

finden wir etwas kleinere Werte. Die Li-Atome sind verzerrt tetraedrisch von 4 O mit einem mittleren Li-O-Abstand von 1.95 Å umgeben. Die SiO<sub>4</sub>- und AlO<sub>4</sub>-Tetraeder sind durchwegs über Ecken verbunden, wobei komplizierte Si<sub>2</sub>O<sub>5</sub>-Schichten gebildet werden, die durch Al miteinander verknüpft sind. Die LiO<sub>4</sub>- und AlO<sub>4</sub>-Tetraeder haben je zwei Kanten gemeinsam.

Nach seiner Kristallstruktur ist Petalit entweder zu den Gerüstsilikaten oder zu den Schichtsilikaten zu stellen, je nachdem, ob man die gemeinsame tetraedrische Koordination um Si und Al oder die Si<sub>2</sub>O<sub>5</sub>-Schichten als wesentlich ansieht. Für die letzte Auffassung spricht auch die vollkommene Spaltbarkeit nach (001).

Diese Arbeit wurde 1951/52 während eines Studienaufenthaltes bei Prof. M. J. Buerger, M. I. T., begonnen. Ihm und den Stipendientiftern (American Association of University Women und Fulbright-

Reisestipendium, bzw. Smith-Mundt Grant und Fulbright-Reisestipendium) sind wir zu grösstem Dank verpflichtet. Prof. Cl. Frondel stellte liebenswürdigerweise Material aus der Harvard-Sammlung zur Verfügung. Die Deutsche Forschungsgemeinschaft hat zum Abschluss dieser Untersuchung durch Sachbeihilfen in dankenswerter Weise beigetragen. Ein beträchtlicher Teil der numerischen Rechenarbeiten lag in den bewährten Händen von Frl. M. Binder.

### Literatur

- GOSSNER, B. & MUSSGNUG, F. (1930). *Z. Kristallogr.* **74**, 62.  
*Hintze's Handbuch der Mineralogie*, (1897), 2. Bd., S. 1595. Leipzig: Veit.  
 SMITH, J. V. (1954). *Acta Cryst.* **7**, 479.  
 TAVORA, E. (1952). *Ann. Acad. bras. Sci.* **24**, 175.  
 ZEMANN-HEDLIK, A. & ZEMANN, J. (1954). *Naturwissenschaften*, **41**, 476.

*Acta Cryst.* (1955). **8**, 787

## The Structures of Molecular Compounds Exhibiting Polarization Bonding. II. The Crystal Structure of the Chloranil-Hexamethylbenzene Complex

BY T. T. HARDING AND S. C. WALLWORK

*Department of Chemistry, The University, Nottingham, England*

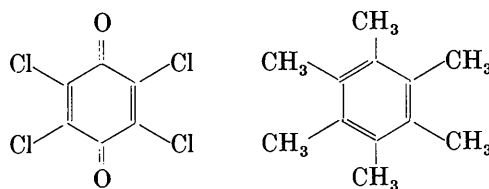
(Received 19 January 1955 and in revised form 26 July 1955)

The structure of the complex formed between chloranil and hexamethylbenzene has been determined by two- and three-dimensional Fourier methods. The cell constants are:  $a_0 = 7.30$ ,  $b_0 = 8.64$ ,  $c_0 = 15.26$  Å,  $\beta = 106^\circ$ , and the space group is  $P2_1/c$ . There are two molecules of each component in the cell, and these are stacked alternately in columns parallel to the  $a$  axis. Both types of molecule are distorted from a planar configuration and the mean molecular planes of adjacent molecules are not quite parallel. This gives rise to some interatomic distances slightly less than normal van der Waals separations. The structure is discussed in terms of the interpretation of polarization bonding developed in Part I.

### Introduction

In the discussion of the crystal structure of phenoquinone, reported in Part I of this series (Harding & Wallwork, 1953), it was suggested that the plane-to-plane stacking of alternate phenol and quinone molecules could be interpreted as evidence of polarization bonding between the two components. This polarization bonding was envisaged as arising from the partial overlap of the  $\pi$  orbitals of the two components, quinone acting as an electron acceptor and phenol as an electron donor. The only difficulty in this formulation was that the greatest  $\pi$ -orbital overlap would be expected when the molecules lie directly over one another, whereas in the phenoquinone structure the centres of adjacent molecules are displaced from this position by about 1.98 Å. This means that the mole-

cules do not lie in planes perpendicular to the line joining their centres but are tilted from this position by about  $30^\circ$ . The distortion of the molecular  $\pi$ -bonds so produced could be explained as being necessary in order to effect a compromise between the packing requirements of polarization bonding and hydrogen bonding. This explanation was supported by evidence from the structure of the chloranil-hexamethylbenzene complex (I)



I

in which no hydrogen bonding is possible. Preliminary work on this structure suggested that the planes of the two component molecules were perpendicular to the line joining their centres so that maximum  $\pi$ -orbital overlap was possible.

In this paper, the detailed structure determination of the chloranil-hexamethylbenzene complex is reported and the results are discussed in terms of the molecular  $\pi$ -bond interpretation of the polarization bonding in molecular compounds.

