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# The Crystal and Molecular Structures of Overcrowded Halogenated Compounds. Part III: 1:4:5:8 Tetrachloronaphthalene

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The crystal structure of 1:4:5:8-tetrachloronaphthalene has been determined by a three-dimensional least-squares analysis, using anisotropic temperature factors. The cell dimensions are

$$a = 9{\cdot}359,\ b = 15{\cdot}100,\ c = 7{\cdot}070\ \text{Å}\ .$$

The space group is *Pccn* and there are four molecules of $C_{10}H_4Cl_4$ in the cell; the molecular symmetry is $C_2$–2. The overcrowding of the chlorine atoms is relieved by both in-plane splaying apart of the C–Cl bonds by 4° each and out-of-plane displacements of the Cl atoms of about 0·2 Å; $d(\text{Cl} \cdots \text{Cl}) = 2{\cdot}99$ Å. The naphthalene ring system is not planar, the $\alpha$-carbon atoms being displaced by 0·05 Å out of the mean plane and the $\beta$-carbons by 0·02 Å; the C–C bond lengths are, however, close to those of naphthalene. The thermal vibrations have been analysed in some detail. The molecules are stacked along [001], with their mean planes parallel to (001); the stacks are packed in an hexagonal arrangement.

## 1. Introduction

The overcrowding in 1:4:5:8-tetrachloronaphthalene results from the presence of bulky substituents in the 1:8 and 4:5 positions of the naphthalene ring system; it belongs to Group IV of the classification due to Harnik, Herbstein, Schmidt & Hirshfeld (1954). The overcrowding is severe as the $\alpha$-substituents are separated by only 2·4 Å in the hypothetical regular and planar model, whereas the closest approach found between chlorine atoms in different molecules is approximately 3·6 Å. As the overcrowded chlorine atoms are bonded to non-adjacent carbon atoms, it is expected that their interaction should approximate to that between chlorine atoms in different molecules. Consequently, expressions for the van der Waals potential derived from inter-molecular interactions should be more applicable to the calculation of steric effects in this type of compound than to those in which the overcrowding results from the proximity of substituents bonded to adjacent carbon atoms in benzene rings.

A preliminary report of this work has been read (Gafner & Herbstein, 1960*a*) and the approximate crystallographic data reported (Gafner & Herbstein, 1960*b*). An independent analysis of this crystal structure has been carried out by Kitaygorodsky and coworkers (Kitaygorodsky, Struchkov, Avoyan & Davydova, 1961; Davydova & Struchkov, 1961) and their results are compared with ours below (Section 6).

## 2. Experimental

(*a*) *Crystallographic data*

Material was supplied by Dr E. Clar, Chemistry Department, University of Glasgow (see Clar & Marschalk, 1950). Crystals of satisfactory quality were grown by slow cooling of toluene–acetic acid solutions. The needle-shaped crystals were elongated along [001], showed straight extinction and were bounded by {110} faces. Accurate cell dimensions (at 20 °C.) were obtained as follows:

*a*, *b* from back-reflection Weissenberg photographs (Herbstein, 1957) using Fe $K\alpha$ radiation.

*c* from normal and inclined-beam rotation photographs, using Cu $K\alpha$ radiation. The film was mounted as suggested by Mathieson (1957).

Following Parrish (1960), the wavelengths given by Lonsdale (1950) have been increased by a factor of 1·000017, and the values used were

$$\text{Cu } K\alpha\ 1{\cdot}5418,\quad \text{Fe } K\alpha_1\ 1{\cdot}93600,\quad \text{Fe } K\alpha_2\ 1{\cdot}93994\ \text{Å}.$$

The density was measured by flotation in potassium mercuric iodide solution. The space group was determined unequivocally from the systematic absences.

The crystallographic data are summarized below. The limits quoted for the cell dimensions are 95% confidence limits taking random errors into account; systematic errors were eliminated by extrapolation to $\theta$ (or $\nu$) = 90°.

$a = 9{\cdot}359 \pm 0{\cdot}001,\ b = 15{\cdot}100 \pm 0{\cdot}001\ ,$
$c = 7{\cdot}070 \pm 0{\cdot}009$ Å .

Space group *Pccn*

$\varrho$(meas.) = 1·76, $\varrho$(X-ray) = 1·78 g.cm.$^{-3}$.

4 molecules of $C_{10}H_4Cl_4$ per unit cell; molecular symmetry either $C_i$–$\bar{1}$ or $C_2$–2.

Linear absorption coefficient for Cu $K\alpha$ = 98 cm.$^{-1}$.

(*b*) *Intensity measurements*

The intensities of 797 *hkl* ($0 \leq l \leq 5$) reflexions were recorded with Cu $K\alpha$ radiation using an equi-inclination Weissenberg camera and the standard multiple-film technique. 120 of these reflections had $I_0 = 0$. The ratio of the largest to the smallest measured intensity was 460. Seven near-in reflections (see Table 2) could not be measured because they were obscured by the beam stop. Absorption corrections were applied as for cylindrical crystals, a procedure which is justified for small crystals of square cross-section. The effective absorption radii for higher layer-line reflexions were calculated according to the method of Buerger & Niizeki (1958). The Lorentz polarization, spot-shape (Phillips, 1954, 1956) and absorption corrections were applied simultaneously to each reflexion using a plot of the reciprocal lattice. The individual layer-lines were put on an approximately absolute

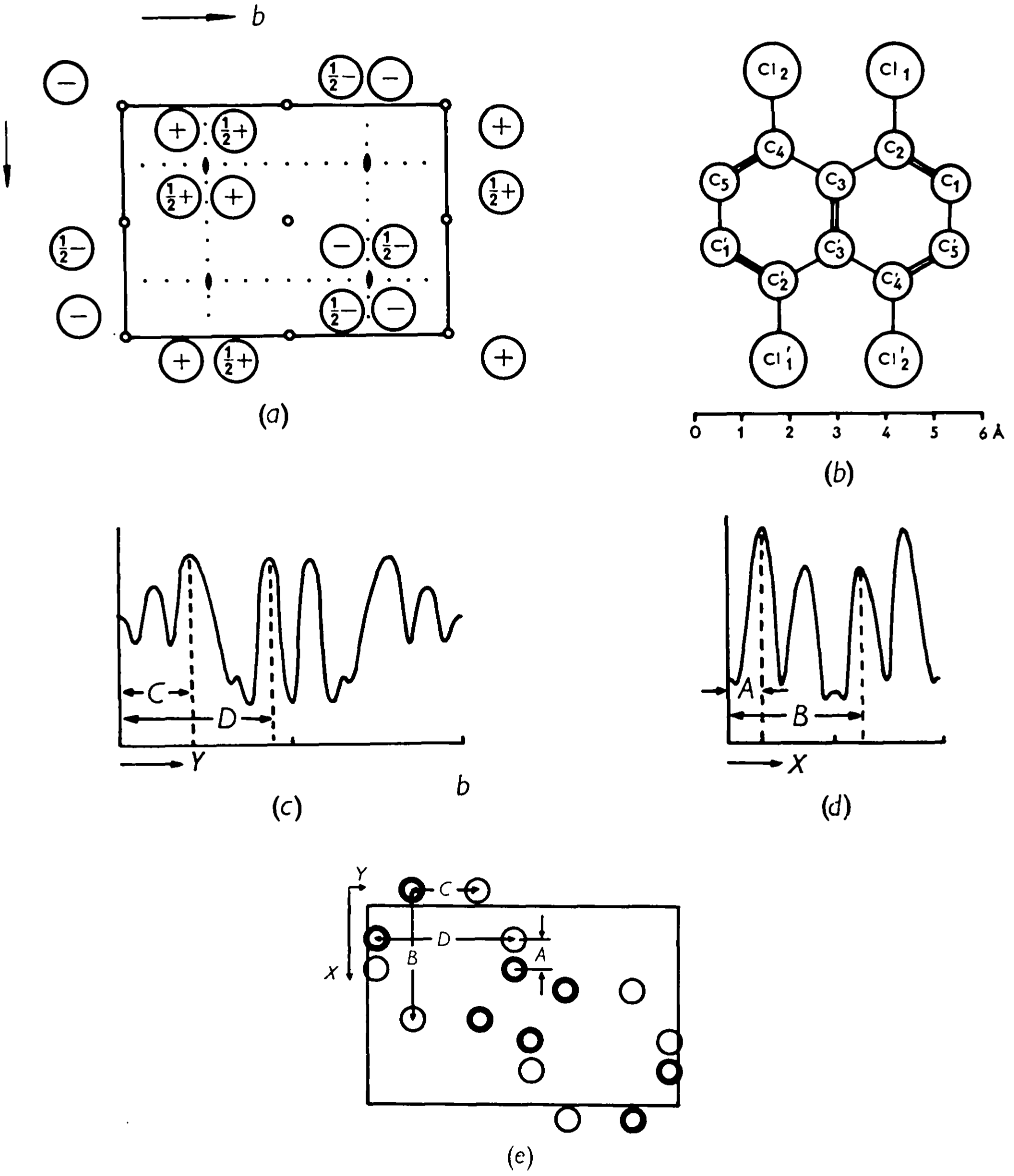


Fig. 1. (*a*) Positions of symmetry-related units in space group *Pccn*, (*b*) hypothetical regular model of molecule with numbering of atoms, (*c*) (0, *v*, ½) Harker section, (*d*) (*u*, 0, ½) Harker section, (*e*) chlorine positions derived from Harker sections.

