# Molecular Complexes Exhibiting Polarization Bonding.
# VII. The Crystal Structure of the 2:1 Complexes formed by p-Chlorophenol and p-Bromophenol with p-Benzoquinone.

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The isomorphous structures of the 2:1 complexes formed by p-chlorophenol and p-bromophenol with p-benzoquinone were determined by Patterson and Fourier syntheses of the bromo-complex. The structure of the chloro-complex was then refined by anisotropic structure-factor least-squares methods. The crystals are monoclinic, space group $P2_1/c$, with two molecules of the quinone and four molecules of the phenol in each unit cell. The component molecules are stacked plane-to-plane discontinuously in groups of three, each group consisting of a quinone molecule between two molecules of the phenol and held together by charge-transfer forces. In addition, each quinone molecule is connected by hydrogen bonds to phenol molecules in two adjacent stacks.

## Introduction

In the previously described crystal structures of quin-hydrone, $C_6H_4O_2 . C_6H_4(OH)_2$ (Matsuda, Osaki & Nitta, 1958; Sakurai, 1965), and phenoquinone $C_6H_4O_2 . 2C_6H_5OH$ (Harding & Wallwork, 1953) it was shown that the molecules are held together by both charge-transfer forces and hydrogen bonds. In both structures, each C=O group of the quinone molecule is hydrogen-bonded to one hydroxyl group of a phenolic molecule, and it was inferred that the number of hydroxyl groups possessed by the phenolic molecule determined the ratio of the components in the complex. It is of interest, therefore, that p-chlorophenol (PCP) and p-bromophenol (PBP) both form 1:1 as well as 2:1 complexes with p-benzoquinone (Q). The present paper describes the determination of the structures of the 2:1 complexes (QdiPCP and QdiPBP). The corresponding 1:1 complexes (QmonoPCP and QmonoPBP) form the subject of the paper following this one.

## Experimental

Warm concentrated solutions of the components in light petroleum were combined in a 2:1 molecular ratio. When the dark solution so formed was cooled, reddish-brown crystals of the 2:1 complex separated. Normally the crystals were needle-like and exhibited pleochroism, the colour varying from deep red to orange-red, but the maximum absorption of light did not appear to be parallel to the needle axis as is often the case for charge-transfer complexes. It was subsequently found that the needle axis corresponds to the direction of hydrogen bonding and not to that of charge-transfer interaction.

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The crystals selected for X-ray photography were loaded into thin-walled glass capillary tubes to prevent volatilization. Oscillation and Weissenberg photographs were taken, with the crystals rotating about each of the three crystal axes. For the QdiPBP complex, zero and first-layer Weissenberg photographs were taken for the determination of the space group. The intensities of the zero-layer reflexions were measured by a photometer method (Wallwork & Standley, 1954). For the QdiPCP complex, higher layer Weissenberg photographs were also taken and the intensities of 0kl to 3kl, h0l to h4l reflexions were estimated visually by comparison with a series of timed exposures of a selected reflexion. Data from the various layers were placed on the same scale by comparison of reflexions in common, and a total of 812 independent intensities was thereby obtained. For each complex the measured intensities were converted into $F_o^2$ values in the usual way, without making any corrections for absorption or extinction.

*Crystal data*

(a) QdiPBP, $C_6H_4O_2.2p\text{-}BrC_6H_4OH$, $M=454\cdot1$
$a=11\cdot91\pm0\cdot03$, $b=6\cdot16\pm0\cdot02$, $c=12\cdot03\pm0\cdot03$ Å
$\beta=96\cdot0\pm0\cdot5°$,
$U=876$ Å³, $F(000)=448$, $D_m=1\cdot68$ g.cm⁻³, $Z=2$,
$D_c=1\cdot72$ g.cm⁻³.

Space group $P2_1/c$ uniquely determined by systematically absent X-ray reflexions; Cu $K\alpha$ ($\lambda=1\cdot542$ Å).

(b) QdiPCP, $C_6H_4O_2 . 2p\text{-}ClC_6H_4OH$, $M=365\cdot2$
$a=11\cdot70$, $b=6\cdot10$, $c=11\cdot83$, all $\pm0\cdot03$ Å
$\beta=97\cdot0\pm0\cdot5°$,
$U=838$ Å³, $F(000)=376$, $D_m=1\cdot44$ g.cm⁻³, $Z=2$,
$D_c=1\cdot44$ g.cm⁻³.

Space group $P2_1/c$ uniquely determined by systematically absent X-ray reflexions; Cu $K\alpha$ ($\lambda=1\cdot542$ Å).

## Structure determination and refinement

The three Patterson projections for the QdiPBP structure revealed the positions of the bromine atoms, and the $h0l$ projections also showed the approximate position of the rest of each phenol molecule. The corresponding Fourier electron density projections, phased on the bromine atom contributions to the structure factors, revealed the approximate positions of all atoms other than hydrogen. These positions were partly refined by successive structure factor and Fourier electron density calculations for the three projections, keeping a constant temperature factor $B = 3.5$ Å² for each atom. The agreement index,

$$R = \Sigma \, ||F_o| - |F_c||/\Sigma \, |F_o|,$$

corresponding to each of the three projections refined in this way, was 0·16 for $h0l$, 0·23 for $0kl$ and 0·25 for $hk0$ reflexions. The Fourier electron density map for the $h0l$ projection, where there is least overlap of atoms, is shown in Fig. 1, and the approximate atomic coordinates ($\sigma \simeq 0.005$) derived from the three projections are given in Table 1. The corresponding calculated structure factors are compared with the observed amplitudes in Table 2.

### Table 1. Fractional atomic coordinates for QdiPBP

|  | $x/a$ | $y/b$ | $z/c$ |
|---|---|---|---|
| C(1) | 0·140 | 0·374 | 0·614 |
| C(2) | 0·203 | 0·502 | 0·689 |
| C(3) | 0·267 | 0·671 | 0·640 |
| C(4) | 0·265 | 0·752 | 0·516 |
| C(5) | 0·198 | 0·623 | 0·448 |
| C(6) | 0·134 | 0·462 | 0·500 |
| C(7) | 0·449 | 0·304 | 0·562 |
| C(8) | 0·447 | 0·344 | 0·429 |
| C(9) | 0·500 | 0·498 | 0·379 |
| O(1) | 0·317 | 0·893 | 0·474 |
| O(2) | 0·407 | 0·138 | 0·612 |
| Br | 0·058 | 0·135 | 0·678 |

A brief study of the $h0l$ and $0kl$ projections for the QdiPCP complex confirmed that it was isomorphous with QdiPBP and provided approximate atomic parameters to use as the starting point of a structure-factor least-squares analysis of the three-dimensional $F_o$ data for QdiPCP. This analysis was commenced on the Oxford University MERCURY computer with the block-diagonal SFLS program written by Dr J.S. Rollett (Pepinsky, Robertson & Speakman, 1961) and continued on the Science Research Council ATLAS computer using a modification of the same program written by Dr R.D. Diamand.