### Preliminary investigation

Crystals of the complex were obtained as purple-red needles by mixing equimolecular proportions of hot concentrated solutions of the two components in benzene and allowing the mixture to cool slowly. When observed under the polarizing microscope the crystals appeared deep red when the electric vector was parallel to the needle axis and yellow-brown at right angles to this position. The crystals decompose very slowly on exposure to the atmosphere, but it was not necessary to seal them in capillary tubes for X-ray photography. Difficulty was experienced in selecting untwinned crystals for the X-ray examination since groups of three crystals were commonly found growing together with needle axes parallel, giving the appearance of a single pseudo-hexagonal prism. Oscillation and Weissenberg photographs were taken using  $\text{CuK}\alpha$  radiation, with the crystal mounted so as to rotate about each of the three crystal axes in turn. Short sections were cut from the needle in all cases where the rotation axis did not coincide with the needle axis.

The crystals are monoclinic and unit-cell dimensions determined from far-out reflexions on Weissenberg photographs are:

$$a_0 = 7.30, b_0 = 8.64, c_0 = 15.26 \text{ \AA}, \beta = 106^\circ.$$

The space group is  $P2_1/c$  and the density of  $1.47 \text{ g.cm.}^{-3}$  corresponds to two molecules of the complex in this cell (density calculated =  $1.466 \text{ g.cm.}^{-3}$ ). Since the general position in  $P2_1/c$  is fourfold, the two molecules of each component in the cell must occupy special positions. These were chosen as follows:

Chloranil centres at  $0, 0, 0$  and  $0, \frac{1}{2}, \frac{1}{2}$ .

Hexamethylbenzene centres at  $\frac{1}{2}, 0, 0$  and  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ .

The relative intensities of reflexions on the Weissenberg photographs obtained by the multiple-film technique were measured by direct photometry of the X-ray negatives (Wallwork & Standley, 1954). No corrections were made for absorption.

In pleochroic molecular compounds of this type it has been shown (Tsuchida, Kobayashi & Nakamoto, 1951; Harding & Wallwork, 1953) that the direction of maximum light absorption corresponds to the direction of stacking of the molecules linked by polarization bonds. In this complex the needle axis

of the crystal is the  $a$  axis and this is also the direction of maximum light absorption. This suggests that the components are stacked alternately in columns parallel to the  $a$  axis—an arrangement consistent with the special positions noted above provided that the molecular planes are approximately perpendicular to the  $a$  axis. With an  $a$  cell dimension of  $7.30 \text{ \AA}$ , such a structural arrangement would give a spacing of approximately  $3.65 \text{ \AA}$  between the molecules, which is about what would be expected for normal van der Waals separations.

Following these indications of the arrangement of the molecules, all that remains to be known in order to establish a trial structure is the orientation of each of the component molecules round the axis through its centre parallel to the  $a$  axis. It was found to be possible to obtain a strong indication of this by a study of the weighted reciprocal lattice for the  $0kl$  zone of reflexions. There were strong reflexions in six, and only six, small regions lying near the position of the 'benzene circle' of radius  $0.83 \text{ \AA}^{-1}$  drawn in reciprocal space (cf. Taylor, 1952). These six strong regions correspond to the Fourier transform of the benzene ring component of the structure. The quinonoid carbon nucleus of the chloranil molecule must have a Fourier transform not greatly different from that of a regular benzene ring, giving again six strong regions near the 'benzene circle'. The fact that there are six strong regions in the weighted reciprocal lattice and not twelve must mean that the benzene ring and the quinonoid carbon ring lying on top of it in the projection along the  $a$  axis must have almost the same orientation. The actual orientation of both is also given by the positions of the six strong regions relative to the  $b^*$  and  $c^*$  reciprocal axes.

### Fourier syntheses

The most convenient Fourier projection for refining the atomic positions of the trial structure, based on all the information gained from the preliminary investigation, is evidently the  $0kl$  projection. The molecules all lie approximately perpendicular to the  $a$  axis and, although it cannot be expected that peaks from atoms of the two component molecules lying over one another will be resolved, it should be possible to obtain a fairly accurate view of the orientation of both molecules together. The  $0kl$  structure factors were calculated on the basis of the trial structure which assumed, in the first instance, that both component molecules were planar and parallel to each other. The calculated  $F_{0kl}$  showed reasonable agreement with the values derived from the observed intensities. From these calculated signs and the observed magnitudes of  $F_{0kl}$  the electron density projected along the  $a$  axis was calculated at intervals of  $1/60$  of  $b_0$  and  $c_0 \sin \beta$ . This projection was refined in the usual way and the final electron-density map is shown in Fig. 1(a). This map has been put on an absolute scale by

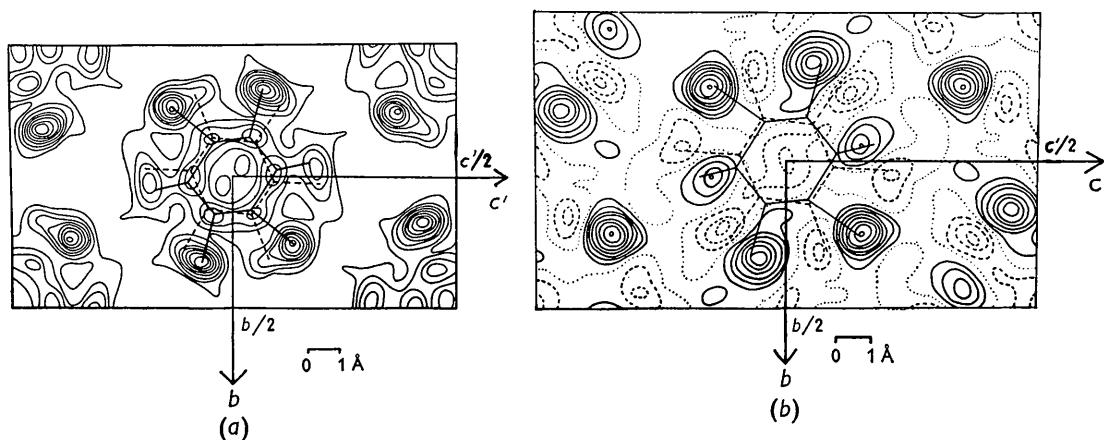


Fig. 1. (a) Fourier electron density projected along the  $a$  axis, showing a molecule of chloranil (full line) overlapping a molecule of hexamethylbenzene (broken line). Contours are drawn at 2, 4, 6, ...  $e \cdot \text{\AA}^{-2}$ .  $c' = c_0 \sin \beta$ .