Table 1. *Comparison of chlorine-atom positions from three-dimensional Patterson synthesis with final values from least-squares refinement*

| | $u$ | | $v$ | | $w$ | |
|---|---|---|---|---|---|---|
| Atom | Patterson | Least-squares | Patterson | Least-squares | Patterson | Least-squares |
| $Cl_1$ | 0·082 | 0·0783 | 0·149 | 0·1478 | 0·164 | 0·1771 |
| $Cl_2$ | 0·167 | 0·1711 | 0·030 | 0·0276 | 0·105 | 0·1226 |

scale by Wilson's (1942) method. Final adjustments were made at a later stage by comparing observed and calculated structure factors. The several layer lines could not be scaled experimentally as the crystals obtained were too thin for satisfactory Weissenberg photography about $a$ and $b$ axes, and a precession camera was not available.

### (c) *Trial structure determination*

The density indicates that there are four molecules in the unit cell and the space group allows these to be centred on the symmetry centres at $0, 0, 0$; $\frac{1}{2}, \frac{1}{2}, 0$; $0, \frac{1}{2}, \frac{1}{2}$ and $\frac{1}{2}, 0, \frac{1}{2}$ or arranged in pairs along the two-fold axes at $\frac{1}{4}, \frac{1}{4}, z$ and $\frac{3}{4}, \frac{3}{4}, z$. The latter arrangement is more likely as buttressing between the