The overall scale factor and atomic positions and anisotropic temperature factors were refined for all atoms other than hydrogen, so a total of 217 parameters were determined from 812 independent observations. The observations were initially all given unit weight, but in the later cycles, terms with $|F_o| > F^*$ were given weights $\sqrt{w} = F^*/F_o$ with $F^*$ first set equal to 2000, and finally 1000 (on a scale 50 times the abso-
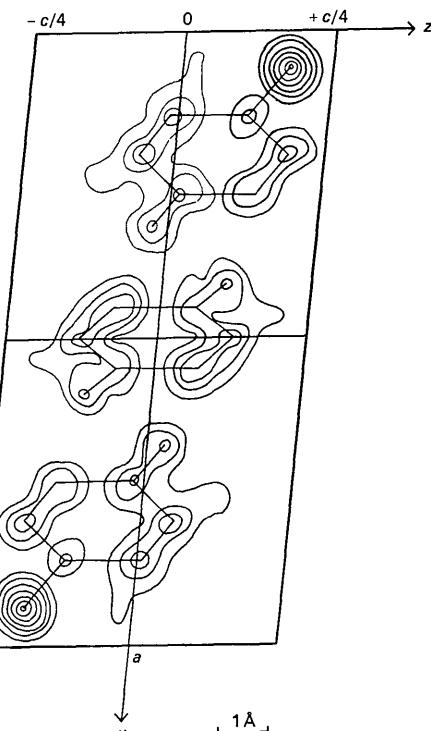


Fig. 1. QdiPBP, $h0l$ Fourier electron density projection. Contours at equal arbitrary intervals.
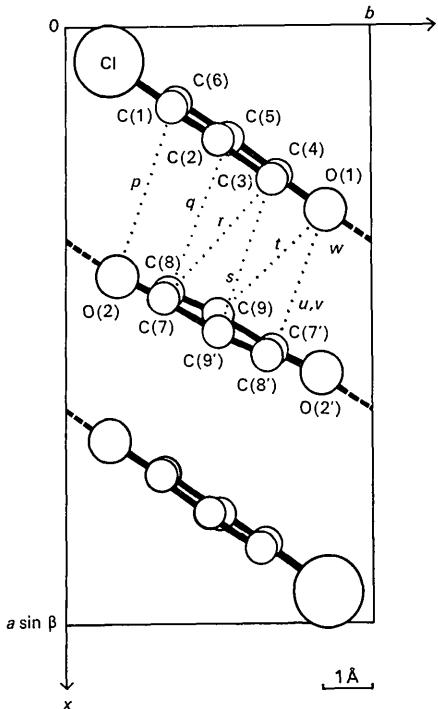


Fig. 2. The QdiPCP structure projected along the $c$ axis showing principal intermolecular contacts:

| | | | | |
|---|---|---|---|---|
| ($p$) | C(1)...O(2) | 3·49 Å, | ($q$) C(5)...C(8) | 3·25 Å |
| ($r$) | C(4)...C(7) | 3·29 | ($s$) C(3)...C(9') | 3·28 |
| ($t$) | O(1)...C(9) | 3·33 | ($u$) O(1)...C(7') | 3·11 |
| ($v$) | O(1)...C(8') | 3·29 | ($w$) O(1)...O(2) | 2·74 |
| | | | | (H bond). |

lute scale). Refinement was discontinued when $R$ was 0·131 and shifts in atomic positions were of the order of 0·1$\sigma$.

The resulting atomic positions and their standard deviations calculated by inversion of the normal equations matrix are shown in Table 3 and the thermal parameters $B_{ij}$ in the expression

$$f=f_0 \exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{23}kl+B_{13}hl+B_{12}hk)\right]$$

are shown in Table 4. A comparison of the observed and final calculated structure factors is given in Table 5.

## Results and discussion

The 2:1 $p$-bromophenol and the $p$-chlorophenol complex both have crystal structures based on the same principle as that of phenoquinone (Harding & Wallwork, 1953). Groups of three molecules, each consisting of a quinone molecule sandwiched between two

Table 2. *Observed structure amplitudes and final calculated structure factors for* QdiPBP ($\frac{1}{4}$ *of absolute scale*)