(b) Fourier  $1kl$  generalized projection. Contours at 0 (dotted line), -2, -4, ... (broken lines), and +2, +4, ... units (full lines) on the absolute electron-density scale. The final positions of a chloranil (full line) and hexamethylbenzene molecule (broken line) are also indicated.  $c' = c_0 \sin \beta$ .

comparison of observed and calculated structure factor values. The disagreement factor,

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

for the refined projection has the value 0.27, excluding all terms for which  $F_o$  is zero.

It is clear from the map that the two overlapping molecules, chloranil and hexamethylbenzene, do not have exactly the same orientation, though both molecules must lie nearly in the plane of projection.

Attempts to obtain atomic  $x$  coordination from Fourier projections along the  $b$  and  $c$  axes gave rise to electron-density maps showing hardly any resolution of separate atoms. Because of this, and the inability to obtain accurate separate molecular orientations from the  $0kl$  Fourier projection, it was decided to obtain atomic coordinates by three-dimensional Fourier methods.

In an attempt to obtain some confirmation of the assumed  $x$ ,  $y$  and  $z$  atomic parameters before embarking on a full three-dimensional structure-factor calculation followed by Fourier section and line syntheses, a 'generalized projection' (Cochran & Dyer, 1952) was calculated on the basis of the  $1kl$  structure factors. In such a first-layer-line generalized projection, an atom with  $x = 0$  should give its full positive electron density, while a similar atom having  $x = \frac{1}{2}$  should appear on the map with equal negative 'electron density'. Thus, from the magnitude and sign of the electron density at the peak centre it should be possible to estimate the approximate  $x$  coordinate.

The generalized projection electron-density map calculated at  $1/60$  intervals of  $b_0$  and  $c_0 \sin \beta$ , is shown in Fig. 1(b). The methyl groups with  $x \approx \frac{1}{2}$  are now resolved from the chlorine and oxygen peaks with  $x \approx 0$ , the former showing as regions of high negative density. The slightly different orientations of the two overlapping molecules are therefore confirmed. At the

positions of the overlapping carbon rings the positive and negative regions are too nearly superimposed to be resolved, and they combine to give regions of almost zero density. Comparison of the maximum electron density values in the  $\text{CH}_3$ , Cl and O peaks indicated that atoms which were expected to have approximately the same  $x$  coordinate were giving peaks of different maximum densities. This was probably due to the rather small number of terms which could be included in the synthesis, and suggested that no great reliance could be placed upon  $x$  coordinates derived from peak densities.

The generalized projection did, however, show that the atomic coordinates which had been assumed in calculating the  $1kl$  structure factors could not be seriously in error. The calculation of general  $hkl$  structure factors was therefore completed. These were used first in the calculation of line syntheses parallel to the  $a$  axis through the positions of the atoms in the refined  $0kl$  Fourier projection. Separate lines were calculated for each of the  $\text{CH}_3$  groups and the Cl and O atoms but, for the overlapping carbon skeletons of the two molecules, lines were calculated for the mean positions of each pair of overlapping carbon atoms. The line electron densities were calculated at intervals of  $a_0/120$ .

The results of these calculations were not very encouraging. Although well resolved maxima were obtained, the  $x$  coordinates were not consistent with planar quinonoid and benzene rings in the respective molecules. It was expected that the chlorine atoms might be moved out of the mean plane of the chloranil molecule because of their large size, but the rest of the chloranil molecule was expected to be planar as was the whole of the hexamethylbenzene molecule (Brockway & Robertson, 1939). It was therefore decided that the  $y$  and  $z$  coordinates of the atoms should first be refined further by means of a Fourier

section before attempting the refinement of the  $x$  coordinates.

The most convenient Fourier section for the refinement of  $y$  and  $z$  parameters was found to be that of the  $(20\bar{1})$  plane. This plane is approximately perpendicular to the  $a$  axis and so should pass close to the atomic centres of the chloranil molecule in the region of  $x = 0$  and  $z = 0$ , and close to the atomic centres of the hexamethylbenzene molecule in the region of  $x = \frac{1}{2}$  and  $z = 1$ . The Fourier expression for this section proved to be rather inconvenient, so the structure was described in terms of a new cell, of which this plane is the  $(100)$  face. The relationship between the

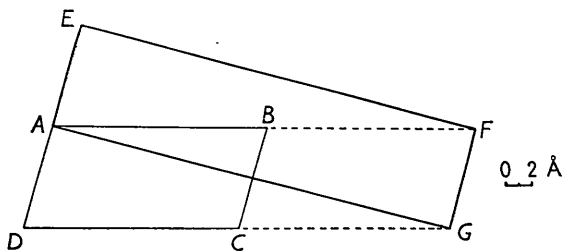


Fig. 2. Relationship between the original cell ( $ABCD$ ) and the new cell ( $AEFG$ ) to which the three-dimensional Fourier section is referred.

new cell and the original cell is shown in Fig. 2. The new cell has dimensions

$$a_0 = 7.30, b_0 = 8.64, c_0 = 29.36 \text{ \AA}, \beta = 92^\circ 11'$$

and it has the space group  $B2_1/d$ . The Fourier electron-

density section in the plane  $(100)$  for this new cell was evaluated at intervals of  $b/60$  and  $c/120$ . Resolution of practically all the atoms of the two component molecules was obtained in the resulting contour map, and new  $y$  and  $z$  parameters were determined.