Table 2. *Observed and calculated structure factors*

| $h\,k\ell$ | $\lvert F_o \rvert$ | $F_c$ |
|---|---|---|
| 1 9 3 | 2.9 | +4.2 |
| 10 | 5.6 | -5.8 |
| 11 | 17.4 | +18.0 |
| 12 | 5.5 | +5.0 |
| 13 | 10.8 | -12.8 |
| 14 | 4.2 | -3.7 |
| 15 | 4.9 | +5.0 |
| 16 | 2.5 | -0.2 |
| 17 | 7.3 | +8.8 |
| 2 1 3 | 21.2 | -21.0 |
| 2 | 26.3 | -22.7 |
| 3 | 14.4 | -12.9 |
| 4 | 13.9 | +14.8 |
| 5 | 14.6 | -14.0 |
| 6 | 44.5 | +39.2 |
| 7 | 5.6 | -5.9 |
| 8 | 5.6 | -5.1 |
| 9 | 1.0 | +1.9 |
| 10 | 9.7 | +10.7 |
| 11 | 6.7 | +6.9 |
| 12 | 9.2 | +11.0 |
| 13 | 3.1 | +4.0 |
| 14 | 4.2 | +4.7 |
| 15 | 4.8 | +5.4 |
| 16 | 2.4 | -2.8 |
| 17 | 5.4 | +7.2 |
| 3 1 3 | 21.9 | +18.9 |
| 2 | 10.3 | +8.8 |
| 3 | 11.8 | +10.5 |
| 4 | 11.6 | +9.7 |
| 5 | 27.8 | +24.0 |
| 6 | 18.8 | +17.1 |
| 7 | 4.4 | -2.7 |
| 8 | 14.9 | +14.6 |
| 9 | 3.7 | -3.7 |
| 10 | 10.8 | +12.0 |
| 11 | 3.2 | +2.8 |
| 12 | 7.7 | +9.7 |
| 13 | 6.8 | -8.0 |
| 14 | 5.4 | +5.5 |
| 15 | 5.6 | -6.1 |
| 16 | 3.5 | +2.7 |
| 17 | 5.9 | -7.5 |
| 4 1 3 | 17.7 | +13.8 |
| 2 | 29.2 | -28.5 |
| 3 | 18.2 | +17.9 |
| 4 | 1.8 | +3.0 |
| 5 | 12.7 | +11.3 |
| 6 | 1.0 | +0.6 |
| 7 | 2.1 | -0.2 |
| 8 | 18.3 | -20.9 |
| 9 | 2.2 | +1.9 |
| 10 | 9.8 | -10.8 |
| 11 | 1.1 | +0.8 |
| 12 | 1.1 | -2.1 |
| 13 | 5.1 | -6.2 |
| 14 | 3.8 | -4.5 |
| 15 | 5.9 | -7.2 |
| 16 | 6.0 | -8.1 |
| 17 | 3.8 | -5.0 |
| 5 1 3 | 1.0 | +0.6 |
| 2 | 5.8 | -5.1 |
| 3 | 21.7 | -20.9 |
| 4 | 5.3 | -4.5 |
| 5 | 3.6 | -3.6 |
| 6 | 6.0 | -5.9 |
| 7 | 10.0 | +11.5 |
| 8 | 5.9 | -6.1 |
| 9 | 11.4 | -14.1 |
| 10 | 6.7 | -7.5 |
| 11 | 1.1 | -1.1 |
| 12 | 4.1 | -4.8 |
| 13 | 5.9 | +6.9 |
| 14 | 3.7 | -4.5 |
| 15 | 1.8 | +2.4 |
| 6 1 3 | 4.7 | -3.4 |
| 2 | 2.1 | -1.4 |
| 3 | 2.1 | -0.8 |
| 4 | 6.5 | -6.5 |
| 5 | 5.4 | -4.3 |
| 6 | 12.2 | +12.8 |
| 7 | 1.1 | -0.8 |
| 8 | 6.7 | -7.5 |
| 9 | 2.2 | -2.6 |
| 10 | 1.1 | +1.8 |
| 11 | 1.0 | -1.0 |
| 12 | 1.0 | -0.1 |
| 13 | 2.1 | -0.7 |
| 14 | 5.3 | +6.5 |
| 7 1 3 | 4.5 | +4.3 |
| 2 | 3.8 | -5.0 |
| 3 | 17.1 | -18.5 |
| 4 | 2.2 | -3.0 |
| 5 | 8.4 | +8.9 |
| 6 | 2.2 | +2.9 |
| 7 | 2.2 | +2.7 |
| 8 | 3.0 | -4.3 |
| 9 | 1.1 | -1.8 |
| 10 | 3.5 | -3.5 |
| 11 | 3.2 | -4.1 |
| 12 | 0.8 | +0.8 |
| 13 | 13.4 | +10.0 |
| 8 1 3 | 3.8 | -5.2 |
| 2 | 10.4 | +13.7 |
| 3 | 3.8 | -3.7 |
| 4 | 1.1 | -0.2 |
| 5 | 1.1 | -0.6 |
| 6 | 4.2 | -4.5 |
| 7 | 1.0 | -0.8 |
| 8 | 9.0 | +10.4 |
| 9 | 0.9 | +0.2 |
| 10 | 4.2 | +5.0 |
| 9 1 3 | 7.7 | +9.2 |
| 2 | 2.4 | +1.8 |
| 3 | 2.5 | -2.2 |
| 4 | 2.5 | +3.0 |
| 5 | 2.4 | +0.9 |
| 6 | 2.3 | +3.9 |
| 7 | 3.7 | +3.6 |
| 8 | 2.8 | +3.9 |
| 9 | 3.2 | +3.7 |
| 10 | 1.7 | +3.1 |
| 11 | 3.5 | -5.7 |
| 10 1 3 | 3.7 | +4.6 |
| 2 | 4.9 | +5.8 |
| 3 | 0.8 | +1.5 |
| 4 | 4.6 | -5.3 |
| 5 | 1.9 | +1.3 |
| 6 | 4.9 | -6.0 |
| 7 | 2.3 | +3.2 |
| 0 0 4 | - | -68.1 |
| 1 | - | +38.0 |
| 2 | 9.1 | -8.9 |
| 3 | 0.7 | +0.2 |
| 4 | 11.2 | -11.4 |
| 5 | 17.5 | -18.1 |
| 6 | 13.3 | -13.1 |
| 7 | 4.2 | -3.7 |
| 8 | 10.4 | -9.9 |
| 9 | 10.1 | +9.2 |
| 10 | 1.4 | +1.3 |
| 11 | 1.4 | +0.1 |
| 12 | 12.6 | +12.7 |
| 13 | 9.6 | -8.2 |
| 14 | 7.3 | +8.2 |
| 15 | 4.4 | +3.8 |
| 16 | 7.4 | +8.6 |
| 1 0 4 | 4.6 | +3.8 |
| 1 | 16.7 | +18.6 |
| 2 | 6.4 | -5.9 |
| 3 | 11.8 | +11.7 |
| 4 | 5.7 | +5.2 |
| 5 | 15.3 | +15.7 |
| 6 | 9.3 | -10.0 |
| 7 | 10.4 | +9.7 |
| 8 | 1.2 | +1.4 |
| 9 | 16.3 | +17.4 |
| 10 | 8.9 | -8.6 |
| 11 | 17.5 | +20.8 |
| 12 | 6.3 | -5.7 |
| 13 | 5.1 | +4.0 |
| 14 | 1.5 | -1.4 |
| 15 | 4.7 | +3.6 |
| 2 0 4 | 11.6 | +13.5 |
| 1 | 12.3 | +12.4 |
| 2 | 13.0 | +15.0 |
| 3 | 0.9 | +0.8 |
| 4 | 8.4 | +7.7 |
| 5 | 6.7 | -6.9 |
| 6 | 6.2 | +5.0 |
| 7 | 5.4 | +3.9 |
| 8 | 7.2 | +6.3 |
| 9 | 7.2 | +6.2 |
| 10 | 2.4 | +1.2 |
| 11 | 4.8 | -3.9 |
| 12 | 10.0 | -9.0 |
| 13 | 1.4 | -0.3 |
| 14 | 1.3 | -0.6 |
| 15 | 1.1 | +2.8 |
| 16 | 3.7 | -0.3 |
| 3 0 4 | 13.7 | -15.7 |
| 1 | 7.4 | -6.0 |
| 2 | 6.1 | +4.6 |
| 3 | 3.9 | -1.6 |
| 4 | 15.7 | +16.5 |
| 5 | 9.8 | +8.1 |
| 6 | 13.8 | -12.5 |
| 7 | 7.2 | -5.9 |
| 8 | 5.3 | -3.6 |
| 9 | 4.8 | -3.8 |
| 10 | 9.3 | +9.0 |
| 11 | 1.5 | -0.6 |
| 12 | 1.4 | -0.1 |
| 13 | 1.3 | +2.4 |
| 14 | 6.9 | -6.7 |
| 15 | 4.2 | -4.3 |
| 4 0 4 | 1.0 | +0.8 |
| 1 | 2.9 | +2.2 |
| 2 | 11.5 | +12.0 |
| 3 | 5.5 | -5.3 |
| 4 | 5.3 | +4.3 |
| 5 | 4.9 | +5.6 |
| 6 | 3.3 | +1.1 |
| 7 | 1.3 | -1.8 |
| 8 | 1.3 | -0.7 |
| 9 | 4.9 | -4.8 |
| 10 | 5.4 | -4.0 |
| 11 | 5.2 | +5.2 |
| 12 | 1.4 | -0.4 |
| 13 | 1.3 | -1.7 |
| 14 | 5.1 | -5.4 |
| 15 | 0.9 | -2.7 |
| 16 | 4.4 | -6.0 |
| 5 0 4 | 3.1 | -0.8 |
| 1 | 3.9 | +3.5 |
| 2 | 3.2 | -2.8 |
| 3 | 7.6 | -7.1 |
| 4 | 8.4 | +8.8 |
| 5 | 6.7 | -7.7 |
| 6 | 8.0 | -7.6 |
| 7 | 12.6 | -13.7 |
| 8 | 1.4 | -1.3 |
| 9 | 7.9 | -7.1 |
| 10 | 4.7 | +5.6 |
| 11 | 3.9 | -4.4 |
| 12 | 1.3 | -1.2 |
| 13 | 5.5 | -6.0 |
| 14 | 1.0 | -3.7 |
| 15 | 3.1 | -3.4 |
| 6 0 4 | 6.3 | -5.6 |
| 1 | 10.0 | -10.6 |
| 2 | 10.7 | -11.7 |
| 3 | 7.5 | -8.1 |
| 4 | 13.5 | -15.7 |
| 5 | 10.5 | +11.3 |
| 6 | 5.4 | -6.1 |
| 7 | 1.4 | +2.0 |
| 8 | 5.8 | +5.1 |
| 9 | 11.8 | -10.9 |
| 10 | 1.4 | -0.8 |
| 11 | 4.6 | +3.5 |
| 12 | 1.1 | +3.1 |
| 13 | 3.9 | +2.8 |
| 14 | 4.5 | +5.7 |
| 7 0 4 | 4.8 | +4.5 |
| 1 | 3.5 | +3.4 |
| 2 | 5.9 | -7.1 |
| 3 | 1.2 | -0.9 |
| 4 | 4.2 | +3.3 |
| 5 | 9.2 | +9.2 |
| 6 | 1.4 | +1.9 |
| 7 | 9.4 | +9.6 |
| 8 | 1.4 | -3.0 |
| 9 | 6.2 | +6.5 |
| 10 | 1.2 | -1.9 |
| 11 | 3.8 | +4.1 |
| 12 | 0.9 | +3.3 |
| 13 | 4.2 | +5.3 |
| 8 0 4 | 7.8 | +7.8 |
| 1 | 6.1 | -6.8 |
| 2 | 1.3 | +2.1 |
| 3 | 1.3 | +0.8 |
| 4 | 7.1 | +7.3 |
| 5 | 1.3 | +3.2 |
| 6 | 1.3 | +0.9 |
| 7 | 1.2 | +2.8 |
| 8 | 1.1 | +3.1 |
| 9 | 4.2 | -4.6 |
| 9 0 4 | 6.8 | +7.1 |
| 1 | 1.3 | -0.8 |
| 2 | 1.3 | -0.9 |
| 3 | 1.2 | +1.4 |
| 4 | 5.4 | -5.1 |
| 5 | 1.1 | -3.0 |
| 6 | 4.9 | +5.7 |
| 1 1 5 | 3.2 | -0.8 |
| 2 | 4.5 | +4.2 |
| 3 | 14.4 | -14.9 |
| 4 | 2.0 | -1.8 |
| 5 | 6.4 | -4.9 |
| 6 | 7.8 | +7.6 |
| 7 | 5.3 | +4.4 |
| 8 | 6.9 | +7.2 |
| 9 | 0.9 | -0.5 |
| 10 | 7.9 | +7.6 |
| 11 | 4.2 | -3.3 |
| 12 | 7.3 | -7.2 |
| 13 | 6.1 | +7.1 |
| 14 | 6.7 | +8.0 |
| 15 | 3.5 | +2.8 |
| 16 | 1.9 | +2.0 |
| 2 1 5 | 3.2 | +3.1 |
| 2 | 11.5 | +12.0 |
| 3 | 15.2 | +15.4 |
| 4 | 5.2 | +3.7 |
| 5 | 16.7 | +15.5 |
| 6 | 4.0 | +3.4 |
| 7 | 10.5 | -9.8 |
| 8 | 15.0 | +15.8 |
| 9 | 3.5 | +3.8 |
| 10 | 7.4 | +8.0 |
| 11 | 2.4 | -3.1 |
| 12 | 2.3 | +2.6 |
| 13 | 1.0 | -2.5 |
| 14 | 3.2 | +3.5 |
| 15 | 3.6 | -4.4 |
| 3 1 5 | 13.2 | +13.4 |
| 2 | 5.7 | -5.6 |
| 3 | 11.4 | +10.8 |
| 4 | 1.2 | +0.1 |
| 5 | 6.2 | +6.4 |
| 6 | 17.2 | -16.3 |
| 7 | 5.5 | +4.5 |
| 8 | 6.6 | -7.1 |
| 9 | 1.2 | +0.5 |
| 10 | 3.4 | -4.1 |
| 11 | 4.6 | -4.1 |
| 12 | 8.2 | -8.3 |
| 13 | 2.0 | -4.0 |
| 14 | 0.9 | -2.8 |
| 15 | 3.8 | -5.2 |
| 4 1 5 | 13.8 | -14.2 |
| 2 | 5.2 | +5.5 |
| 3 | 1.2 | +1.1 |
| 4 | 9.6 | -10.6 |
| 5 | 6.0 | -6.7 |
| 6 | 13.6 | -14.1 |
| 7 | 6.4 | -5.8 |
| 8 | 3.5 | -2.0 |
| 9 | 1.2 | +0.8 |
| 10 | 3.7 | -3.8 |
| 11 | 1.1 | +1.7 |
| 12 | 9.0 | -9.9 |
| 13 | 2.6 | +2.3 |
| 14 | 3.5 | -4.5 |
| 5 1 5 | 8.4 | -9.5 |
| 2 | 2.5 | -3.2 |
| 3 | 1.2 | -1.1 |
| 4 | 4.9 | +5.3 |
| 5 | 4.3 | -4.5 |
| 6 | 5.6 | +7.7 |
| 7 | 6.0 | -6.4 |
| 8 | 5.4 | -6.0 |
| 9 | 1.2 | +1.8 |
| 10 | 6.2 | +7.5 |
| 11 | 1.0 | +0.8 |
| 12 | 4.5 | +4.4 |
| 6 1 5 | 1.2 | +0.2 |
| 2 | 1.2 | +1.3 |
| 3 | 1.2 | -2.4 |
| 4 | 1.2 | +1.2 |
| 5 | 6.5 | +8.7 |
| 6 | 1.2 | -1.0 |
| 7 | 6.2 | -7.3 |
| 8 | 3.2 | +3.0 |
| 9 | 3.7 | +4.9 |
| 10 | 1.0 | +1.0 |
| 11 | 0.9 | -0.4 |
| 12 | 0.7 | +3.1 |
| 13 | 2.1 | +3.3 |
| 7 1 5 | 4.8 | -5.7 |
| 2 | 2.4 | -3.7 |
| 3 | 3.3 | +5.5 |
| 4 | 8.7 | +11.1 |
| 5 | 1.2 | +0.1 |
| 6 | 3.1 | -4.4 |
| 7 | 3.0 | -3.6 |
| 8 | 1.0 | +2.2 |
| 9 | 0.9 | +1.5 |
| 10 | 0.8 | +1.6 |
| 11 | 3.6 | +3.2 |
| 8 1 5 | 3.4 | +7.8 |
| 2 | 1.1 | -1.1 |
| 3 | 1.1 | -1.8 |
| 4 | 3.6 | +4.0 |
| 5 | 3.3 | -1.9 |
| 6 | 2.7 | +3.8 |
| 7 | 5.2 | +6.0 |
| 9 1 5 | 0.9 | +2.1 |
| 2 | 4.9 | -5.0 |
| 3 | 4.2 | +4.2 |