| hkℓ | \|Fo\| | Fc | hkℓ | \|Fo\| | Fc | hkℓ | \|Fo\| | Fc | hkℓ | \|Fo\| | Fc | hkℓ | \|Fo\| | Fc | hkℓ | \|Fo\| | Fc |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| h0ℓ projection | | | 704 | 14.1 | +12.1 | $\bar{1}$306 | 1.4 | -2.9 | 8012 | 1.7 | -2.8 | 027 | 12.2 | +13.9 | 1110 | 4.7 | +5.3 |
| 1500 | 2.4 | +4.8 | 604 | 18.5 | +18.8 | $\bar{1}$406 | 1.2 | +0.4 | 7012 | 2.0 | -2.3 | 025 | 9.6 | -13.7 | 810 | 5.7 | -2.6 |
| 1300 | 1.9 | -0.9 | 504 | 14.3 | +14.0 | 1208 | 2.6 | +2.6 | 6012 | 4.9 | -6.0 | 022 | 7.6 | -2.1 | 710 | 10.4 | -7.1 |
| 1200 | 3.8 | -3.2 | 304 | 15.4 | +16.2 | 1108 | 1.6 | +2.2 | 5012 | 3.6 | -4.7 | 021 | 20.0 | +19.9 | 610 | 7.9 | -10.8 |
| 1100 | 7.5 | -6.8 | 204 | 5.7 | +5.0 | 1008 | 4.3 | +6.5 | 4012 | 2.6 | -2.4 | 020 | 8.5 | -2.2 | 510 | 12.2 | -16.1 |
| 1000 | 11.4 | -8.4 | 104 | 18.5 | +18.7 | 808 | 10.3 | +9.7 | 3012 | 1.6 | -2.6 | 0313 | 4.4 | -2.7 | 410 | 3.2 | -5.2 |
| 900 | 12.2 | -12.7 | 004 | 10.8 | -9.5 | 708 | 7.3 | +7.7 | 2012 | 1.2 | -1.5 | 0311 | 6.3 | +6.9 | 310 | 23.1 | -40.5 |
| 800 | 16.4 | -15.4 | $\bar{1}$04 | 15.7 | -14.7 | 608 | 1.5 | +4.4 | 1012 | 1.8 | +2.0 | 039 | 3.6 | -2.4 | 210 | 14.9 | -12.4 |
| 700 | 1.2 | -8.3 | $\bar{2}$04 | 25.7 | -31.2 | 508 | 10.4 | -8.1 | 0012 | 1.5 | +2.7 | 038 | 5.0 | -4.5 | 110 | 4.2 | -1.0 |
| 600 | 13.5 | -12.0 | $\bar{3}$04 | 14.1 | -10.8 | 408 | 9.1 | -7.6 | $\bar{1}$012 | 7.8 | +8.0 | 036 | 3.4 | -4.0 | 1020 | 6.1 | +4.1 |
| 500 | 6.6 | -7.0 | $\bar{7}$04 | 21.0 | -21.1 | 308 | 8.7 | -6.5 | $\bar{2}$012 | 7.8 | +8.4 | 035 | 9.6 | +13.2 | 720 | 6.3 | -2.9 |
| 400 | 11.1 | +6.1 | $\bar{5}$05 | 20.0 | -20.0 | 208 | 15.2 | -14.1 | $\bar{3}$012 | 8.5 | +6.5 | 034 | 6.8 | +6.1 | 620 | 7.7 | +8.4 |
| 300 | 7.8 | -0.6 | $\bar{8}$04 | 13.8 | -11.8 | 108 | 12.5 | -11.7 | $\bar{7}$012 | 2.0 | +2.7 | 033 | 16.0 | -16.0 | 320 | 11.0 | -7.5 |
| 200 | 13.8 | +14.3 | $\bar{7}$04 | 12.7 | -10.0 | 008 | 11.0 | -9.8 | $\bar{5}$012 | 3.7 | +2.8 | 032 | 12.7 | -13.5 | 220 | 4.3 | -1.2 |
| 100 | 9.7 | +15.3 | $\bar{8}$04 | 3.4 | -0.2 | $\bar{1}$08 | 11.2 | -12.1 | $\bar{6}$012 | 2.5 | +2.5 | 031 | 7.3 | +7.7 | 120 | 3.1 | +1.4 |
| 1402 | 2.4 | +2.8 | $\bar{9}$04 | 10.3 | +10.0 | $\bar{2}$08 | 7.0 | -5.4 | $\bar{7}$012 | 2.7 | -2.7 | 048 | 4.3 | +7.2 | 020 | 6.6 | -2.2 |
| 1302 | 4.6 | +4.1 | $\bar{10}$04 | 7.4 | +4.8 | $\bar{3}$08 | 3.4 | -1.2 | $\bar{10}$012 | 2.1 | -4.7 | 046 | 8.0 | -6.5 | 1330 | 2.2 | +2.6 |
| 1202 | 5.3 | +5.9 | $\bar{11}$04 | 6.6 | +6.5 | $\bar{7}$08 | 2.7 | +2.3 | 2014 | 1.6 | -3.2 | 043 | 3.3 | +0.3 | 1230 | 4.2 | +2.8 |
| 1102 | 8.9 | +9.1 | $\bar{12}$04 | 3.7 | +4.8 | $\bar{5}$08 | 8.1 | +6.8 | 1014 | 2.8 | -3.6 | 043 | 3.4 | +5.9 | 1130 | 4.2 | +3.5 |
| 1002 | 4.8 | +7.5 | $\bar{13}$04 | 6.4 | +6.5 | $\bar{6}$08 | 10.8 | +9.0 | 0014 | 4.3 | -4.8 | C41 | 6.5 | -4.7 | 630 | 4.0 | -4.8 |
| 902 | 7.6 | +9.0 | $\bar{14}$04 | 2.8 | +3.3 | $\bar{7}$08 | 11.0 | +11.2 | $\bar{1}$014 | 4.0 | -4.8 | 040 | 15.5 | -18.6 | 530 | 7.8 | -9.0 |
| 702 | 11.8 | +11.0 | $\bar{15}$04 | 1.8 | +2.6 | $\bar{8}$08 | 13.8 | +14.7 | $\bar{2}$014 | 2.4 | -2.7 | C57 | 3.7 | -0.1 | 430 | 10.5 | -7.4 |
| 602 | 7.1 | -3.0 | 1106 | 3.4 | -1.7 | $\bar{9}$08 | 8.5 | +5.1 | $\bar{3}$014 | 1.9 | -3.5 | 054 | 6.5 | -7.1 | 330 | 10.2 | -6.2 |
| 502 | 17.7 | -17.5 | 1006 | 2.6 | -2.5 | $\bar{10}$08 | 3.3 | +2.8 | $\bar{6}$014 | 1.1 | +1.9 | 053 | 4.4 | -4.9 | 230 | 9.9 | -10.0 |
| 402 | 15.7 | -16.5 | 906 | 9.6 | -8.3 | $\bar{11}$08 | 3.4 | -2.2 | $\bar{7}$014 | 2.3 | +3.2 | 052 | 7.0 | +9.0 | 130 | 4.0 | -5.1 |
| 302 | 21.4 | -29.7 | 806 | 4.1 | -4.3 | $\bar{12}$08 | 2.0 | +3.2 | 0kℓ projection | | | 051 | 5.3 | +6.0 | 1240 | 1.9 | +1.4 |
| 202 | 22.0 | -31.0 | 706 | 11.9 | -9.3 | 10010 | 1.7 | -1.6 | 0014 | 4.8 | -4.8 | 061 | 4.6 | -6.5 | 1140 | 3.7 | +4.1 |
| 102 | 22.4 | -45.1 | 606 | 10.9 | -10.7 | 9010 | 2.5 | -3.1 | 0012 | 3.0 | +2.7 | 060 | 6.9 | +6.4 | 1040 | 6.5 | +5.1 |
| 002 | 8.3 | +5.6 | 506 | 13.5 | -14.1 | 7010 | 5.6 | +4.3 | 0010 | 4.3 | +4.0 | hk0 projection | | | 940 | 4.9 | +5.9 |
| $\bar{1}$02 | 6.6 | -4.6 | 406 | 3.5 | -3.9 | 6010 | 6.2 | +3.9 | 008 | 12.8 | -9.8 | 1500 | 2.2 | +4.8 | 840 | 6.3 | +10.4 |
| $\bar{3}$02 | 11.3 | +13.4 | 306 | 5.2 | +4.8 | 5010 | 5.3 | +4.3 | 006 | 19.0 | +19.5 | 1300 | 1.8 | -0.9 | 640 | 5.7 | +6.5 |
| $\bar{4}$02 | 13.9 | +11.4 | 206 | 3.4 | -4.1 | 4010 | 6.3 | +7.3 | 004 | 9.3 | -9.5 | 1200 | 3.6 | -3.2 | 540 | 4.7 | +1.0 |
| $\bar{5}$02 | 18.1 | +17.2 | 106 | 23.7 | +25.2 | 3010 | 6.7 | +7.0 | 002 | 5.9 | +5.6 | 1100 | 7.1 | -6.8 | 340 | 7.2 | -8.7 |
| $\bar{6}$02 | 18.6 | +19.5 | 006 | 19.5 | +19.5 | 2010 | 8.6 | +7.8 | 0112 | 6.5 | -4.4 | 1000 | 10.8 | -8.4 | 240 | 8.2 | -9.9 |
| $\bar{7}$02 | 18.4 | +16.1 | $\bar{1}$06 | 20.4 | +18.5 | 1010 | 6.4 | +5.7 | 0111 | 6.4 | -5.0 | 900 | 11.4 | -12.7 | 140 | 10.4 | -12.1 |
| $\bar{8}$02 | 15.4 | +14.1 | $\bar{2}$06 | 10.1 | +12.6 | 0010 | 3.5 | +4.0 | 0110 | 6.5 | +6.2 | 800 | 15.4 | -15.4 | 040 | 12.1 | -13.6 |
| $\bar{9}$02 | 12.1 | +9.2 | $\bar{3}$06 | 16.5 | +16.5 | $\bar{1}$010 | 1.3 | +0.5 | 019 | 6.8 | +6.2 | 700 | 7.7 | -8.3 | 750 | 4.0 | +2.9 |
| $\bar{10}$02 | 2.9 | +0.2 | $\bar{4}$06 | 12.9 | +10.7 | $\bar{2}$010 | 4.2 | -4.4 | 018 | 3.4 | -3.7 | 600 | 12.7 | -12.0 | 650 | 3.7 | +5.2 |
| $\bar{11}$02 | 3.0 | -2.4 | $\bar{5}$06 | 4.0 | +2.4 | $\bar{3}$010 | 7.7 | -7.3 | 016 | 5.3 | -6.5 | 500 | 6.2 | -7.0 | 550 | 5.5 | +9.2 |
| $\bar{12}$02 | 3.3 | -4.6 | $\bar{6}$06 | 2.3 | +0.5 | $\bar{7}$010 | 13.1 | -13.1 | 015 | 8.5 | -11.4 | 400 | 10.4 | +6.1 | 350 | 8.6 | +8.7 |
| $\bar{13}$02 | 3.2 | -4.2 | $\bar{7}$06 | 7.1 | -6.4 | $\bar{5}$010 | 8.4 | -7.6 | 014 | 10.3 | +11.4 | 300 | 7.4 | -0.6 | 250 | 5.5 | +3.9 |
| $\bar{14}$02 | 4.4 | -6.2 | $\bar{8}$06 | 11.3 | -9.2 | $\bar{6}$010 | 8.3 | -8.5 | 013 | 11.1 | +12.5 | 200 | 12.9 | +14.3 | 150 | 3.6 | +3.8 |
| 1404 | 3.8 | -4.7 | $\bar{9}$06 | 8.6 | -9.0 | $\bar{7}$010 | 8.5 | -6.8 | 012 | 16.1 | -24.2 | 100 | 9.1 | +15.3 | 060 | 5.8 | +6.4 |
| 1304 | 3.1 | -4.1 | $\bar{10}$06 | 10.7 | -9.2 | $\bar{10}$010 | 3.4 | +1.0 | 011 | 9.6 | -3.2 | 1410 | 3.3 | +2.0 | | | |
| 1204 | 3.3 | -5.2 | $\bar{11}$06 | 6.6 | -7.3 | $\bar{11}$010 | 2.5 | +0.0 | 0213 | 5.0 | +5.4 | 1310 | 7.2 | +5.2 | | | |
| 804 | 3.5 | +0.· | $\bar{12}$06 | 4.4 | -2.8 | $\bar{12}$010 | 2.2 | +4.0 | 029 | 5.5 | -4.8 | 1210 | 5.8 | +6.6 | | | |