At this stage it was also possible to obtain a plausible estimate of the  $x$  coordinates of all the atoms by correlation of the information from the Fourier section, the  $1kl$  generalized projection, and the  $h01$  and  $hk0$  projections. Still assuming that both molecules were planar, since there was no reliable evidence to the contrary, a consistent set of  $x$ ,  $y$  and  $z$  parameters was obtained and used in a second calculation of  $F_{hkl}$ . These structure factors enabled refinements of the Fourier line and section syntheses to be carried out. The electron-density function in the section at  $(100)$  for the new cell of space group  $B2_1/d$  is shown in Fig. 3(a). It will be seen that all atoms are resolved except the carbon atoms adjacent to the oxygen atoms in the chloranil molecule. The small extra peaks are nearly all in positions corresponding to atoms of adjacent molecules at some distance above or below the plane of the section.

The atomic positions derived from these syntheses showed clearly that both the chloranil and the hexamethylbenzene molecules must be non-planar. The coordinates derived from the Fourier line and section syntheses were corrected for non-orthogonality (Parry & Pitt, 1948), and the atomic parameters so obtained were used in a third calculation of  $F_{hkl}$ . The signs of all but two small structure factors were

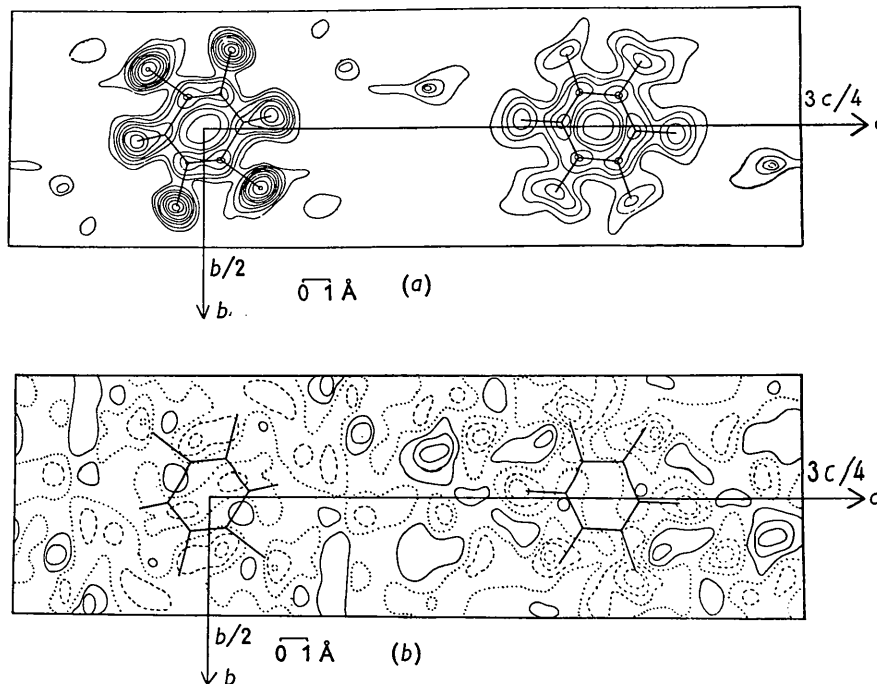


Fig. 3. (a) Fourier electron-density section at  $(100)$  in the new cell, showing a complete chloranil molecule at  $0, 0, 0$  and a complete hexamethylbenzene molecule at  $0, 0, \frac{1}{2}$ . Contours at  $\frac{1}{2}, 1, 1\frac{1}{2}, \dots e.\text{\AA}^{-3}$ .

(b)  $(F_o - F_c)$  synthesis for the section at  $(100)$  in the new cell. The positions of the molecules are indicated as in Fig. 3(a). Contours at  $0$  (dotted line),  $-\frac{1}{2}, -1, \dots$  (broken lines), and  $+\frac{1}{2}, +1, \dots e.\text{\AA}^{-3}$  (full lines).

the same as those obtained in the second  $F_{hkl}$  calculation, so no further direct refinement was attempted. Instead,  $(F_o - F_c)$  difference syntheses were calculated both for the lines and for the section. The difference map obtained for the section, calculated at intervals of  $1/60$ th of  $b_0$  and  $c_0$  of the new cell, is shown in Fig. 3(b). Besides showing thermal effects, which are discussed below, the map indicated that small movements should be made in the positions of some of the atoms. Similar indications, affecting the  $x$  parameters, were obtained from the line difference syntheses.

