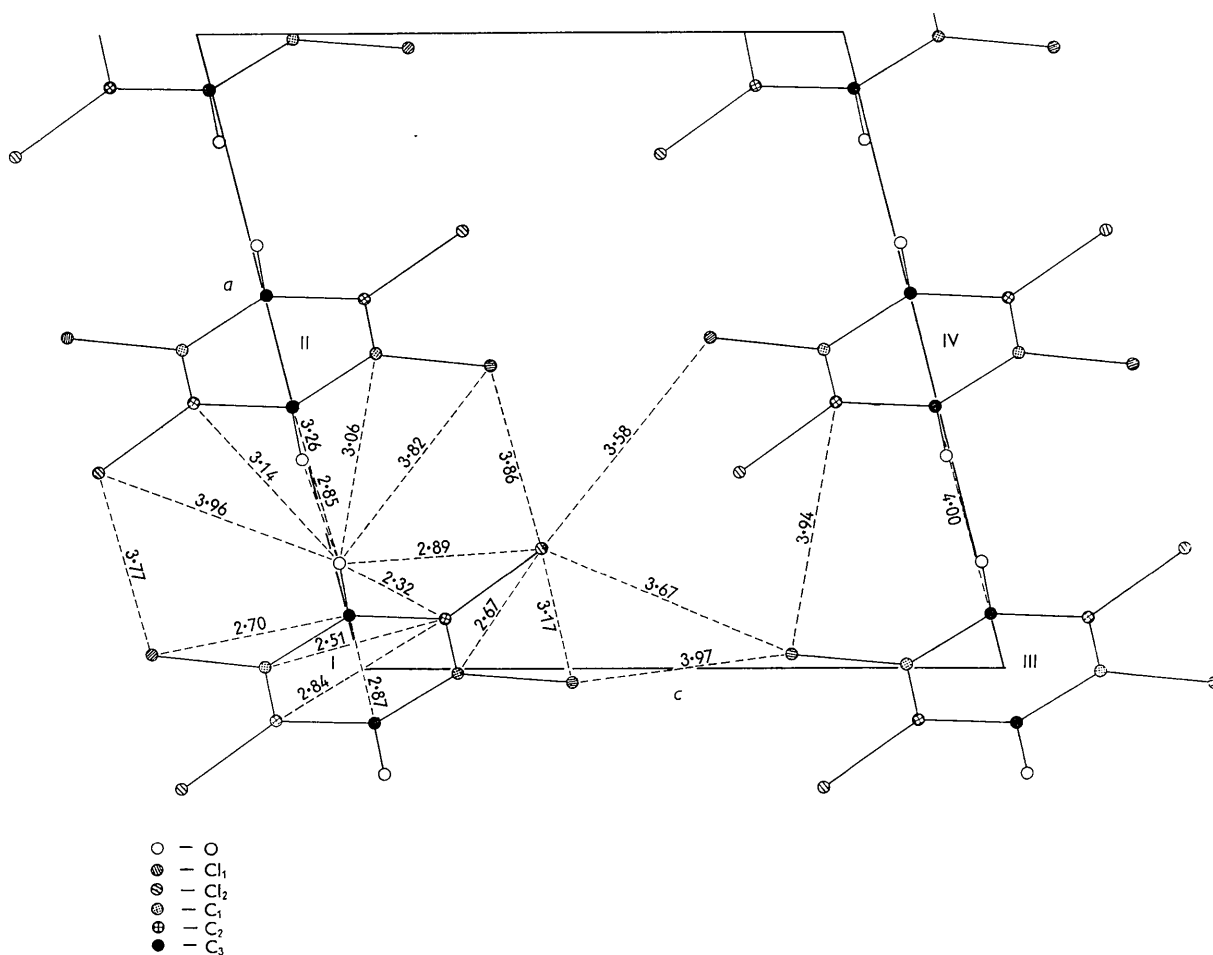


Fig. 4. The shorter intra- and inter-molecular distances in the crystal structure of tetrachloro *p*-benzoquinone.