Table 3. *Final fractional atomic coordinates and their standard deviations for* QdiPCP

| | $x/a$ | $\sigma(x/a)$ | $y/b$ | $\sigma(y/b)$ | $z/c$ | $\sigma(z/c)$ |
|---|---|---|---|---|---|---|
| C(1) | 0·1320 | 0·0008 | 0·3450 | 0·0020 | 0·6148 | 0·0010 |
| C(2) | 0·1913 | 0·0010 | 0·5011 | 0·0022 | 0·6875 | 0·0010 |
| C(3) | 0·2504 | 0·0010 | 0·6742 | 0·0024 | 0·6401 | 0·0010 |
| C(4) | 0·2450 | 0·0009 | 0·6870 | 0·0020 | 0·5238 | 0·0010 |
| C(5) | 0·1864 | 0·0009 | 0·5326 | 0·0020 | 0·4477 | 0·0009 |
| C(6) | 0·1293 | 0·0009 | 0·3582 | 0·0023 | 0·5000 | 0·0009 |
| C(7) | 0·4521 | 0·0009 | 0·3185 | 0·0019 | 0·5557 | 0·0010 |
| C(8) | 0·4411 | 0·0009 | 0·3317 | 0·0021 | 0·4316 | 0·0009 |
| C(9) | 0·4864 | 0·0009 | 0·4987 | 0·0019 | 0·3761 | 0·0010 |
| O(1) | 0·3009 | 0·0007 | 0·8489 | 0·0015 | 0·4693 | 0·0007 |
| O(2) | 0·4141 | 0·0007 | 0·1640 | 0·0014 | 0·6052 | 0·0007 |
| Cl | 0·0557 | 0·0003 | 0·1394 | 0·0006 | 0·6753 | 0·0003 |

phenol molecules, are stacked in columns along the $a$ axis, with the axis which passes through the centres of the three molecules of a group making an angle of about 13° with the $a$ axis.

The orientations of the molecules in each group are such that the C–O bonds of the two phenol molecules are arranged almost centrally above and below the quinone ring of the central molecule, approximately in the same direction as its O–O axis, and each C = O group of the quinone molecule is almost centrally above or below the aromatic ring of a phenol molecule. This feature is common to all structures of the quin-hydrone type and suggests a specific interaction between the C–O or C = O groups and the $\pi$ electron clouds of the adjacent six-membered rings (Prout & Wallwork, 1966). These interactions, together with the general charge-transfer interactions within each group of three molecules cause close inter-planar separations. The large halogen substituent at one end of each phenol molecule causes its plane to be about 6° from parallelism with the quinone molecule, but the average perpendicular separation in the region of overlap is about 3·20 Å. Interatomic distances less than 3·4 Å between adjacent molecules in the QdiPCP group are shown in Figs. 2 & 3. Between successive groups the interatomic distances are all greater than 3·4 Å, except for the hydrogen bonds of length 2·74 Å between the phenolic OH groups and quinone oxygen atoms in adjacent columns along the $b$ axis, and van der Waals contacts of 3·36 Å between O(2) and C(9) in glide-plane-related molecules.

The dimensions of the component molecules in Qdi-PCP are shown in Fig. 4. The standard deviations of bond lengths are all about 0·02 Å, apart from that of the C–Cl bond which is 0·012 Å, and the standard deviations of bond angles are all about 1·5°. The differences between the dimensions of chemically similar bonds are not significant, and the only bond angle which differs significantly from 120° is $\angle$ C(5)C(4)O(1) which has a value of 113°. This can be explained in terms of repulsion between the OH group and C(3)H causing the C(4)–O(1) bond to bend slightly in the direction of C(5). In the quinone molecule the mean length of the C–C bonds adjacent to the C = O group is $1·48_5$ Å. This and the C = C and C = O bond lengths of 1·35 and 1·22 Å respectively compare favourably with pre-

viously determined dimensions of $p$-benzoquinone (Trotter, 1960; Sakurai, 1965).

As in the structures of quinhydrone and phenoquinone, it is clear that charge-transfer forces, hydrogen bonding and van der Waals forces all contribute to the stability of these 2:1 phenol-quinone complexes. The charge-transfer forces hold the molecules together
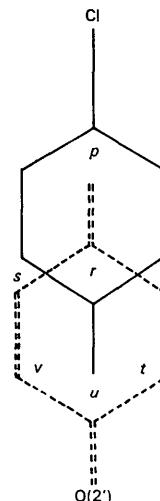


Fig. 3. Projection of both components of QdiPCP on to their mean plane showing the mode of overlap in relation to the close approaches designated as in Fig. 2.
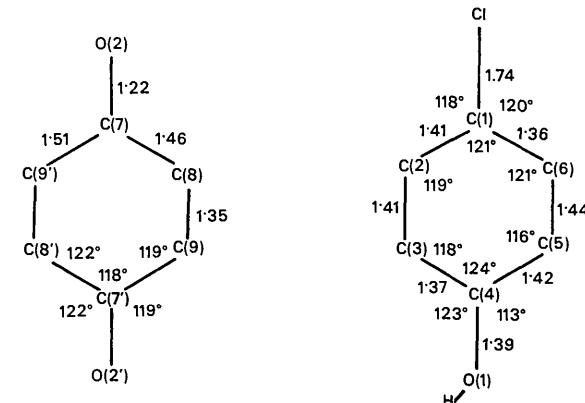


Fig. 4. Molecular dimensions of $p$-benzoquinone and $p$-chlorophenol in QdiPCP (distances in Å).

Table 4. *Final anisotropic thermal parameters for* QdiPCP

|        | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{23}$ | $B_{13}$ | $B_{12}$ |
|--------|----------|----------|----------|----------|----------|----------|
| C(1)   | 0·0041   | 0·0176   | 0·0090   | 0·0018   | 0·0047   | −0·0022  |
| C(2)   | 0·0073   | 0·0266   | 0·0064   | −0·0078  | 0·0037   | 0·0050   |
| C(3)   | 0·0077   | 0·0312   | 0·0076   | −0·0041  | 0·0050   | 0·0021   |
| C(4)   | 0·0061   | 0·0199   | 0·0070   | −0·0046  | −0·0020  | −0·0000  |
| C(5)   | 0·0062   | 0·0208   | 0·0069   | 0·0026   | 0·0021   | −0·0048  |
| C(6)   | 0·0057   | 0·0289   | 0·0064   | 0·0011   | 0·0003   | 0·0015   |
| C(7)   | 0·0059   | 0·0145   | 0·0089   | 0·0015   | 0·0016   | 0·0001   |
| C(8)   | 0·0069   | 0·0201   | 0·0054   | −0·0023  | 0·0004   | 0·0014   |
| C(9)   | 0·0073   | 0·0147   | 0·0066   | −0·0017  | 0·0049   | −0·0049  |
| O(1)   | 0·0094   | 0·0244   | 0·0085   | 0·0110   | 0·0062   | −0·0096  |
| O(2)   | 0·0098   | 0·0217   | 0·0071   | 0·0057   | 0·0058   | −0·0089  |
| Cl     | 0·0079   | 0·0321   | 0·0074   | 0·0119   | 0·0032   | −0·0067  |

Table 5. *Comparison of observed and final calculated structure factors on fifty times the absolute scale for* QdiPCP.