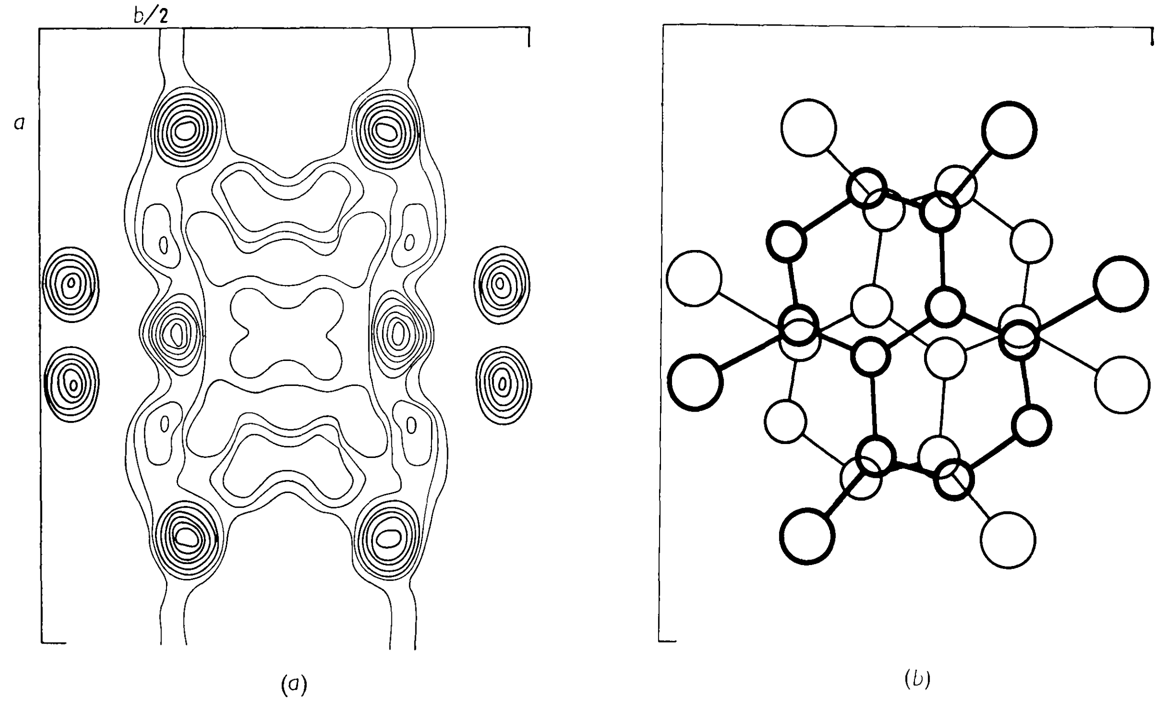
Table 2 (*cont.*)