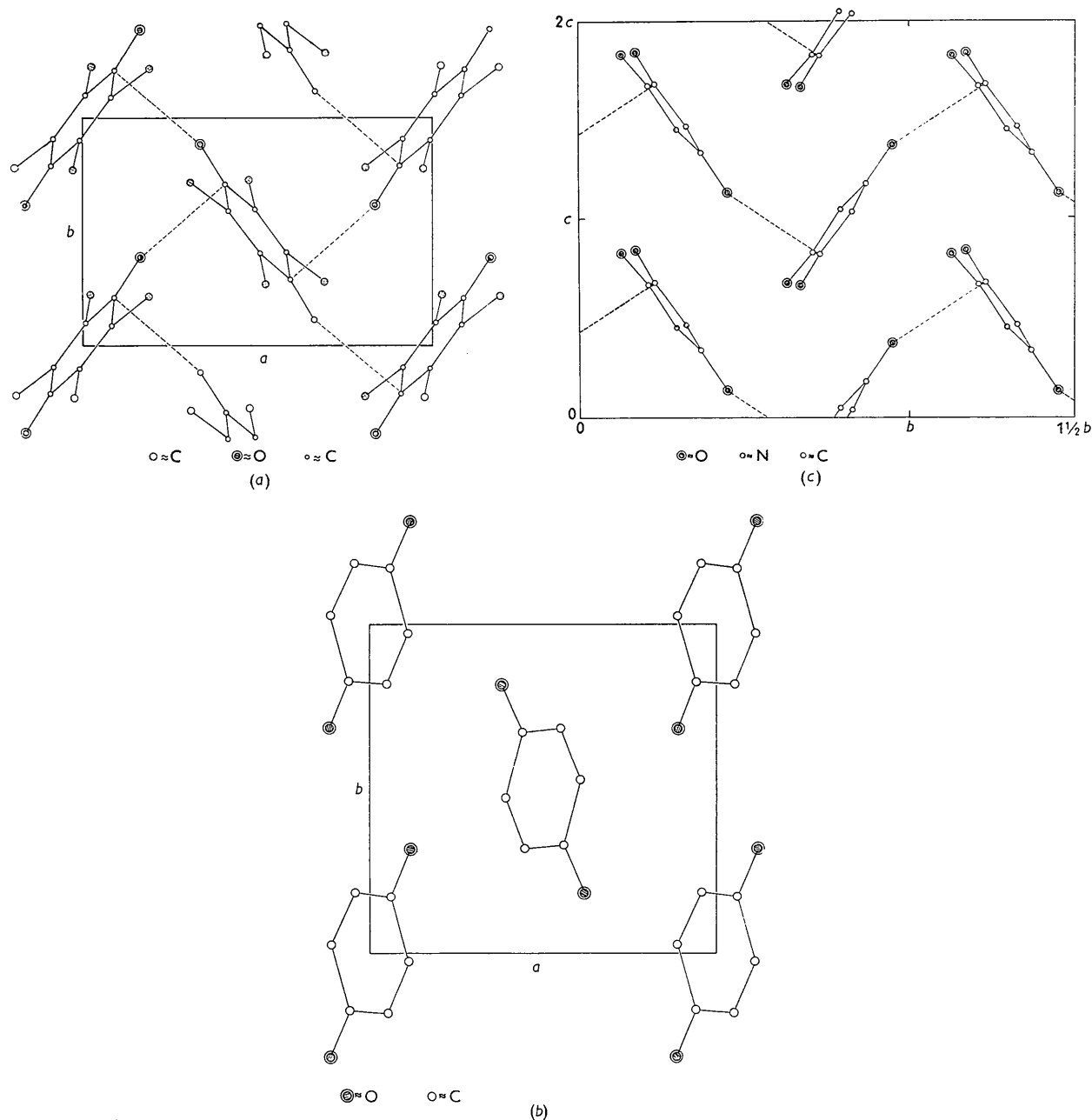


Fig. 5. The molecular arrangement in (a) tetrachloro *p*-benzoquinone, (b) *p*-benzoquinone, (c) parabanic acid.

The angles between the two C-Cl bonds in chloranil is  $64.9^\circ$  in close agreement with that of  $63.6^\circ$  observed in 1245 tetrachlorobenzene (Dean, Pollak, Craven & Jeffrey, 1958). This is presumably a consequence of the repulsion of the chlorine atoms, and this feature is discussed in these terms in considerable detail in Ueda's paper (1961).

The molecular structure of chloranil in the gaseous state has been determined by the electron diffraction method (Barricelli & Bastiansen, 1949). With the exception of the C-Cl bond lengths, which agreed

with the present values, these data were not sufficiently accurate to indicate any significant differences between the molecules in the solid and gaseous state.