Asterisked line gives k, l. Other lines give values in the order h,Fo,F.

| h | Fo | F | h | Fo | F | h | Fo | F | h | Fo | F |
|---|---|---|---|---|---|---|---|---|---|---|---|
| • 0 | 0 | | | | | | | | | | |
| 1 | 405 | 423 | 2 | 606 | 781 | 3 | -2112 | -2482 | 4 | 1005 | 1127 |
| 5 | -498 | -345 | 6 | -1199 | -1299 | 7 | 353 | 323 | 6 | -1225 | -1142 |
| 9 | -667 | -526 | 10 | -870 | -600 | 11 | -743 | -600 | 12 | -507 | -384 |
| 13 | -313 | -249 | | | | | | | | | |
| • 0 | 2 | | | | | | | | | | |
| 0 | 2247 | 3448 | 1 | -3623 | -5721 | 2 | -2660 | -5569 | 3 | -2264 | -3500 |
| 4 | -904 | -811 | 5 | -1858 | -2110 | 6 | -1022 | -999 | 7 | 1731 | 1925 |
| 9 | 726 | 549 | 10 | -270 | -133 | 11 | 743 | 611 | 12 | 422 | 288 |
| 13 | 414 | 399 | 14 | 270 | 207 | -3 | 695 | 911 | -4 | 617 | 489 |
| -5 | 1106 | 1191 | -6 | 1191 | 1297 | -7 | 1326 | 1191 | -8 | 1199 | 1113 |
| -9 | 1326 | 1186 | -10 | 524 | 472 | -11 | -532 | -411 | -12 | -507 | -448 |
| -14 | -456 | -441 | -15 | -296 | -355 | | | | | | |
| • 0 | 4 | | | | | | | | | | |
| 0 | -1470 | -1445 | 1 | 2534 | 2902 | 2 | -513 | -191 | 3 | 921 | 936 |
| 4 | 1216 | 1170 | 5 | 496 | 529 | 6 | 1563 | 1562 | 7 | 1512 | 1550 |
| 8 | 355 | 350 | 9 | -380 | -217 | 10 | -372 | -279 | -1 | -1579 | -1549 |
| -2 | -3471 | -4272 | -3 | 220 | 210 | -4 | -1647 | -1575 | -5 | -1706 | -1521 |
| -6 | -743 | -755 | -7 | -1326 | -1288 | -8 | -726 | -573 | -9 | 1360 | 1145 |
| -10 | 794 | 749 | -11 | 693 | 552 | -13 | 552 | 546 | -14 | 296 | 208 |
| • 0 | 6 | | | | | | | | | | |
| 0 | 1757 | 1629 | 1 | 3201 | 3467 | 2 | -1022 | -889 | 3 | 633 | 549 |
| 4 | 389 | 273 | 5 | -1191 | -1256 | 6 | -752 | -723 | 7 | -1081 | -979 |
| 8 | 465 | 376 | 9 | -870 | -859 | 11 | -459 | -522 | -1 | 1731 | 1576 |
| -2 | 566 | 174 | -3 | 1233 | 1133 | -4 | 1047 | 826 | -6 | 557 | 490 |
| -7 | -600 | -501 | -8 | -929 | -964 | -9 | -524 | -417 | -10 | -988 | -987 |
| -11 | -574 | -517 | -12 | -329 | -337 | | | | | | |
| • 0 | 8 | | | | | | | | | | |
| 0 | -693 | -605 | 1 | 667 | -581 | 2 | -1284 | -1163 | 3 | -498 | -324 |
| 4 | -777 | -632 | 5 | -1368 | 1379 | 6 | -580 | -264 | 7 | 524 | 457 |
| 8 | 1470 | 1337 | 9 | -338 | -141 | 10 | 414 | 251 | -1 | -946 | -820 |
| -2 | 465 | 70 | -3 | -329 | -269 | -5 | 608 | 400 | -6 | 769 | 792 |
| -7 | 743 | 717 | -8 | 1402 | 1444 | -9 | 946 | 919 | -10 | 253 | 110 |
| -11 | -963 | -932 | -12 | 203 | 171 | | | | | | |
| • 0 | 10 | | | | | | | | | | |
| 1 | 456 | 288 | 2 | 650 | 523 | 3 | 380 | 370 | 7 | 465 | 631 |
| 8 | 684 | 296 | 9 | -338 | -186 | 10 | -169 | -160 | -2 | -270 | -253 |
| -3 | -642 | -615 | -4 | -1427 | -1629 | -5 | -380 | -361 | -6 | -532 | -576 |
| -7 | -828 | -753 | -8 | 253 | 172 | -9 | 338 | 269 | -10 | 709 | 629 |
| -11 | -617 | -506 | | | | | | | | | |
| • 0 | 12 | | | | | | | | | | |
| 0 | 355 | 90 | 5 | -716 | -249 | -1 | 929 | 941 | -2 | 769 | 703 |
| -3 | 921 | 824 | -4 | -498 | -475 | -9 | -355 | -353 | | | |
| • 0 | 14 | | | | | | | | | | |
| 0 | -380 | -347 | 1 | -253 | -316 | -1 | -270 | -223 | | | |
| • 1 | 0 | | | | | | | | | | |
| 2 | -1275 | -1286 | 3 | -5076 | 6622 | 4 | 1022 | 945 | 5 | -1005 | -947 |
| 7 | -743 | -767 | 8 | -481 | -419 | 10 | -405 | -325 | 12 | 329 | 175 |
| 13 | 667 | 727 | 14 | 513 | 346 | | | | | | |
| • 1 | 1 | | | | | | | | | | |
| 0 | 2280 | 2412 | 1 | -912 | -846 | 2 | -769 | -653 | 3 | -1343 | -1135 |
| 4 | 1334 | 1267 | 5 | 1563 | 1557 | 6 | 1064 | 1195 | 7 | 473 | 484 |
| 8 | 684 | 701 | 9 | 389 | 342 | 10 | -296 | -275 | 12 | -380 | -318 |
| 13 | -313 | -243 | 14 | -203 | -224 | -1 | 338 | 137 | -2 | -355 | -425 |
| -3 | -4324 | -5649 | -4 | -769 | -823 | -5 | -1005 | -971 | -6 | 296 | 176 |
| -7 | -532 | -503 | -8 | 532 | 468 | -9 | 541 | 496 | -11 | 574 | 469 |
| -12 | 389 | 283 | | | | | | | | | |
| • 1 | 2 | | | | | | | | | | |
| 0 | -2728 | -2937 | 1 | -236 | -66 | 2 | -1596 | -1599 | 3 | -1731 | -1861 |
| 4 | 2779 | 3325 | 5 | 769 | 817 | 6 | 1022 | 1163 | 7 | 236 | 220 |
| 8 | 1073 | 975 | 9 | 546 | 271 | 10 | -296 | -147 | 12 | 253 | 56 |
| 13 | 169 | 164 | -1 | -2179 | -2162 | -2 | -2660 | -2723 | -3 | 1140 | 1057 |
| -4 | -1132 | -1128 | -5 | -591 | -598 | -6 | -997 | -959 | -7 | -524 | -518 |
| -8 | 667 | 528 | -9 | 794 | 793 | -10 | 405 | 437 | -11 | 608 | 658 |
| -12 | 653 | 725 | | | | | | | | | |
| • 1 | 3 | | | | | | | | | | |
| 3 | 878 | 817 | 3 | 2213 | 2037 | 2 | 1216 | 1222 | 3 | 938 | 955 |
| 4 | -1650 | -1904 | 5 | 296 | 239 | 6 | -490 | -458 | 7 | 313 | 126 |
| 8 | -541 | -500 | 9 | -600 | -581 | 10 | -701 | -732 | -1 | 1503 | 1558 |
| -2 ! | 1917 | 1958 | -3 | 220 | 143 | -4 | 1022 | 936 | -5 | 389 | 294 |
| -6 | -1557 | -1479 | -7 | -743 | -765 | -8 | -541 | -520 | -9 | 279 | 192 |
| -10 | -574 | -502 | -11 | -279 | -311 | -12 | -380 | -319 | | | |
| • 1 | 4 | | | | | | | | | | |
| 3 | 625 | 461 | 1 | 2931 | 2802 | 2 | 574 | 636 | 3 | 1030 | 1056 |
| 4 | 414 | 511 | 5 | 448 | 468 | 6 | -490 | -428 | 7 | -642 | -687 |
| 9 | -642 | -579 | 10 | -397 | -394 | 11 | -270 | -345 | -1 | 921 | 828 |
| -2 | 2390 | 2058 | -3 | -380 | -259 | -5 | -414 | -245 | -6 | -735 | -636 |
| -7 | -1064 | -1120 | -8 | -912 | -904 | -10 | -735 | -844 | -11 | -279 | -278 |
| • 1 | 5 | | | | | | | | | | |
| 3 | -735 | -604 | 2 | -693 | -664 | 3 | -1064 | -1191 | 4 | -1503 | -1703 |
| 13 | 279 | 289 | 12 | 296 | 379 | -1 | -448 | -362 | -2 | -1284 | -1393 |
| -3 | 279 | 333 | -4 | 878 | 856 | -5 | 2154 | 2168 | -7 | 617 | 671 |
| -9 | 574 | 554 | -12 | -253 | -330 | 13 | -220 | -263 | | | |
| • 1 | 6 | | | | | | | | | | |
| 3 | -441 | -390 | 1 | 541 | 127 | 2 | -1427 | -1351 | 3 | -1157 | -1163 |
| 4 | -1651 | -1718 | 5 | 524 | 549 | 6 | -701 | -853 | -1 | -938 | -838 |
| -2 | 1745 | 1993 | -4 | 743 | 663 | -5 | 338 | 593 | -6 | 752 | 651 |
| -7 | 961 | 879 | -8 | 745 | 694 | -9 | 405 | 406 | -13 | -355 | -377 |
| • 1 | 7 | | | | | | | | | | |
| 2 | 929 | 942 | 5 | 439 | 584 | 4 | 642 | 665 | 5 | -279 | -240 |
| 6 | 397 | 419 | 8 | 667 | 735 | 12 | -186 | -38 | -1 | 329 | 139 |
| -2 | -1512 | -1128 | -3 | -963 | -863 | -4 | -921 | -854 | -5 | -439 | -634 |
| -6 | -650 | -654 | -8 | 701 | 731 | -12 | 236 | 280 | -13 | 253 | 314 |
| • 1 | 8 | | | | | | | | | | |
| 2 | -557 | -526 | 4 | 279 | 294 | 5 | 1326 | 1434 | 7 | 397 | 495 |
| 8 | 270 | 390 | 11 | -279 | -312 | -1 | -642 | -546 | -2 | -355 | -342 |