After making these small adjustments, the atomic coordinates shown in Table 1 were obtained. From

Table 1. *Final atomic parameters*

No.	Type	$x$	$y$	$z$
1	C	0.076	-0.147	0.040
2	C	0.075	-0.007	0.093
3	C	-0.016	0.132	0.043
4	Cl	-0.020	0.253	0.142
5	Cl	0.123	-0.333	0.069
6	O	0.083	-0.053	0.173
7	C	0.554	-0.127	0.052
8	C	0.528	0.019	0.094
9	C	0.478	0.145	0.047
10	CH <sub>3</sub>	0.428	0.307	0.083
11	CH <sub>3</sub>	0.615	-0.275	0.110
12	CH <sub>3</sub>	0.594	0.029	0.199

these the final structure factors  $F_{hkl}$  shown in Table 2 were calculated. In Table 2 the calculated values are those for the contribution of one asymmetric unit, i.e. they are all one quarter of the absolute value for the whole unit cell. The  $F_o$  values have been put on the same scale as the  $F_c$  values by making  $\Sigma|F_o| = \Sigma|F_c|$ . For the calculation of the final structure-factor values the temperature factor,  $B = 5.04 \text{ \AA}^2$ , was obtained by comparing  $F_o$  with uncorrected  $F_c$  values for regions of reciprocal space of successively increasing  $\sin \theta$  values. This temperature factor was applied to the Hartree scattering factors for carbon and chlorine. Previously, empirical unitary scattering factors had been employed.

The disagreement factor  $R$ , calculated for all the  $hkl$  reflections except those for which  $F_o$  is zero, had a value 0.21. From the errors in the structure factors, the standard deviations of atomic positions were calculated (Cruickshank, 1949) and gave the values for carbon  $\sigma_x = 0.0214$ ,  $\sigma_y = 0.0242 \text{ \AA}$ , and for chlorine  $\sigma_x = 0.0256$ ,  $\sigma_y = 0.0291 \text{ \AA}$ . Assuming that  $\sigma_x$ ,  $\sigma_y$  and  $\sigma_z$  all have approximately the same value, the standard deviation for any C-C distance not related by a centre of symmetry is about  $0.0323 \text{ \AA}$ . Similarly, the standard deviation for any C-Cl distance not related by a centre of symmetry is  $0.0357 \text{ \AA}$ . However, these figures almost certainly underestimate the errors in the structure since their calculation did not include terms for which  $F_o$  is zero. An attempt was made to estimate the effect of such terms on the Fourier syntheses by calculating a further electron-density section using  $F_c$  in place of  $F_o$ , as in the

estimation of termination-of-series error. The  $F_c$  synthesis showed surprisingly large differences from the  $F_o$  synthesis. If these differences are used to modify the atomic positions obtained from the  $F_o$  syntheses, as in the termination-of-series correction, interatomic distances are altered by an average of  $0.05 \text{ \AA}$  (maximum alteration  $0.11 \text{ \AA}$ ). These alterations almost certainly overestimate the errors in atomic positions since the  $F_c$  synthesis must include spurious effects due to the inadequacy of the model used in calculating structure factors (e.g. failure to use anisotropic temperature factors, and the inclusion of each CH<sub>3</sub> group in the structure-factor calculation as one atom of atomic number 9). Nevertheless it is clear that the interatomic distances derived in this structure determination cannot be relied upon to an accuracy of greater than about  $0.05 \text{ \AA}$ . That this limit is so large for a structure determination employing three-dimensional Fourier methods is not altogether surprising when the large thermal effect, and consequently the small total number of independent reflexions (185), is taken into consideration.

### Description of the structure

In the following description of the structure the positions of the molecules are those in the original unit cell of space group  $P2_1/c$ . The structure consists of alternate chloranil and hexamethylbenzene molecules stacked in columns parallel to the  $a$  axis of the crystal. The columns are at  $y = 0$ ,  $z = 0$  and  $y = \frac{1}{2}$ ,  $z = \frac{1}{2}$ , the molecules in one column being related to those in the other by the  $c$  glide plane at  $y = \frac{1}{2}$ . The shorter intermolecular distances within one such column are shown in Fig. 4(a). The dimensions of the separate molecules are given in Fig. 4(b) and (c). Owing to the non-resolution of the C<sub>2</sub> peak of the chloranil molecule in the Fourier section, its  $y$  and  $z$  coordinates are only estimated values. No significance can therefore be attached to the lengths of the bonds joining C<sub>2</sub> to its neighbouring atoms. The central carbon rings of both molecules are planar to within experimental error, but all the substituent groups, with the exception of methyl group No. 11, are moved out of these planes by the amounts shown in Fig. 4(b) and (c).

The molecules are not arranged perpendicular to the line parallel to the  $a$  axis joining their centres, as the preliminary work seemed to indicate. The plane of the carbon skeleton of the chloranil molecule at  $0, 0, 0$  is tilted downwards out of the (100) plane through an angle of  $19^\circ$ , so that the line which would have been coincident with the  $c$  axis now makes an angle of  $87^\circ$  with the  $a$  axis. The molecule is also twisted about this line through an angle of  $16\frac{1}{2}^\circ$  so that atoms with positive  $y$  coordinates have their  $x$  coordinates made more negative. Similarly, the plane of the benzene ring of the hexamethylbenzene molecule at  $\frac{1}{2}, 0, 0$  is tilted and twisted from a position parallel to (100) in the same directions but through angles of