The intermolecular distances less than  $4.0 \text{ \AA}$  are listed in Table 7, and some are shown in Fig. 4. Of particular interest are the carbon to oxygen distances of  $2.85$ ,  $3.06$ , and  $3.14 \text{ \AA}$ . While all of these are shorter than the usual van der Waals separations, one in particular is exceptional being that normally associated with a hydrogen bond.



Table 7. *Intermolecular distances less than 4.0 Å*

Cl <sub>I</sub> (I) ... Cl <sub>II</sub> (II)	3.77 Å	O(I) ... Cl <sub>II</sub> (II)	3.82 Å
Cl <sub>II</sub> (I) ... Cl <sub>I</sub> (II)	3.86	Cl <sub>I</sub> (I) ... Cl <sub>II</sub> (II)	3.94
Cl <sub>II</sub> (I) ... Cl <sub>I</sub> (IV)	3.58	O(I) ... C <sub>I</sub> (II)	3.06
Cl <sub>II</sub> (I) ... Cl <sub>I</sub> (III)	3.67	O(I) ... C <sub>II</sub> (II)	3.14
Cl <sub>I</sub> (I) ... Cl <sub>I</sub> (III)	3.97	O(I) ... O(II)	3.26
O(I) ... Cl <sub>I</sub> (II)	3.96	C <sub>III</sub> (I) ... C <sub>III</sub> (II)	4.00
O(I) ... C <sub>III</sub> (II) 2.85 Å			
(I)	( <i>x, y, z</i> )		
(II)	(½ + <i>x, ½ - y, z</i> )		
(III)	( <i>x, y, 1 + z</i> )		
(IV)	(½ + <i>x, ½ - y, 1 + z</i> )		

A somewhat similar situation has been found in parabanic acid, (CO)<sub>2</sub>N<sub>2</sub>H<sub>2</sub> (Davies & Blum, 1955). In that structure also, the shorter intermolecular distances, excluding the hydrogen bond distances are between carbonyl oxygens and  $\pi$ -bonded ring carbon atoms. One of these distances is unusually short, 2.77 Å; the others are 3.01, 3.02, 3.12, 3.16 Å. The non-hydrogen bonded oxygen to nitrogen and oxygen intermolecular distances are 3.03, 3.04, 3.07, 3.13 Å. As in chloranil, there is the herring-bone type of molecular packing and the similarity in the orientation of the close approach with respect to the molecular packing is illustrated in Fig. 5.

In benzoquinone, however, which has a similar molecular packing arrangement, the shortest oxygen to carbon separation between molecules is 3.34 Å and all other intermolecular distances are greater.

#### Verification of the structure analysis

There have been three crystal structure analyses in which anomalously short intermolecular distances were reported. Of these, two, triphenylene (Klug, 1950)

and *p*-nitroaniline (Abrahams & Robertson, 1948) proved on re-examination to be false solutions to the phase problem. The third example is parabanic acid (CO)<sub>2</sub>N<sub>2</sub>H<sub>2</sub> (Davies & Blum, 1955) which is discussed above. This was a complete three-dimensional analyses carried through the anisotropic least squares stage of refinement to an *R*-factor of 0.09. There is no reason, either from the method of analysis or the self-consistency of the results, to believe that this can be other than a true solution.

One of the characteristics of the two false solutions, which were based on two-dimensional analyses only, was the poor agreement for certain reflexions and zones of reflexions, and the differences in peak heights of chemically equivalent atoms. These criteria were checked in this analysis and no discrepancies were found.

A completely independent check on the orientation of the chloranil molecule in the crystal was also provided by the nuclear quadrupole resonance measurements which are discussed below. These measurements independently confirmed the directions of the C-Cl bonds with respect to the two-fold symmetry axis.