| h k $\ell$ | $\lvert F_o \rvert$ | $F_c$ |
|---|---|---|
| 0 2 0 | 11.4 | -11.0 |
| 4 | 13.2 | -11.7 |
| 6 | 32.9* | +44.3 |
| 8 | 24.5 | +29.7 |
| 10 | 17.0 | -15.7 |
| 12 | 21.2 | -21.4 |
| 14 | 5.5 | - 3.1 |
| 16 | 12.7 | -15.9 |
| 18 | 8.7 | -10.7 |
| 1 1 0 | - | -36.3 |
| 3 | 18.4 | -18.3 |
| 5 | 36.9* | -47.5 |
| 7 | 13.5 | -11.4 |
| 9 | 22.1 | -19.8 |
| 11 | 29.8* | -37.9 |
| 13 | 8.8 | - 8.8 |
| 15 | 1.4 | - 1.1 |
| 17 | 1.2 | - 3.2 |
| 19 | 3.5 | - 4.0 |
| 2 0 0 | 12.5 | + 9.3 |
| 2 | 30.9* | -47.0 |
| 4 | 25.7 | -30.9 |
| 6 | 0.9 | + 2.4 |
| 8 | 6.4 | - 4.1 |
| 10 | 12.4 | - 9.4 |
| 12 | 12.2 | +10.2 |
| 14 | 8.3 | + 7.4 |
| 16 | 6.1 | + 3.5 |
| 18 | 4.2 | + 4.1 |
| 3 1 0 | 29.3 | +33.0 |
| 3 | 16.6 | +17.1 |
| 5 | 36.5 | -42.4 |
| 7 | 18.3 | +14.8 |
| 9 | 20.8 | +21.3 |
| 11 | 9.0 | - 8.8 |
| 13 | 8.5 | - 8.0 |
| 15 | 11.2 | +13.2 |
| 17 | 5.5 | + 4.7 |
| 4 0 0 | 8.7 | - 6.4 |
| 2 | 19.5 | -23.0 |
| 4 | 4.0 | + 2.9 |
| 6 | 10.9 | - 8.6 |
| 8 | 1.3 | - 2.2 |
| 10 | 13.6 | +13.1 |
| 12 | 1.4 | - 1.9 |
| 14 | 6.0 | + 5.2 |
| 16 | 10.0 | +10.7 |
| 5 1 0 | 4.2 | + 2.2 |
| 3 | 19.6 | +21.3 |
| 5 | 1.2 | - 2.7 |
| 7 | 21.3 | +24.2 |
| 9 | 20.2 | +20.9 |
| 11 | 5.5 | + 2.8 |
| 13 | 5.4 | + 3.4 |
| 15 | 7.3 | + 8.0 |
| 6 0 0 | 13.2 | -10.8 |
| 2 | 22.2 | +21.8 |
| 4 | 34.2* | +41.1 |
| 6 | 3.6 | - 1.1 |
| 8 | 15.7 | -15.5 |
| 10 | 12.2 | +12.3 |
| 12 | 5.4 | - 5.1 |
| 14 | 11.3 | -14.2 |
| 16 | 3.5 | - 4.0 |
| 7 1 0 | 11.7 | -10.8 |
| 3 | 6.0 | + 4.4 |
| 5 | 12.2 | -11.3 |
| 7 | 16.7 | -18.3 |
| 9 | 10.4 | - 9.9 |
| 11 | 1.3 | - 2.0 |
| 13 | 8.7 | - 8.5 |
| 15 | 8.0 | -10.3 |
| 8 0 0 | 17.7 | -21.7 |
| 2 | 1.4 | - 1.1 |
| 4 | 1.4 | - 2.3 |
| 6 | 5.5 | - 5.3 |
| 8 | 11.3 | -11.1 |
| 10 | 6.2 | + 6.3 |
| 12 | 3.6 | + 3.0 |
| 14 | 5.7 | - 5.4 |
| 9 1 0 | 8.2 | - 8.1 |
| 3 | 4.7 | - 4.0 |
| 5 | 11.4 | +13.1 |
| 7 | 1.3 | - 3.0 |
| 9 | 6.8 | - 7.6 |
| 11 | 9.1 | +10.5 |
| 10 0 0 | 4.5 | + 3.6 |
| 2 | 5.0 | - 3.8 |
| 4 | 1.2 | - 2.6 |
| 6 | 6.0 | + 6.0 |
| 8 | 5.5 | - 4.2 |
| 10 | 3.9 | + 3.1 |
| 11 1 0 | 5.0 | - |
| 3 | 1.0 | - 0.1 |
| 5 | 6.8 | + 7.8 |
| 12 0 0 | 5.5 | + 7.7 |
| 1 1 1 | 25.4 | +22.8 |
| 2 | 20.6* | -29.9 |
| 3 | 6.0 | + 5.6 |
| 4 | 8.3 | + 8.7 |
| 5 | 14.0 | +15.1 |
| 6 | 3.8 | - 3.8 |
| 7 | 10.8 | + 9.9 |
| 8 | 20.5 | -25.6 |
| 9 | 4.4 | - 3.6 |
| 10 | 16.7 | -16.1 |
| 11 | 14.0 | -13.2 |
| 12 | 15.1 | +16.1 |
| 13 | 7.0 | + 6.0 |
| 14 | 11.6 | -12.5 |
| 15 | 6.4 | - 5.4 |
| 16 | 7.5 | - 6.4 |
| 17 | 7.8 | - 7.6 |
| 18 | 5.0 | + 4.6 |
| 2 1 1 | 2.4 | + 2.3 |
| 2 | 14.1 | +14.2 |
| 3 | 36.0* | -57.3 |
| 4 | 16.5 | -18.6 |
| 5 | 26.4* | -34.2 |
| 6 | 28.4* | -38.5 |
| 7 | 22.7 | +26.7 |
| 8 | 6.5 | - 6.0 |
| 9 | 8.9 | - 8.3 |
| 10 | 14.7 | -13.9 |
| 11 | 1.1 | - 0.6 |
| 12 | 11.9 | -11.5 |
| 13 | 10.4 | +10.2 |
| 14 | 6.9 | - 5.6 |
| 15 | 9.7 | + 9.4 |
| 16 | 1.0 | - 1.3 |
| 17 | 5.0 | + 3.5 |
| 3 1 1 | 25.0* | -30.0 |
| 2 | 12.0 | +10.8 |
| 3 | 16.9 | -19.1 |
| 4 | 5.3 | + 3.8 |
| 5 | 21.8 | -26.1 |
| 6 | 25.4 | +33.4 |
| 7 | 0.9 | - 1.2 |
| 8 | 15.9 | +16.1 |
| 9 | 4.4 | + 2.9 |
| 10 | 8.8 | + 7.1 |
| 11 | 1.1 | + 0.3 |
| 12 | 16.5 | +15.8 |
| 13 | 9.9 | + 8.9 |
| 14 | 6.5 | + 6.3 |
| 15 | 8.5 | + 8.3 |
| 16 | 4.6 | + 3.2 |
| 17 | 8.4 | + 8.4 |
| 18 | 2.4 | - 1.9 |
| 4 1 1 | 32.3* | -42.6 |
| 2 | 22.0 | +23.5 |
| 3 | 11.0 | -11.5 |
| 4 | 6.2 | + 5.2 |
| 5 | 9.2 | + 8.5 |
| 6 | 8.8 | + 7.8 |
| 7 | 21.7 | +24.5 |
| 8 | 20.8 | +20.3 |
| 9 | 5.4 | - 4.3 |
| 10 | 13.8 | +13.0 |
| 11 | 11.8 | - 9.7 |
| 12 | 8.0 | + 7.0 |
| 13 | 1.3 | - 1.0 |
| 14 | 7.0 | + 6.4 |
| 15 | 1.2 | - 2.0 |
| 16 | 6.7 | + 6.1 |
| 17 | 11.2 | -12.6 |
| 18 | 2.8 | - 2.8 |
| 5 1 1 | 7.8 | + 6.2 |
| 2 | 14.4 | +15.0 |
| 3 | 17.9 | +20.1 |
| 4 | 18.8 | -18.8 |
| 5 | 6.7 | + 5.6 |
| 6 | 14.8 | +16.0 |
| 7 | 5.7 | - 5.2 |
| 8 | 10.4 | +11.5 |
| 9 | 11.0 | +10.3 |
| 10 | 13.3 | -12.3 |
| 11 | 1.3 | + 0.5 |
| 12 | 12.6 | -12.8 |
| 13 | 7.1 | - 5.8 |
| 14 | 1.2 | - 0.9 |
| 15 | 4.2 | - 3.4 |
| 16 | 1.0 | + 0.3 |
| 17 | 3.8 | - 2.1 |
| 6 1 1 | 1.0 | + 0.3 |
| 2 | 1.0 | + 0.5 |
| 3 | 1.0 | - 1.5 |
| 4 | 4.4 | + 3.8 |
| 5 | 14.7 | -13.4 |
| 6 | 11.4 | - 9.5 |
| 7 | 10.9 | + 9.8 |
| 8 | 4.4 | + 3.4 |
| 9 | 6.3 | + 5.1 |
| 10 | 2.2 | - 2.2 |
| 11 | 3.3 | - 2.6 |
| 12 | 3.7 | - 1.9 |
| 13 | 4.9 | - 4.4 |
| 14 | 6.2 | - 5.5 |
| 15 | 4.9 | + 4.9 |
| 7 1 1 | 1.0 | - 1.0 |
| 2 | 14.4 | +14.9 |
| 3 | 13.2 | +12.1 |
| 4 | 17.3 | -19.3 |
| 5 | 7.5 | - 6.3 |
| 6 | 4.0 | - 2.5 |
| 7 | 1.3 | - 1.6 |
| 8 | 5.9 | + 4.1 |
| 9 | 1.4 | + 0.7 |
| 10 | 1.5 | - 0.3 |
| 11 | 1.3 | + 0.7 |
| 12 | 10.6 | -10.9 |
| 13 | 7.7 | - 7.5 |
| 14 | 3.6 | + 3.9 |
| 15 | 2.4 | - 2.4 |
| 8 1 1 | 14.5 | -14.7 |
| 2 | 11.5 | -10.4 |