Table 2. Comparison of observed and calculated structure factors

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
100	8.4	+12.2	0,1,12	2.5	+ 2.6	31 $\bar{2}$	8.0	+ 9.4
200	33.5	+38.0				31 $\bar{5}$	4.7	- 4.8
			021	1.8	- 1.7			
002	21.0	+22.3	022	10.0	- 5.0	412	6.9	- 7.0
004	19.2	-20.0	023	7.3	- 6.3			
006	8.6	- 7.7	024	12.0	+10.2	121	4.0	- 1.0
008	10.6	- 9.2	025	9.0	- 7.1	123	10.2	-11.1
0,0,10	3.1	- 4.2	028	6.3	- 4.0	124	8.0	+ 6.5
			029	2.8	+ 2.1	125	3.5	- 4.4
102	2.5	- 5.1	0,2,10	7.1	+ 6.8			
104	16.2	-16.3				12 $\bar{1}$	5.7	- 3.8
			031	11.6	+11.6	12 $\bar{2}$	3.3	+ 3.5
202	11.2	-11.1	032	10.6	+ 9.8	12 $\bar{3}$	4.5	+ 3.6
204	14.8	-14.5	033	11.2	-10.0	12 $\bar{5}$	13.2	+11.2
206	5.3	- 5.1	034	5.3	- 4.5	12 $\bar{6}$	7.5	- 5.0
			035	12.6	- 8.7			
302	6.9	-10.8	036	4.3	- 4.5	222	3.3	- 4.5
304	8.4	-12.1	037	7.6	- 7.6	224	9.2	+12.0
			038	5.1	+ 5.9	225	4.1	+ 4.0
10 $\bar{2}$	5.3	+ 6.6	039	3.1	+ 0.9			
10 $\bar{6}$	11.6	+ 8.9	0,3,11	5.1	+ 5.7	22 $\bar{1}$	3.9	- 5.9
1,0,10	10.2	-14.6				22 $\bar{2}$	4.3	+ 3.2
			041	4.7	+ 3.5	22 $\bar{4}$	3.7	- 3.4
20 $\bar{2}$	27.4	+28.3	042	13.4	-10.5	22 $\bar{5}$	6.1	+ 9.0
20 $\bar{4}$	3.3	- 4.3	043	4.5	+ 5.5	22 $\bar{6}$	6.7	- 3.1
20 $\bar{6}$	9.2	+ 8.4	044	14.3	-12.2	22 $\bar{7}$	6.5	+ 7.4
20 $\bar{8}$	7.5	- 5.3	046	4.1	+ 4.5			
2,0,10	8.4	- 9.8	048	8.6	+ 7.3	321	6.5	+ 5.5
			049	3.7	- 1.0	324	8.6	+10.0
30 $\bar{2}$	3.7	- 3.3	0,4,10	4.7	+ 3.3			
30 $\bar{6}$	12.4	+15.8				32 $\bar{2}$	5.5	+ 4.7
30 $\bar{8}$	8.9	+ 8.5	051	7.5	- 6.1	32 $\bar{3}$	7.9	- 7.8
			052	6.5	- 6.5	32 $\bar{6}$	8.8	-11.4
40 $\bar{4}$	3.7	- 2.4	054	3.3	- 2.1			
40 $\bar{6}$	7.3	+11.8	055	4.7	+ 3.3	421	3.7	+ 3.7
			057	3.5	+ 2.1			
50 $\bar{2}$	6.5	- 7.4	058	2.6	- 1.2			
						132	11.3	+13.0
020	14.3	-13.6	062	7.1	+ 6.2	133	5.5	- 5.7
040	2.9	+ 6.0	064	4.3	+ 3.7	134	7.7	- 8.8
060	3.9	- 0.5	066	6.3	- 6.9	135	5.3	- 5.3
			068	4.1	- 6.2			
110	5.7	+ 5.7				13 $\bar{1}$	6.5	+ 5.0
210	24.1	+25.7	071	3.7	+ 3.4	13 $\bar{2}$	13.5	-15.2
310	5.3	+ 5.2	072	4.7	+ 4.3	13 $\bar{3}$	9.2	+ 8.9
410	5.7	+ 9.4				13 $\bar{4}$	7.5	+ 6.1
			111	3.3	+ 0.1	13 $\bar{6}$	6.7	+ 8.0
120	10.0	- 9.5	114	8.8	+11.8	13 $\bar{8}$	4.5	- 4.1
220	3.5	- 6.2	115	5.7	+ 4.9	1,3,10	3.5	+ 0.2
320	3.5	- 6.1	116	7.5	+10.5			
			118	5.1	-10.1	231	7.8	- 7.8
130	3.7	+ 5.5				232	10.2	+ 9.0
330	1.4	+ 4.8	11 $\bar{1}$	5.1	- 3.9	233	10.8	-10.9
			11 $\bar{2}$	7.5	+ 5.9	235	7.1	- 4.5
240	1.4	+ 5.0	11 $\bar{3}$	7.2	- 3.5			
340	4.1	+ 7.4	11 $\bar{4}$	11.8	-10.6	23 $\bar{1}$	4.7	+ 7.8
540	1.4	+ 4.5	11 $\bar{5}$	5.5	- 3.7	23 $\bar{2}$	7.0	- 8.1
			11 $\bar{6}$	13.6	-15.5	23 $\bar{4}$	9.0	+ 7.4
250	2.5	- 3.3	11 $\bar{7}$	4.9	+ 5.5	23 $\bar{6}$	7.1	+ 7.7
360	3.1	- 6.6	211	5.3	+ 2.2	331	6.3	- 5.9
			212	3.9	- 0.5	333	3.7	- 7.4
011	16.6	+16.7	214	5.9	- 5.4			
012	2.6	- 2.0				33 $\bar{2}$	5.9	- 5.6
013	8.8	- 7.0	21 $\bar{1}$	22.0	+19.5	33 $\bar{5}$	6.5	+ 6.5
014	11.4	+11.3	21 $\bar{2}$	26.9	+24.6			
015	8.2	+ 7.3	21 $\bar{4}$	7.4	- 8.9	431	4.5	- 8.4
016	8.2	+ 7.3	21 $\bar{5}$	5.5	- 3.6			
017	5.1	- 0.5	21 $\bar{6}$	12.2	-13.8	141	10.2	+10.1
018	5.5	- 9.6				145	3.1	+ 2.6
0,1,10	4.5	- 4.4						
0,1,11	4.5	+ 0.5	312	8.1	- 8.0	14 $\bar{2}$	8.0	- 7.2