#### The nuclear quadrupole resonance analysis

(By T. SAKURAI)

The Zeeman splitting of the n.q.r. spectrum of the chlorine atoms can be used to determine the carbon-chlorine  $\sigma$ -bond directions (Dean, Pollak, Craven & Jeffrey, 1958; Dass & Hahn, 1958). When the bonds have a certain amount of  $\pi$  bond character also, this contributes to the electric field gradient and destroys the axial symmetry. It is therefore possible to determine the direction of the asymmetry normal to the  $\sigma$ -bond (which we call the  $\pi$  bond direction) and the

Table 8

Direct comparison of n.q.r. and X-ray analysis results		
Angles between	n.q.r.	X-ray
[ <i>b</i> ] and Cl <sub>I</sub> $\sigma$ bond	63.6 ± 0.8°	63.9°
[ <i>b</i> ] and Cl <sub>II</sub> $\sigma$ bond	65.4 ± 0.8	65.1
Cl <sub>I</sub> $\sigma$ bond and Cl <sub>II</sub> $\sigma$ bond	64.8 ± 0.8	64.9
Cl <sub>I</sub> $\pi$ bond and Cl <sub>II</sub> $\pi$ bond	10.7 ± 2.3	

Value of asymmetry parameter,  $\eta = 0.21 \pm 0.03$ .

Direction cosines of molecular axes (1, 2, 3) with respect to orthogonal crystallographic axes, (*a'*, *b*, *c*)

	n.q.r. results*			X-ray results		
	<i>a'</i>	<i>b</i>	<i>c</i>	<i>a'</i>	<i>b</i>	<i>c</i>
Axis 1	0.476	0.871	-0.117	0.5390	0.8306	0.1399
Axis 2	-0.847	0.491	0.207	-0.8011	0.5569	0.2197
Axis 3	0.237	0.000	0.971	0.2604	-0.0064	0.9655
Cl <sub>1</sub> $\pi$ bond	-0.844	0.449	0.129	-0.799	0.568	0.198†
Cl <sub>2</sub> $\pi$ bond	-0.803	0.527	0.280	-0.787	0.568	0.239
Cl <sub>1</sub> $\sigma$ bond	0.094	0.441	-0.893	0.092	0.440	-0.893
Cl <sub>2</sub> $\sigma$ bond	0.530	0.413	0.741	0.528	0.421	0.737

\* *a'* and *c* axes in n.q.r. study are so determined that the direction cosines of  $\sigma$  bonds agree with X-ray results, as closely as possible.

† The X-ray chlorine  $\pi$  bond direction is obtained by assuming that the bond is perpendicular to the  $\sigma$  bond and coplanar with axis 2.

magnitude of an asymmetry parameter,  $\eta$  which is related to the percentage of double-bond character in the C-Cl bonds.

The n.q.r. measurements alone determine the angles between the two C-Cl bonds and their relationship to the two-fold symmetry axis. These data are given in Table 8 and compared with the X-ray analysis results. The agreement is within the estimated errors of the n.q.r. data.

The molecular axes for the n.q.r. study, shown in Fig. 1, were defined as follows; axes 1 and 3 bisect the two C-Cl  $\sigma$  bond directions, axis 2 bisects the two  $\pi$  bond directions (i.e. the polar axis of the  $p$ -orbitals at the chlorine atoms, assuming these to be in planes normal to the respective C-Cl  $\sigma$  bond). The direction cosines of these molecular axes with respect to the orthogonal crystal axes,  $b$ ,  $a'$  ( $=a \sin \beta$ ) and  $c$  are given in Table 8 for comparison with those for the molecular axes previously defined with reference to the X-ray analysis.

Since the directions of the two non-unique crystallographic axes cannot be determined from the n.q.r. measurements alone, these two sets of orientation data are not independent. The approximate orientation of the crystal on the n.q.r. spectrometer could be determined from the prominent crystal faces, (100) and (001). A more precise orientation was then deduced by minimizing the discrepancies between the direction cosines for the C-Cl  $\sigma$  bonds from the n.q.r. and X-ray data.

The mean discrepancy between the data from the two techniques is  $0.2^\circ$  for the Cl  $\sigma$  bond directions. For the less precise Cl  $\pi$  bond information it is  $4.0^\circ$ .

### The anomalous dipole moment of chloranil and *p*-benzoquinone

Chloranil and *p*-benzoquinone are both examples of molecules which are centrosymmetrical in the crystal but possess definite dipole moments in solution. That of chloranil is 0.6 D. (Le Fevre, 1948), and of *p*-benzoquinone is 0.7 D. (Hassel & Naeshagen, 1929; Le Fevre & Le Fevre, 1935; Hammick, Hampson & Jenkins, 1935). This problem has been discussed more recently by Paolini (1958), who concludes that the experimental evidence is such that the observations must be accepted as real. He ascribes the effect to an abnormally high electron polarizability of the lone pair electrons of the oxygen atoms associated with the particular arrangement of the carbonyl groups in *p*-benzoquinone and chloranil. There is no evidence of any difference in behaviour of these two molecules, with respect to an external electric field in solution.