590    MOLECULAR COMPLEXES EXHIBITING POLARIZATION BONDING. VII

Table 5 *(cont.)*

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| -3 | -726 | -747 | -4 | •524 | •604 | •5 | •997 | -564 | •6 | •878 | •869 |
| -7 | -405 | -562 | -8 | 929 | 875 | •11 | 236 | 372 | •12 | 253 | 325 |
| • 1 | 9 | | | | | | | | | | |
| 0 | 541 | 514 | 1 | 389 | 396 | 2 | 897 | 551 | 4 | •405 | •353 |
| 5 | -997 | -608 | 10 | •236 | •244 | -1 | 695 | 950 | -2 | 389 | 365 |
| -3 | 481 | 367 | -4 | 617 | 542 | •5 | •490 | -577 | -6 | •296 | •213 |
| -7 | •574 | •571 | -8 | 566 | 510 | •11 | •650 | -701 | •12 | •253 | •289 |
| • 1 | 10 | | | | | | | | | | |
| 0 | 346 | 353 | 4 | 346 | 271 | 5 | 338 | 157 | 6 | •329 | •274 |
| 9 | -296 | -247 | -1 | 1140 | 1177 | •2 | 470 | 409 | -3 | 405 | 352 |
| -4 | 574 | 510 | -6 | •405 | •398 | •7 | •861 | •957 | -8 | 270 | 219 |
| -9 | -397 | -409 | | | | | | | | | |
| • 1 | 11 | | | | | | | | | | |
| 0 | -490 | •457 | 1 | •346 | •379 | 2 | •557 | •986 | 4 | •380 | •313 |
| -1 | 279 | 295 | •6 | 279 | 347 | -8 | 304 | 281 | •10 | 186 | 204 |
| • 1 | 12 | | | | | | | | | | |
| 0 | •473 | •516 | 1 | •422 | •544 | 2 | •363 | -411 | 3 | •253 | •277 |
| -4 | 380 | 455 | -5 | 255 | 306 | •6 | 304 | 391 | -8 | 304 | 353 |
| • 1 | 13 | | | | | | | | | | |
| 3 | 481 | 392 | -4 | •405 | •427 | •5 | •313 | •359 | •6 | •355 | •410 |
| -7 | 270 | 295 | | | | | | | | | |
| • 1 | 14 | | | | | | | | | | |
| -4 | -255 | -195 | -7 | 236 | 54 | | | | | | |
| • 2 | 0 | | | | | | | | | | |
| 1 | 380 | 484 | 2 | •439 | -285 | 3 | •1858 | •1514 | 4 | 186 | 144 |
| 5 | 405 | 295 | 6 | 1672 | 1488 | 7 | •980 | -989 | 8 | •279 | •216 |
| 9 | -422 | -419 | 10 | 709 | 799 | 11 | 355 | 356 | 13 | •220 | •208 |
| • 2 | 1 | | | | | | | | | | |
| 0 | 2078 | 2843 | 1 | 684 | 532 | 2 | 1605 | 1405 | 3 | 1132 | 971 |
| 4 | 887 | 932 | 5 | 1343 | 1320 | 6 | 912 | 926 | 7 | •1090 | •945 |
| 8 | -659 | -667 | 9 | •785 | -807 | 10 | •802 | -806 | 11 | •743 | •757 |
| 12 | -270 | -79 | 13 | 270 | 313 | -1 | 1326 | 1185 | -2 | 1098 | 894 |
| -5 | 1799 | 1614 | -4 | 676 | 589 | •5 | •1216 | •1161 | •6 | •2998 | •3468 |
| -7 | •253 | -292 | -8 | •1022 | •1018 | -9 | •557 | •502 | -13 | •372 | •458 |
| • 2 | 2 | | | | | | | | | | |
| 0 | •1456 | -1226 | 1 | 1858 | 1681 | 2 | 346 | 261 | 3 | 878 | 770 |
| 4 | -625 | -503 | 5 | 735 | 683 | 7 | •380 | -380 | -2 | 456 | 459 |
| -3 | -144 | -245 | -4 | 270 | 235 | •5 | •659 | •526 | •6 | 329 | 369 |
| -7 | -255 | -216 | -9 | •836 | -865 | •13 | •236 | -241 | | | |
| • 2 | 3 | | | | | | | | | | |
| 0 | 1005 | 845 | 1 | •269 | •156 | 2 | •861 | -773 | 3 | •1149 | •1059 |
| 4 | •1115 | -1094 | 5 | •1081 | •1047 | 6 | •828 | -786 | 7 | •279 | •290 |
| 8 | -414 | -442 | 10 | 296 | 196 | 12 | 422 | 515 | 13 | 270 | 355 |
| -1 | 431 | 211 | -3 | 2559 | 2436 | •4 | 2179 | 2095 | •5 | 2162 | 2056 |
| -6 | -557 | •504 | -7 | 1216 | 1159 | •8 | 279 | 274 | -9 | •203 | •139 |
| •11 | -296 | -271 | •13 | •513 | -441 | | | | | | |
| • 2 | 4 | | | | | | | | | | |
| 0 | -253 | -255 | 1 | 1030 | 1108 | 2 | 203 | 152 | 3 | •270 | •154 |
| 4 | •1050 | -1742 | 5 | 431 | 308 | 7 | 498 | 429 | 8 | •372 | •358 |
| -1 | -498 | -479 | -2 | -1014 | -933 | -3 | 769 | 673 | -4 | 828 | 728 |
| -5 | 1360 | 1087 | -6 | •709 | -710 | -7 | 270 | 313 | -9 | 296 | 317 |
| -13 | -220 | -171 | | | | | | | | | |
| • 2 | 5 | | | | | | | | | | |
| 0 | -811 | -751 | 1 | -1174 | •1113 | 2 | 144 | 73 | 3 | 405 | 407 |
| 4 | 253 | 401 | 5 | 532 | 558 | 6 | 802 | 855 | 7 | 938 | 971 |
| 8 | 203 | 297 | 9 | 600 | 608 | 11 | •236 | -246 | -1 | •802 | •868 |
| •2 | •2103 | -2223 | -3 | •650 | -557 | •4 | •1149 | •1077 | -5 | •1368 | •1261 |
| -6 | -270 | -257 | -7 | 397 | 406 | •8 | 684 | 666 | -10 | 701 | 710 |
| -11 | 346 | 373 | •13 | 253 | 405 | | | | | | |
| • 2 | 6 | | | | | | | | | | |
| 1 | -667 | -715 | 2 | 684 | 648 | 3 | •372 | -306 | 4 | •329 | •112 |
| 5 | 279 | 359 | 6 | 414 | 320 | 7 | 296 | 228 | 8 | •296 | •244 |
| -1 | -236 | -230 | -3 | •638 | -256 | -4 | •524 | -517 | -6 | •389 | •429 |
| -8 | -296 | -243 | | | | | | | | | |
| • 2 | 7 | | | | | | | | | | |
| 0 | 1275 | 1264 | 1 | 1639 | 1472 | 2 | •380 | -360 | 3 | 557 | 623 |
| 5 | 296 | 249 | 8 | •355 | -334 | 11 | •270 | -514 | 12 | •203 | •59 |
| -1 | 1588 | 1400 | -2 | 515 | 464 | -3 | 802 | 774 | -4 | 541 | 543 |
| -5 | -1765 | -1979 | -6 | •405 | -345 | -7 | •600 | -605 | -9 | •600 | •631 |
| -10 | -296 | -328 | •12 | •270 | -401 | | | | | | |
| • 2 | 8 | | | | | | | | | | |
| 1 | -279 | -300 | 2 | 1115 | 1078 | 5 | •504 | •251 | -1 | •650 | •573 |
| -2 | 1030 | 925 | -3 | 557 | 639 | •4 | 667 | 612 | -5 | •802 | •881 |
| • 2 | 9 | | | | | | | | | | |
| 1 | -422 | -531 | 2 | -1655 | •1913 | 3 | •203 | •213 | 4 | •372 | •454 |
| 6 | -296 | -291 | -2 | 414 | 400 | -3 | 515 | 462 | -4 | 1182 | 1323 |
| -5 | -372 | -289 | -6 | 431 | 595 | -8 | 507 | 508 | -9 | 338 | 377 |
| • 2 | 10 | | | | | | | | | | |
| -1 | -709 | -570 | -4 | 709 | 670 | •5 | •296 | -252 | | | |
| • 2 | 11 | | | | | | | | | | |
| 1 | •296 | -316 | 2 | •296 | -326 | 3 | 422 | 474 | 4 | 414 | 429 |
| 5 | 346 | 416 | 7 | 236 | 274 | -1 | •422 | -468 | -2 | •296 | •355 |
| -5 | -422 | -474 | -4 | •290 | -363 | •5 | •405 | •500 | •6 | •279 | •306 |
| -7 | -270 | -182 | | | | | | | | | |
| • 2 | 12 | | | | | | | | | | |
| 3 | 346 | 364 | -3 | •338 | •85 | •5 | •313 | -254 | | | |
| • 2 | 13 | | | | | | | | | | |
| 5 | 397 | 523 | -1 | 169 | 511 | -2 | 236 | 244 | -3 | 296 | 418 |
| • 2 | 14 | | | | | | | | | | |
| -3 | 236 | 313 | | | | | | | | | |
| • 3 | 0 | | | | | | | | | | |
| 1 | -144 | -221 | 2 | •785 | -811 | 3 | •819 | •740 | 4 | •785 | •759 |
| 5 | -515 | •456 | 6 | •236 | -238 | 11 | 329 | 300 | | | |
| • 3 | 1 | | | | | | | | | | |
| 0 | 304 | 417 | 1 | •186 | -166 | 2 | -169 | -101 | 3 | •389 | •351 |
| 4 | -448 | -297 | 5 | •676 | -588 | 6 | -597 | -570 | 7 | •1149 | •1220 |
| 8 | -1267 | -1301 | 9 | •456 | -399 | 10 | 795 | 824 | -1 | 144 | 89 |
| -2 | 617 | 521 | -3 | 2554 | 2481 | -4 | 633 | 604 | -5 | 1081 | 985 |
| -6 | 1715 | 1845 | -8 | •549 | -540 | -9 | •1461 | •1506 | -10 | 659 | 747 |
| -11 | -270 | -367 | •13 | •529 | -387 | | | | | | |
| • 3 | 2 | | | | | | | | | | |
| 0 | -938 | -967 | 1 | •490 | •525 | 2 | -186 | -131 | 3 | 186 | 114 |