Table 2 (cont.)

$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$
143	6.3	- 6.2	241	7.3	+ 8.6	252	8.8	- 7.7
144	5.1	- 6.8	242	6.1	- 5.7	254	7.9	- 5.8
146	4.3	+ 1.9	244	12.9	- 13.0	162	6.7	+ 7.4
241	6.5	+ 7.8	247	4.9	- 5.6	172	6.7	+ 9.6
242	4.9	- 4.8	343	8.2	- 3.8			
243	5.3	- 1.9	152	6.3	- 9.6			

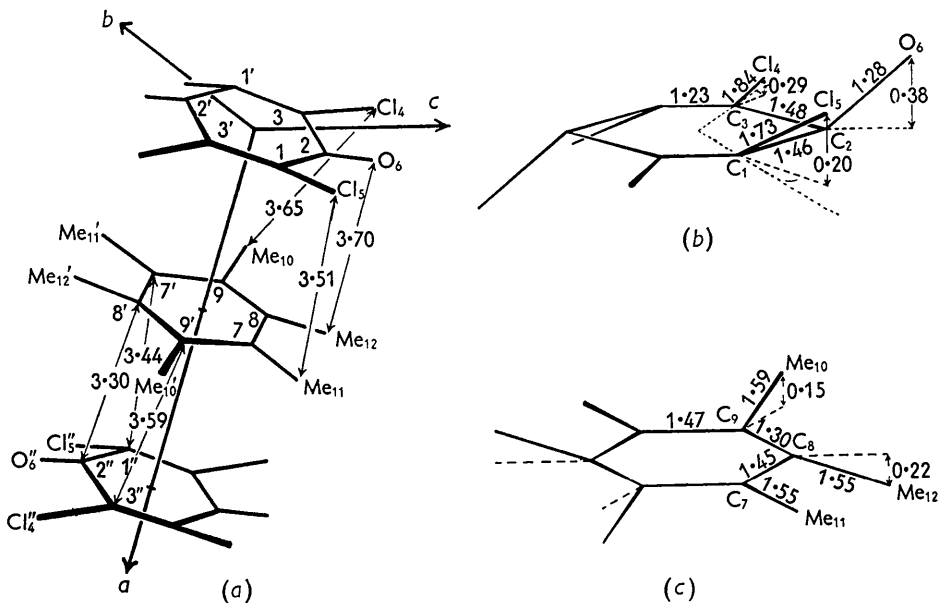


Fig. 4. (a) The arrangement of molecules in one column parallel to the  $a$  axis, showing short intermolecular distances. (b) Dimensions of the chloranil molecule. (c) Dimensions of the hexamethylbenzene molecule.

$10^\circ$  and  $14^\circ$  respectively. The result of these slightly different orientations of the two molecules is that one half of the hexamethylbenzene molecule approaches the chloranil molecule above it rather closely, and the other half approaches the chloranil molecule below. It is also clear that, in this structure, as in phenanthrene, the maximum overlap of  $\pi$ -orbitals between the two components is not being attained. The two molecules differ in orientation round the  $a$  axis by  $16^\circ$  and, when viewed in a direction approximately perpendicular to both molecular planes, the centre of the chloranil molecule is off-set from the centre of the hexamethylbenzene molecule by about  $0.9 \text{ \AA}$ .

### Discussion

In view of the rather large uncertainty in interatomic distances, mentioned above, it is clear that the actual numerical values can have no precise significance. Nevertheless, it appears that certain bonds which are chemically identical in the isolated molecules must differ in bond length. The bond  $C_8-C_9$  in hexamethylbenzene is evidently shorter than the bond  $C_9-C_7$ , but it is impossible at present to say whether this is a result of direct electronic interaction between the hexamethylbenzene and chloranil molecules or whether

it arises indirectly from the general distortion of the molecule.

There is no doubt that the chloranil molecule is considerably distorted from a planar configuration. As might be expected, adjacent chlorine atoms are moved respectively up and down from the plane of the carbon skeleton. This is due to the large size of the chlorine atoms, which also causes a small sideways distortion of the C-Cl bonds. The surprising feature about the molecule is that the oxygen atoms are moved out of the plane of the carbon skeleton in the same directions as their adjacent chlorine atoms. The amount of movement is such as to make the two oxygen atoms lie in the same plane as the four chlorine atoms. This presumably allows the molecule as a whole to pack more efficiently with its adjacent hexamethylbenzene molecules. In spite of this, the formation of the complex has the effect of distorting the hexamethylbenzene molecules which are normally planar (Brockway & Robertson, 1939). One pair of methyl groups remains in the plane of the benzene ring but a second pair is above the ring and the third pair below.