### The infra-red spectra of chloranil and *p*-benzoquinone

The infra-red spectra of *p*-benzoquinone and its substituents have been studied (Josien, Fuson, Lebas &

Gregory, 1953; Bascheroitz, Tatibouet & Souchay, 1953; Yates, Ardao & Fieser, 1956).

The C=O stretching frequency in *p*-benzoquinone is  $1667 \text{ cm.}^{-1}$  in solution (carbon tetrachloride or carbon disulfide) and  $1665 \text{ cm.}^{-1}$  in the crystalline solid. For chloranil the corresponding values of  $1695 \text{ cm.}^{-1}$  and  $1684 \text{ cm.}^{-1}$  are reported. We repeated this measurement in chloroform solution and powdered in Nujol and obtained  $1686 \text{ cm.}^{-1}$  and  $1674 \text{ cm.}^{-1}$ . While this difference of  $12 \text{ cm.}^{-1}$ , as compared with  $2 \text{ cm.}^{-1}$  for benzoquinone, is consistent with a difference in environment for the carbonyl groups in solution and in the solid for chloranil but not for benzoquinone, it is difficult to ascribe any quantitative evaluation to these observations.

### Chloranil in complex formation

Both chloranil and benzoquinone form charge transfer molecular complexes with polynitro and polycyclic aromatic hydrocarbons (e.g. Peticolas, 1957). The crystal structures of two of these chloranil complexes have been studied; chloranil-hexamethylbenzene by Harding & Wallwork (1955) and chloranil-pyrene by Pepinsky, Okaya & Krstanovic (1961).

In the chloranil-hexamethylbenzene complex both molecules are reported to be severely distorted from planarity, but this result cannot now be accepted without a further refinement to include the thermal analysis, for which more experimental data is required. In the pyrene complex, the chloranil molecule is planar except for a small distortion of the oxygen atoms of the same magnitude as we find in chloranil alone (i.e.  $0.05 \text{ \AA}$ ).

Both these complexes are of the sandwich type with alternate molecules, stacked in columns. There are no unusually short intermolecular separations.

### Conclusions

The molecule of chloranil is quinoidal and very nearly planar. The small distortions from planarity, although consistent with an overcrowding effect, are in fact, no larger than are commonly found in formally planar molecules in which there is no possibility of strong intramolecular steric interactions.

The unusual feature of this crystal structure analysis is a short carbon to oxygen intermolecular separation of  $2.85 \text{ \AA}$ . We have applied the tests of (1) self-consistency of data and results, (2) confirmation by an independent X-ray analysis, (by Ueda, 1961), (3) confirmation by an independent technique (nuclear quadrupole resonance), and have come to the conclusion that the analysis represents a true solution to the phase problem and that the refinement gives a true representation of the precision of the results.

It appears then that under certain circumstances, which depend upon the electronic configuration of the molecule (i.e. chloranil *vis-à-vis* *p*-benzoquinone) and

upon the intermolecular arrangement (i.e. chloranil *vis-à-vis* the chloranil-pyrene molecular complex), a polar type of interaction can occur between adjacent molecules in crystals which leads to an interatomic distance less than that normally associated with van der Waal forces. This distance is of the same order as that associated with hydrogen bonding.

The intermolecular configuration requirement appears to be such that the molecules pack in a way as to permit a carbonyl oxygen to approach an  $sp^2$  carbon atom approximately along the direction of the polar axis of the  $\pi$  bonded orbital, and that there is a chain of such interactions throughout the crystal structure, as illustrated in Fig. 5.

Chloranil is well-known to be a strong electron acceptor (e.g. Hausser & Mulliken, 1960). In the crystal, it forms an associated structure in which the same molecule appears to be acting both as electron donor and acceptor. A somewhat analogous situation is found in parabanic acid, except that the close approach in that structure is between a carbonyl oxygen and a  $\pi$  bonded carbon atom at opposite ends of the molecule. There is a striking similarity between the geometrical arrangement of the molecules, as shown in Fig. 5. In chloranil, however, the short distances link the molecules in a two-dimensional net, while in parabanic acid there is a continuous chain of associated molecules. Fig. 5, also shows the structure of *p*-benzoquinone, where there is no short inter-molecular distance despite the similarity in molecular packing.

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