## Table 5 (cont.)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 346 | 217 | 5 | 422 | 386 | 6 | 422 | 426 | 7 | 532 | 562 |
| 8 | 279 | 365 | -1 | -1123 | 1045 | -2 | -358 | -275 | -3 | 279 | 283 |
| -4 | -380 | -251 | -5 | 220 | -128 | -8 | 338 | 242 | -9 | 566 | 582 |
| -10 | 557 | 526 | | | | | | | | | |
| • 3 | 3 | | | | | | | | | | |
| 0 | -1799 | -1916 | 1 | 676 | 513 | 2 | -667 | -606 | 3 | 338 | 293 |
| 5 | -236 | -229 | 6 | 253 | 322 | 7 | 777 | 923 | 9 | 490 | 608 |
| 11 | 346 | 390 | -1 | -1867 | -1728 | -2 | -3176 | 2975 | -3 | 1613 | 1305 |
| -4 | -785 | -693 | -5 | 384 | -354 | -6 | 735 | 720 | -7 | 253 | 209 |
| -8 | 785 | 736 | -10 | 743 | 734 | | | | | | |
| • 3 | 4 | | | | | | | | | | |
| 0 | 220 | 240 | 1 | 532 | 513 | 2 | 667 | 731 | 3 | 481 | 498 |
| 4 | 220 | 301 | -1 | 186 | 192 | -2 | 667 | 657 | -3 | 186 | 125 |
| -4 | -490 | -439 | -5 | 659 | -632 | -6 | -397 | -329 | -7 | 633 | 578 |
| -8 | -439 | -377 | | | | | | | | | |
| • 3 | 5 | | | | | | | | | | |
| 0 | 693 | 641 | 1 | 1571 | 1905 | 2 | 220 | 324 | 3 | 481 | 502 |
| 4 | 507 | 534 | 6 | 338 | 532 | 7 | 279 | 304 | 8 | 397 | 561 |
| 9 | -380 | -409 | 10 | -346 | -375 | -1 | 490 | 423 | -2 | 253 | 261 |
| -3 | 279 | 309 | -4 | -481 | -596 | -5 | -769 | -655 | -6 | 372 | 417 |
| -7 | -1030 | -1027 | -8 | -1056 | -1059 | -12 | -304 | -386 | | | |
| • 3 | 6 | | | | | | | | | | |
| 0 | -169 | -166 | 1 | -236 | -299 | 2 | -253 | -251 | 3 | 313 | 370 |
| 4 | -329 | -335 | 5 | 279 | -399 | -1 | 220 | 208 | -2 | 954 | 860 |
| -3 | 574 | 586 | -4 | 405 | 329 | -5 | 329 | 263 | -6 | 279 | 274 |
| -12 | -279 | -272 | | | | | | | | | |
| • 3 | 7 | | | | | | | | | | |
| 0 | -253 | -188 | 1 | -608 | -626 | 2 | -270 | -227 | 3 | 473 | 523 |
| 4 | -397 | -359 | 5 | -279 | -279 | 6 | -279 | -373 | 7 | 279 | 301 |
| 8 | -372 | -373 | -1 | -1005 | -1045 | -2 | 1954 | 2271 | -3 | 785 | 775 |
| -4 | 929 | 834 | -6 | 650 | 762 | -7 | 448 | 483 | -8 | 481 | 421 |
| -9 | 369 | 536 | -12 | -236 | -293 | | | | | | |
| • 3 | 8 | | | | | | | | | | |
| 0 | -473 | -485 | 1 | -583 | -469 | 2 | -279 | -162 | 4 | 279 | 203 |
| 5 | 279 | 224 | 6 | 336 | 272 | 7 | 313 | 212 | -1 | 329 | 243 |
| -3 | -338 | -385 | -4 | -481 | -556 | | | | | | |
| • 3 | 9 | | | | | | | | | | |
| 0 | -346 | -364 | 1 | -490 | -391 | 2 | 566 | 391 | 4 | 279 | 242 |
| 5 | 541 | 653 | 7 | 220 | 287 | -1 | -2052 | 2256 | -2 | 397 | 267 |
| -3 | -279 | -209 | -5 | -490 | -515 | -6 | -279 | -280 | -9 | 296 | 357 |
| -10 | 203 | 265 | -11 | 279 | 312 | | | | | | |
| • 3 | 10 | | | | | | | | | | |
| 2 | 279 | 285 | -1 | 279 | 340 | -2 | 346 | 409 | -4 | 439 | 478 |
| -6 | -270 | -295 | -8 | -279 | -267 | | | | | | |
| • 3 | 11 | | | | | | | | | | |
| 0 | 465 | 431 | 1 | 414 | 428 | 2 | 313 | 276 | 4 | 279 | 304 |
| 5 | 203 | 318 | 6 | -380 | -397 | -3 | 270 | 222 | -8 | 186 | 324 |
| -9 | -220 | -443 | -10 | 220 | -433 | | | | | | |
| • 3 | 12 | | | | | | | | | | |
| 2 | -270 | -121 | | | | | | | | | |
| • 3 | 13 | | | | | | | | | | |
| 0 | -448 | -498 | -1 | 279 | 234 | -3 | 380 | 364 | -4 | 186 | -44 |
| • 4 | 0 | | | | | | | | | | |
| 0 | -1520 | -1630 | 1 | -819 | -900 | 2 | -650 | -610 | 3 | 929 | 935 |
| • 4 | 1 | | | | | | | | | | |
| 0 | -1030 | -859 | -1 | -338 | -237 | -3 | -887 | -890 | | | |
| • 4 | 2 | | | | | | | | | | |
| 0 | -481 | -325 | 1 | 1064 | 1066 | 2 | 1059 | 1081 | 3 | 1385 | 1251 |
| -3 | -853 | -792 | | | | | | | | | |
| • 4 | 3 | | | | | | | | | | |
| 0 | -684 | -542 | 1 | 861 | 955 | 2 | 439 | 516 | 3 | 524 | 373 |
| -2 | 802 | 703 | -3 | -709 | -667 | | | | | | |
| • 4 | 4 | | | | | | | | | | |
| 1 | 456 | 451 | 3 | -431 | -405 | -1 | 515 | 503 | -2 | 304 | 316 |
| -3 | 645 | 785 | | | | | | | | | |
| • 4 | 5 | | | | | | | | | | |
| -2 | 1073 | 982 | | | | | | | | | |
| • 4 | 6 | | | | | | | | | | |
| 0 | -752 | -633 | 1 | -997 | 1180 | -1 | -549 | -509 | -2 | 481 | 466 |
| -3 | -549 | -501 | | | | | | | | | |
| • 4 | 7 | | | | | | | | | | |
| 0 | -465 | -477 | 1 | -617 | -833 | 2 | 583 | 398 | -1 | 397 | 319 |
| -3 | -456 | -366 | | | | | | | | | |
| • 4 | 8 | | | | | | | | | | |
| 2 | 887 | 1054 | 3 | 541 | 507 | -2 | 473 | 384 | | | |
| • 4 | 9 | | | | | | | | | | |
| 2 | 853 | 888 | -1 | 473 | 453 | | | | | | |
| • 4 | 11 | | | | | | | | | | |
| 0 | -253 | -207 | | | | | | | | | |
| • 4 | 12 | | | | | | | | | | |
| 0 | -355 | -431 | | | | | | | | | |
| • 5 | 0 | | | | | | | | | | |
| 1 | 473 | 462 | 2 | 667 | 660 | 3 | 1647 | 1613 | | | |
| • 5 | 1 | | | | | | | | | | |
| 0 | 954 | 1000 | 1 | 481 | -508 | 2 | -473 | -289 | 3 | 456 | 409 |
| -2 | 473 | 412 | -3 | -633 | -608 | | | | | | |
| • 5 | 2 | | | | | | | | | | |
| 0 | 904 | 830 | 1 | 389 | 298 | 2 | 667 | 512 | 3 | 557 | 428 |
| -1 | 481 | 397 | -2 | 667 | 585 | | | | | | |
| • 5 | 3 | | | | | | | | | | |
| 0 | -313 | -259 | 1 | -389 | -299 | -1 | -389 | -308 | | | |
| • 5 | 4 | | | | | | | | | | |
| 0 | -465 | -441 | 1 | -785 | -990 | 3 | -456 | -305 | -1 | 481 | 406 |
| -2 | -667 | -632 | | | | | | | | | |
| • 5 | 5 | | | | | | | | | | |
| -2 | -684 | -620 | | | | | | | | | |
| • 5 | 6 | | | | | | | | | | |
| 2 | 574 | 648 | 3 | 625 | 670 | -1 | 389 | 209 | -2 | 667 | 587 |
| -3 | 456 | 265 | | | | | | | | | |
| • 5 | 7 | | | | | | | | | | |
| -1 | 473 | 459 | -3 | 439 | 436 | | | | | | |
| • 5 | 9 | | | | | | | | | | |