Although it is clear from the colour, the pleochroism and the general structural arrangement that some interaction must be taking place between the mole-

cules in the same column, any attempt to interpret the arrangement in detail must be only very conjectural. It seems possible that the movement of the chloranil oxygen atoms into the plane of the chlorine atoms allows some electronic interaction to take place between part of the quinonoid ring of chloranil and the benzene ring of the hexamethylbenzene molecule on the side remote from the chlorine and oxygen atoms, i.e. between  $C_1$  and  $C_7$ ,  $C_2$  and  $C_8$ ,  $C_3$  and  $C_9$  in Fig. 4(a). Between these atoms we have distances of 3.44, 3.30 and 3.59 Å respectively. The same atoms of the chloranil molecule have a much wider separation from the hexamethylbenzene molecule on the same side as the chlorine and oxygen atoms (i.e.  $C'_1$  to  $C'_7$ ,  $C'_2$  to  $C'_8$  and  $C'_3$  to  $C'_9$  are approximately 3.89, 4.00 and 3.71 Å respectively).

This arrangement is consistent with the interpretation of polarization bonding as involving a partial overlap of  $\pi$ -orbitals of the two components. Because of the large size of the chlorine atoms and the fact that they cannot be coplanar with the carbon skeleton of chloranil, it would presumably be impossible for a pair of hexamethylbenzene molecules, one on either side, both to approach close enough to the chloranil molecule for  $\pi$ -orbital overlap to occur over the whole of the area of the  $C_6$  rings. A compromise is therefore made, as described above, so that one half of the chloranil molecule interacts strongly with the molecule above it, while the other half interacts strongly with the molecule below, leading to a zigzag arrangement of molecules and polarization bonds.

#### Thermal motion of the molecules

There is information from various sources which indicates that the molecules undergo a considerable amount of thermal motion in the crystal. First, the temperature factor is high, having  $B = 5.04 \text{ \AA}^2$ . Secondly, there are diffuse thermal patches on overexposed X-ray photographs in the region of the reflexions from the planes (200) and (202), which are both approximately parallel to the molecular planes. Thirdly, many of the atomic peaks in the electron-density section map (Fig. 3(a)) are elongated in directions approximately perpendicular to the bonds joining these atoms to the rest of the molecule, suggesting vibration in these directions. Fourthly, the nature of the  $(F_o - F_c)$  difference map for the same section (Fig. 3(b)) in the region of the atomic positions indicates anisotropic thermal motion for many of the atoms. Similar indications are obtained from the line difference syntheses also.

Since the calculation of the  $F_c$  electron-density section map, it has become clear that part of what had been interpreted as anisotropic thermal motion on the  $F_o$  and the  $(F_o - F_c)$  section maps is, in fact, a spurious effect due to the omission of all terms for which  $F_o = 0$ . However, not all the elongation of peaks on the  $F_o$  section map is attributable to this spurious effect, so there must actually be some anisotropic

thermal motion. It appears that the methyl groups vibrate principally in the plane of the benzene ring, whereas the chlorine atoms vibrate principally in the direction perpendicular to the plane of the central carbon ring.

#### General conclusions

It is not yet possible to ascertain in detail what structural features are characteristic of polarization bonding in molecular compounds. In the structure of phenanthroquinone, described in Part I, a compromise has to be made between the packing requirements of the polarization bonding and the hydrogen bonding. In the chloranil-hexamethylbenzene complex it is found that the large size of the substituent groups in the chloranil molecule is preventing the molecules from packing in columns in a simple manner. An attempt must now be made to find a complex in which neither hydrogen-bonding nor steric hindrance can modify the effects of polarization bonding.

Nevertheless, it is clear that in the present structure there must be some attractive force between the two molecules because (a) they approach each other more closely in places than would be expected from the operation of van der Waals forces alone, (b) the force is sufficient to cause the hexamethylbenzene molecule to lose its normal planar configuration. It is not possible to prove that this force arises from the partial overlap of molecular  $\pi$ -orbitals, but the structural arrangement is not inconsistent with this view, and the modification of the shapes of the two molecules may be indicative of some direct electronic interaction. It is unfortunate that not as much significance as was hoped can be attached to the molecular dimensions, in view of the rather large possible error. This situation arises mainly because of the rather large thermal motion of the molecules, and it is probable that more accurate atomic positions could be derived by repeating the structure determination at a lower temperature. It is not considered, however, that such a repetition would be justified in this case in view of the structural distortions which arise mainly from the large size of the chlorine atoms of the chloranil molecules.

#### References

- BROCKWAY, L. O. & ROBERTSON, J. M. (1939). *J. Chem. Soc.* p. 1324.  
 COCHRAN, W. & DYER, H. B. (1952). *Acta Cryst.* **5**, 634.  
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.  
 CRUICKSHANK, D. W. J. & JEFFREY, G. A. (1954). Third International Congress, International Union of Crystallography, Paris.  
 HARDING, T. T. & WALLWORK, S. C. (1953). *Acta Cryst.* **6**, 791.  
 PARRY, G. S. & PITT, G. J. (1948). *Acta Cryst.* **2**, 145.  
 TAYLOR, C. A. (1952). *Nature, Lond.* **169**, 1087.  
 TSUCHIDA, R., KOBAYASHI, M. & NAKAMOTO, K. (1951). *Nature, Lond.* **167**, 726.  
 WALLWORK, S. C. & STANDLEY, K. J. (1954). *Acta Cryst.* **7**, 272.