| 3 | 8.3 | + 7.1 |
| 4 | 1.1 | - 1.7 |
| 5 | 1.1 | + 0.6 |
| 6 | 1.1 | + 0.9 |
| 7 | 11.9 | -11.1 |
| 8 | 9.6 | - 8.7 |
| 9 | 4.6 | + 4.0 |
| 10 | 4.8 | - 4.8 |
| 11 | 6.5 | + 6.4 |
| 12 | 1.0 | - 0.5 |
| 13 | 0.9 | - 1.1 |
| 14 | 3.1 | - 2.4 |
| 9 1 1 | 9.8 | - 8.5 |
| 2 | 10.4 | + 9.9 |
| 3 | 1.3 | - 0.8 |
| 4 | 1.3 | + 1.1 |
| 5 | 3.6 | - 2.0 |
| 6 | 1.3 | + 0.1 |
| 7 | 4.5 | - 3.0 |
| 8 | 5.5 | + 4.1 |
| 9 | 3.2 | - 1.9 |
| 10 | 9.3 | + 9.9 |
| 11 | 4.6 | + 4.4 |
| 10 1 1 | 1.2 | - 1.6 |
| 2 | 1.2 | - 2.7 |
| 3 | 11.5 | +11.2 |
| 4 | 5.4 | + 4.6 |
| 5 | 4.6 | + 3.2 |
| 6 | 5.5 | + 5.1 |
| 7 | 5.2 | - 5.5 |
| 8 | 1.0 | + 0.5 |
| 9 | 4.1 | + 3.0 |
| 10 | 3.7 | + 3.0 |
| 11 1 1 | 2.9 | + 3.0 |
| 2 | 3.6 | - 3.5 |
| 3 | 1.0 | + 0.4 |
| 4 | 0.9 | + 0.8 |
| 5 | 0.9 | + 1.0 |
| 6 | 0.8 | + 2.2 |
| 7 | 4.2 | + 4.4 |
| 0 0 2 | - | -57.5 |
| 1 | - | -106.3 |
| 2 | 18.5 | +24.6 |
| 3 | 22.8 | -27.6 |
| 4 | 18.2 | +20.7 |
| 5 | 2.4 | + 2.3 |
| 6 | 11.3 | -10.3 |
| 7 | 24.1 | -23.8 |
| 8 | 9.5 | - 9.5 |
| 9 | 32.0* | -41.3 |
| 10 | 8.2 | + 7.1 |
| 11 | 22.9 | -23.7 |
| 12 | 5.4 | + 5.9 |
| 13 | 5.9 | - 4.2 |
| 14 | 7.4 | - 6.6 |
| 15 | 10.0 | -10.9 |
| 1 0 2 | - | -70.0 |
| 1 | - | + 1.7 |
| 2 | 22.8 | -27.5 |
| 3 | 5.8 | - 5.8 |
| 4 | 22.2* | -31.0 |
| 5 | 9.1 | + 8.9 |
| 6 | 0.8 | - 0.8 |
| 7 | 6.8 | - 6.5 |
| 8 | 13.1 | -12.3 |
| 9 | 6.8 | - 5.6 |
| 10 | 8.9 | - 8.6 |
| 11 | 7.6 | + 6.3 |
| 12 | 17.9 | +19.4 |
| 13 | 1.3 | - 0.7 |
| 14 | 10.6 | +11.5 |
| 15 | 1.5 | - 3.2 |
| 16 | 6.8 | + 6.3 |
| 17 | 1.1 | - 0.3 |
| 18 | 5.4 | + 6.4 |
| 2 0 2 | 18.0 | -20.5 |
| 1 | 15.0 | -15.2 |
| 2 | 7.6 | + 6.9 |
| 3 | 11.3 | +13.1 |
| 4 | 7.1 | + 6.8 |
| 5 | 17.9 | +22.3 |
| 6 | 7.8 | - 7.6 |
| 7 | 8.7 | + 8.4 |
| 8 | 3.6 | - 3.0 |
| 9 | 10.0 | + 9.7 |
| 10 | 6.2 | + 5.7 |
| 11 | 18.1 | +18.6 |
| 12 | 1.3 | - 0.2 |
| 13 | 6.3 | + 4.2 |
| 14 | 1.3 | - 2.7 |
| 15 | 5.0 | + 3.0 |
| 3 0 2 | 24.1 | +30.8 |
| 1 | 13.2 | -14.9 |
| 2 | 6.4 | - 4.7 |
| 3 | 8.0 | - 8.3 |
| 4 | 18.6 | -21.1 |
| 5 | 17.9 | +19.1 |
| 6 | 22.2 | +26.3 |
| 7 | 5.1 | - 3.4 |
| 8 | 6.9 | + 6.3 |
| 9 | 9.5 | - 9.1 |
| 10 | 11.5 | -11.5 |
| 11 | 6.2 | + 6.0 |
| 12 | 1.3 | - 0.1 |
| 13 | 6.3 | + 4.5 |
| 14 | 10.2 | +11.0 |
| 15 | 4.4 | - 4.7 |
| 16 | 1.1 | - 2.6 |
| 17 | 1.0 | - 0.4 |
| 18 | 5.4 | - 4.8 |
| 4 0 2 | 0.8 | + 0.7 |
| 1 | 6.0 | - 5.5 |
| 2 | 4.9 | + 2.9 |
| 3 | 13.0 | +14.7 |
| 4 | 5.7 | - 5.9 |
| 5 | 5.0 | + 3.8 |
| 6 | 5.3 | + 4.5 |
| 7 | 10.0 | + 9.5 |
| 8 | 1.2 | + 1.9 |
| 9 | 11.7 | +11.9 |
| 10 | 5.9 | - 5.1 |
| 11 | 1.3 | - 1.8 |
| 12 | 1.3 | + 2.9 |
| 13 | 6.1 | + 6.2 |
| 14 | 1.2 | + 1.1 |
| 15 | 3.3 | + 3.3 |
| 16 | 1.0 | - 2.2 |
| 17 | 5.0 | - 5.4 |
| 5 0 2 | 13.9 | +14.7 |
| 1 | 3.1 | - 2.2 |
| 2 | 17.0 | +21.3 |
| 3 | 7.4 | - 6.2 |
| 4 | 3.9 | + 3.0 |
| 5 | 10.0 | + 9.7 |
| 6 | 16.3 | +17.4 |
| 7 | 3.7 | - 1.8 |
| 8 | 1.3 | - 1.3 |
| 9 | 6.2 | - 5.5 |
| 10 | 10.0 | -10.2 |
| 11 | 1.3 | + 3.3 |
| 12 | 4.9 | - 3.8 |
| 13 | 1.3 | + 2.5 |
| 14 | 4.4 | - 3.6 |
| 15 | 1.1 | - 2.7 |
| 16 | 8.0 | - 9.0 |
| 6 0 2 | 14.6 | +14.2 |
| 1 | 12.3 | +12.9 |
| 2 | 2.9 | - 1.6 |
| 3 | 5.4 | + 3.7 |
| 4 | 12.3 | -12.0 |
| 5 | 23.3 | -28.4 |
| 6 | 6.5 | + 6.1 |
| 7 | 17.1 | -19.9 |
| 8 | 8.0 | + 7.1 |
| 9 | 1.3 | + 2.0 |
| 10 | 7.7 | - 8.0 |
| 11 | 13.0 | -14.6 |
| 12 | 1.2 | - 0.4 |
| 13 | 10.3 | -10.8 |
| 14 | 4.2 | + 3.5 |
| 7 0 2 | 16.2 | -18.0 |
| 1 | 4.9 | + 4.5 |
| 2 | 4.9 | - 3.9 |
| 3 | 4.4 | - 4.5 |
| 4 | 13.7 | -16.6 |
| 5 | 1.3 | - 0.6 |
| 6 | 10.0 | - 9.1 |
| 7 | 1.3 | + 2.7 |
| 8 | 1.3 | + 1.9 |
| 9 | 1.3 | - 0.6 |
| 10 | 3.1 | + 4.0 |
| 11 | 1.2 | - 3.5 |
| 12 | 1.2 | - 1.4 |
| 13 | 1.0 | + 0.5 |
| 14 | 2.8 | + 2.1 |
| 8 0 2 | 6.8 | + 6.8 |
| 1 | 8.4 | + 9.4 |
| 2 | 1.2 | - 3.3 |
| 3 | 1.3 | + 1.4 |
| 4 | 4.1 | - 4.1 |
| 5 | 1.3 | + 2.8 |
| 6 | 1.3 | + 1.3 |
| 7 | 1.3 | + 1.6 |
| 8 | 6.1 | + 4.3 |
| 9 | 10.7 | +11.7 |
| 10 | 3.3 | - 4.0 |
| 11 | 4.1 | + 3.2 |
| 9 0 2 | 6.1 | - 4.4 |
| 1 | 5.4 | + 5.4 |
| 2 | 4.3 | + 3.2 |
| 3 | 1.3 | + 2.3 |
| 4 | 8.9 | + 9.2 |
| 5 | 3.9 | - 3.9 |
| 6 | 5.6 | - 5.3 |
| 7 | 1.2 | + 2.2 |
| 8 | 1.1 | - 0.5 |
| 9 | 5.1 | + 4.7 |
| 10 | 9.0 | + 9.9 |
| 11 | 3.5 | - 3.3 |
| 10 0 2 | 1.2 | - 1.2 |
| 1 | 3.3 | - 3.3 |
| 2 | 1.2 | + 1.3 |
| 3 | 1.1 | + 1.3 |
| 4 | 1.1 | + 0.9 |
| 5 | 5.0 | + 4.9 |
| 6 | 1.0 | - 2.5 |
| 7 | 4.5 | - 3.2 |
| 8 | 2.5 | + 2.4 |
| 9 | 5.0 | + 4.5 |
| 11 0 2 | 0.9 | - 2.8 |
| 1 | 0.9 | + 3.7 |
| 2 | 3.6 | + 4.2 |
| 3 | 0.9 | + 1.1 |
| 4 | 4.0 | + 4.5 |
| 5 | 3.2 | - 3.2 |
| 1 1 3 | 22.0 | -19.5 |
| 2 | 5.5 | + 5.5 |
| 3 | 7.3 | + 6.9 |
| 4 | 9.2 | - 9.1 |
| 5 | 12.7 | -12.1 |
| 6 | 16.4 | -14.9 |
| 7 | 14.1 | -12.9 |
| 8 | 5.7 | - 5.5 |