Table 5 (*cont.*)

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| U | -3o9 | -320 | | | | | | | | | |
| 5 | 10 | | | | | | | | | | |
| -1 | -515 | -541 | | | | | | | | | |
| o | 0 | | | | | | | | | | |
| 0 | 1537 | 1o21 | 1 | -589 | -301 | 3 | -439 | -401 | | | |
| o | 1 | | | | | | | | | | |
| 0 | -513 | -547 | 3 | -524 | -515 | -1 | -549 | -657 | -2 | 473 | 459 |
| 6 | 2 | | | | | | | | | | |
| 0 | 397 | 373 | 1 | -667 | -781 | 2 | -465 | -297 | 3 | 431 | 316 |
| o | 3 | | | | | | | | | | |
| 1 | 465 | 477 | -1 | -580 | -272 | -2 | -465 | -399 | | | |
| o | 4 | | | | | | | | | | |
| 1 | 456 | 488 | -2 | -448 | -469 | -3 | 414 | 311 | | | |
| o | 5 | | | | | | | | | | |
| 1 | 355 | 361 | -1 | 355 | 208 | -2 | 439 | 445 | | | |
| o | 6 | | | | | | | | | | |
| 1 | 473 | 495 | -1 | 346 | 279 | | | | | | |
| o | 7 | | | | | | | | | | |
| 0 | -355 | -421 | -1 | -589 | -424 | | | | | | |
| 7 | c | | | | | | | | | | |
| 3 | -461 | -490 | | | | | | | | | |
| 7 | 1 | | | | | | | | | | |
| -2 | 448 | 105 | -3 | -583 | -696 | | | | | | |

in groups of three along the stacking direction. Hydrogen bonds OH $\cdots$ O$=$C link the molecules sideways in different groups of three. By means of these two types of interaction, bands of molecules are formed which are one unit cell wide (approximately in the $x$ direction) and which extend indefinitely in the $y$ direction. These bands are held together only by van der Waals forces. The structural relationship between the 1:1 and 2:1 complexes will be described in the paper on the 1:1 complexes.

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