* These reflections were omitted from the final stages of the refinement because of extinction. In $F_o$ column dash indicates a reflection that was not recorded. In $F_c$ column this indicates a structure factor that was not calculated in the final stages of the refinement. Those reflections with $0{\cdot}7 \le F_o \le 1{\cdot}5$ were not observed, but were inserted as $\frac{1}{2}F_{\min}$. The values in the table must be doubled to give the correct absolute scale (i.e. for $F(000) = 528$).

peripheral atoms would prevent the molecules from having a centre of symmetry and thus necessitate their being positioned along the two-fold axes. Further information regarding the arrangement of the molecules follows from the fact that the crystals have an excellent cleavage plane parallel to (001), indicating that the molecules lie approximately parallel to this plane.

This information assisted in the interpretation of a three-dimensional Patterson synthesis which was calculated on a Stantec Zebra computer using a programme due to Dr D. W. Smits and Dr J. C. Schoone. The trial structure was derived from this Patterson synthesis by considering only the peaks due to Cl $\cdots$ Cl vectors. In space group *Pccn* symmetry-related atoms with the same $u$ or $v$ coordinates are $\frac{1}{2}$ apart in $w$



(a) (b)

Fig. 2. Fourier projection down [001] and explanatory linediagram. Contours at arbitrary intervals, with the intervals doubled at the chlorine atoms.

(see Fig. 1(*a*)). The two independent chlorine atoms in the asymmetric unit will therefore give rise to two independent peaks, and their mirror images across $u=\frac{1}{2}$ and $v=\frac{1}{2}$ in each of the $(0, v, \frac{1}{2})$ and $(u, 0, \frac{1}{2})$ Harker sections. The prominence of these peaks can be seen in Figs. 1(*c*) and 1(*d*).

The only interpretation of the Harker sections which is consistent with the approximate molecular conformation as shown in Fig. 1(*b*), is given in Fig. 1(*e*). Having thus determined the *u* and *v* coordinates of the chlorine atoms, their *w* coordinates follow from the Patterson peaks at $(2u, 2v, 2w)$ arising from the operation of the centres of symmetry at (0, 0, 0) etc. The positions of the chlorine atoms in the trial structure are listed in Table 1; these values compare well with the final values given in the same Table.

The naphthalene nucleus was assumed to be planar, regular and symmetrically disposed with respect to the chlorine atoms i.e. passing through $w=0{\cdot}135$. A two-dimensional Fourier synthesis down [001] substantiated the *u* and *v* trial coordinates (see Fig. 2).

Table 3. *Final atomic parameters from least-squares refinement and their e.s.d.'s*

These parameters are referred to the crystallographic axes

| | Fractional coordinates | | | Thermal vibration parameters | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Atom | $u$ | $v$ | $w$ | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{23}$ | $b_{31}$ | $b_{12}$ |
| $Cl_1$ | $\overline{0{\cdot}07827}$ | 0·14784 | 0·17707 | 0·00932 | 0·00475 | 0·03306 | $\overline{0{\cdot}00338}$ | 0·00261 | $\overline{0{\cdot}00558}$ |
| | 0·00027 | 0·00015 | 0·00049 | 0·00026 | 0·00011 | 0·00097 | 0·00051 | 0·00088 | 0·00032 |
| $Cl_2$ | 0·17110 | 0·02764 | 0·12256 | 0·01614 | 0·00270 | 0·01956 | $\overline{0{\cdot}00007}$ | $\overline{0{\cdot}00367}$ | $\overline{0{\cdot}00468}$ |
| | 0·00030 | 0·00015 | 0·00041 | 0·00038 | 0·00007 | 0·00074 | 0·00040 | 0·00086 | 0·00030 |
| $C_1$ | 0·00110 | 0·31214 | 0·15658 | 0·01117 | 0·00557 | 0·02073 | $\overline{0{\cdot}00548}$ | 0·00889 | $\overline{0{\cdot}00152}$ |
| | 0·00114 | 0·00072 | 0·00152 | 0·00119 | 0·00049 | 0·00323 | 0·00197 | 0·00328 | 0·00123 |
| $C_2$ | 0·05145 | 0·22881 | 0·16029 | 0·00787 | 0·00354 | 0·01019 | $\overline{0{\cdot}00251}$ | $\overline{0{\cdot}00388}$ | 0·00037 |
| | 0·00080 | 0·00049 | 0·00125 | 0·00101 | 0·00050 | 0·00335 | 0·00198 | 0·00331 | 0·00124 |
| $C_3$ | 0·20283 | 0·21286 | 0·15349 | 0·00839 | 0·00431 | $\overline{0{\cdot}00014}$ | 0·00159 | 0·00078 | 0·00021 |
| | 0·00080 | 0·00053 | 0·00118 | 0·00089 | 0·00036 | 0·00213 | 0·00127 | 0·00218 | 0·00097 |
| $C_4$ | 0·26861 | 0·12569 | 0·14480 | 0·01181 | 0·00270 | 0·00731 | $\overline{0{\cdot}00451}$ | $\overline{0{\cdot}00315}$ | $\overline{0{\cdot}00035}$ |
| | 0·00099 | 0·00049 | 0·00133 | 0·00112 | 0·00031 | 0·00253 | 0·00128 | 0·00248 | 0·00093 |
| $C_5$ | 0·41001 | 0·11386 | 0·15089 | 0·01266 | 0·00308 | 0·01992 | 0·00420 | $\overline{0{\cdot}00188}$ | $\overline{0{\cdot}00053}$ |
| | 0·00106 | 0·00057 | 0·00160 | 0·00122 | 0·00033 | 0·00305 | 0·00152 | 0·00324 | 0·00108 |

### *(d) Structure refinement*

A preliminary three-dimensional least-squares refinement was carried out on the Stantec Zebra computer using an overall isotropic temperature factor. The results of this refinement were used to adjust the data from the various layer lines on to an improved absolute scale.

The final stages of the refinement were carried out on the Deuce computer at the National Physical Laboratory, Teddington, using the least-squares programme with anisotropic temperature-factor refinement facilities described by Rollett (1961). The atomic scattering factor used for chlorine was that of Dawson (1960), obtained by the polydetor method, with a Hönl correction for anomalous scattering of $-0{\cdot}2$; that of Berghuis *et al.* (1955), which includes the effect of exchange, was used for carbon. The hydrogen atoms were excluded from the refinement. The observed structure amplitudes were weighted by a factor $F_o/8$ or its reciprocal depending respectively on whether $F_o$ was smaller or greater than 8. Unobserved reflexions were included as one-half of the smallest observed structure amplitude, as suggested by Hamilton (1955). Zero weight was given to thirteen strong reflexions, because discrepancies between their observed and calculated values indicated severe extinction. The refinement was stopped after the sixth cycle. Convergence was essentially complete at this stage as judged by the following criteria:

(*a*) $R=0{\cdot}147$, 0·146 after 5th and 6th cycles.

(*b*) $\Sigma w(F_o-F_c)^2/\Sigma kF_o=0{\cdot}0201$, 0·0197 after 5th and 6th cycles. (This quotient is the most suitable quantity that can be calculated from the available output data).

(*d*) During the last three cycles of refinement, the atomic coordinates were stationary or oscillated with small amplitudes about their mean positions; some thermal parameters ($b_{ij}$) were still shifting slowly but the differences between the results of the 5th and 6th cycles were small.

## 3. Results of the least-squares refinement

The final observed and calculated structure factors are listed in Table 2 and the refined position and motion parameters in Table 3. The $b_{ij}$ are such that they give the temperature factor when inserted into the expression

$$\exp-(b_{11}h^2+b_{12}hk+b_{13}hl+b_{22}k^2+b_{23}kl+b_{33}l^2)\,.$$

The numbering used for the atoms is shown in Fig. 1. Before these results can be used to establish the molecular configuration and thermal motion, the fractional coordinates have to be converted to absolute coordinates $(x, y, z)$ and the $b_{ij}$ transformed to $U_{ij}$ (Cruickshank, 1956*a*) using equations of the type

$$2\pi^2a^{*2}U_{11}=b_{11},\ 2(2\pi^2a^*b^*U_{12})=b_{12}\ \text{etc.}$$

Table 4. *Atomic coordinates and thermal-vibration parameters referred to molecular axes (see text for definition)*

Calculated $V_{ij}$ values derived from translational and librational tensors

| | Coordinates in Å | | | Thermal-vibration parameters in Å² | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $V_{11}$ | | $V_{22}$ | | $V_{33}$ | | $V_{12}$ | | $V_{13}$ | | $V_{23}$ | |
| Atom | *X* | *Y* | *Z* | obs. | calc. | obs. | calc. | obs. | calc. | obs. | calc. | obs. | calc. | obs. | calc. |
| $Cl_1$ | $\overline{3\cdot142}$ | 1·473 | 0·166 | 0·0307 | 0·0393 | 0·0671 | 0·0698 | 0·0838 | 0·0815 | 0·0113 | 0·0099 | $\overline{0\cdot0092}$ | $\overline{0\cdot0078}$ | $\overline{0\cdot0045}$ | $\overline{0\cdot0005}$ |
| $Cl_2$ | $\overline{3\cdot115}$ | $\overline{1\cdot509}$ | $\overline{0\cdot218}$ | 0·0331 | 0·0397 | 0·0716 | 0·0681 | 0·0496 | 0·0514 | $\overline{0\cdot0168}$ | $\overline{0\cdot0125}$ | 0·0048 | 0·0007 | $\overline{0\cdot0040}$ | $\overline{0\cdot0054}$ |
| $C_1$ | $\overline{0\cdot714}$ | 2·430 | 0·021 | 0·0542 | 0·0483 | 0·0616 | 0·0463 | 0·0525 | 0·0565 | 0·0084 | 0·0029 | $\overline{0\cdot0211}$ | $\overline{0\cdot0025}$ | $\overline{0\cdot0024}$ | $\overline{0\cdot0054}$ |
| $C_2$ | $\overline{1\cdot416}$ | 1·273 | 0·047 | 0·0405 | 0·0379 | 0·0366 | 0·0500 | 0·0528 | 0·0276 | 0·0025 | 0·0031 | 0·0009 | $\overline{0\cdot0028}$ | $\overline{0\cdot0094}$ | $\overline{0\cdot0025}$ |
| $C_3$ | $\overline{0\cdot720}$ | 0·000 | 0·000 | 0·0464 | 0·0340 | 0·0420 | 0·0463 | $\overline{0\cdot0004}$ | 0·0003 | 0·0059 | $\overline{0\cdot0613}$ | 0·0037 | $\overline{0\cdot0007}$ | 0·0026 | $\overline{0\cdot0018}$ |
| $C_4$ | $\overline{1\cdot375}$ | $\overline{1\cdot309}$ | $\overline{0\cdot061}$ | 0·0387 | 0·0382 | 0·0463 | 0·0495 | 0·0185 | 0·0162 | $\overline{0\cdot0104}$ | $\overline{0\cdot0056}$ | $\overline{0\cdot0034}$ | $\overline{0\cdot0003}$ | $\overline{0\cdot0129}$ | $\overline{0\cdot0029}$ |
| $C_5$ | $\overline{0\cdot687}$ | $\overline{2\cdot469}$ | $\overline{0\cdot017}$ | 0·0424 | 0·0487 | 0·0511 | 0·0462 | 0·0505 | 0·0469 | $\overline{0\cdot0099}$ | $\overline{0\cdot0054}$ | 0·0096 | 0·0001 | 0·0070 | $\overline{0\cdot0053}$ |

## 4. Analysis of the thermal motion

The thermal motions of each atom have been combined to give the translational and librational rigid-body motions of the molecule by the method of Cruickshank (1956*b*). The first step in this procedure is the geometrical transformation of the atomic coordinates, and the orthonormal tensor transformation of the $U_{ij}$, from the crystallographic to the molecular axes. The molecular axes ($X$, $Y$, $Z$) have been chosen as follows (see Fig. 3).

Origin at $(\frac{1}{4}, \frac{1}{4}, z_{C_3})$.
Positive $X$ from the origin to $C_3'$;
$Y$ perpendicular to $X$ and [001], with its positive direction approximately in the $[\bar{1}10]$ direction;
$Z$ parallel to the crystallographic [001] axis.

The origin defined above is referred to as the 'molecular origin' in the rest of this paper. The $(x, y, z)$ and $U_{ij}$ have been designated $(X, Y, Z)$ and $V_{ij}$ respectively with respect to the molecular axes and their values are listed in Table 4.

The $X$, $Y$, $Z$ and $V_{ij}$ (all weighted equally) were then used to obtain the twelfth-order* normal equations which were solved for the $T_{ij}$ components of the translational tensor and the $\omega_{ij}$ components of the librational tensor using a Stantec Zebra computer. The standard deviations of the $T_{ij}$ and $\omega_{ij}$ were obtained according to the method outlined by Cruickshank (1956*b*) which involves the reconstruction of the $V_{ij}$ from the $T_{ij}$ and $\omega_{ij}$. The differences between the calculated and observed $V_{ij}$ (see Table 4) are then used to determine the variance of $V_{ij}(\sigma^2(V))$ which then leads to the variances of the $T_{ij}$ or $w_{ij}(\sigma^2(A_p))$ when substituted in the equation

$$\sigma^2(A_p) = C_{pp}^{-1}\sigma^2(V)\ .$$

Here $C_{pp}^{-1}$ is the appropriate diagonal element of the matrix inverse to that constituting the left-hand side of the normal equations. Table 5 gives the values of $T_{ij}$ and $\omega_{ij}$ and their standard deviations.

Table 5. *Elements of translational* ($T_{ij}$) *and vibrational* ($\omega_{ij}$) *tensors and their standard deviations*

| $ij$ | $T_{ij}$ (Å$^2$) | $\sigma(T_{ij})$ | $\omega_{ij}$ (rad.$^2$) | $\sigma(\omega_{ij})$ |
|---|---|---|---|---|
| 11 | 0·034 | 0·003 | 0·0085 | 0·0005 |
| 22 | 0·045 | 0·004 | 0·0051 | 0·0002 |
| 33 | $\overline{0{\cdot}002}$ | 0·006 | 0·0024 | 0·0002 |
| 12 | 0·006 | 0·003 | 0·0016 | 0·0002 |
| 23 | $\overline{0{\cdot}001}$ | 0·004 | 0·0001 | 0·0002 |
| 13 | $\overline{0{\cdot}002}$ | 0·004 | 0·0005 | 0·0003 |

Table 6. *Diagonal elements of translational and vibrational tensors after transformation of the tensors to their principal axes*

| $ij$ | $T_{ij}$ (Å$^2$) | $(T_{ij})^{\frac{1}{2}}$ (Å) | $\omega_{ij}$ (rad.$^2$) | $(\omega_{ij})^{\frac{1}{2}}$ (°) |
|---|---|---|---|---|
| 11 | 0·031 | 0·18 | 0·0092 | 5·5 |
| 22 | 0·048 | 0·22 | 0·0045 | 3·8 |
| 33 | $\overline{0{\cdot}002}$ | 0·04<br>imaginary | 0·0024 | 2·8 |

Transforming these tensors to their principal axes eliminates the non-diagonal terms. This has been done and the resultant tensors are given in Table 6 together with the square root of each term which represents the root-mean-square translational or librational amplitude respectively along or about the two sets of appropriate axes.

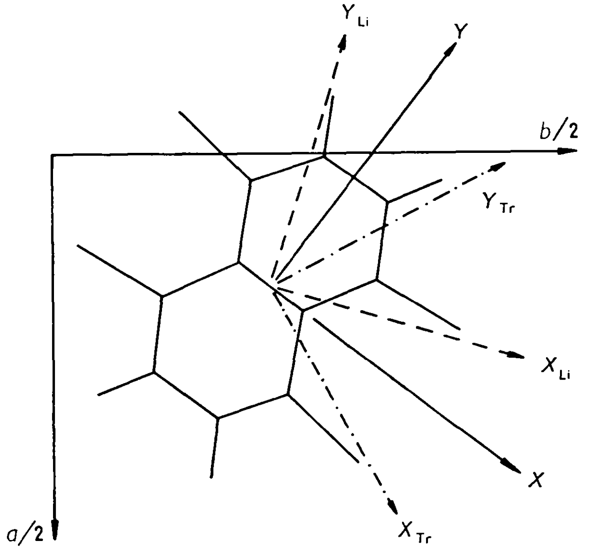


Fig. 3. Molecular axes and principal axes of the translational ($T_{ij}$) and librational tensors ($\omega_{ij}$).

The principal axes ($X_{Tr}$, $Y_{Tr}$ and $Z_{Tr}$ (see Fig. 3)) of the translational tensor $T_{ij}$ are insignificantly displaced (within 5°) from the situation where

$X_{Tr}$ is normal to $Y_{Tr}$ and parallel to (001).
$Y_{Tr}$ is parallel to $[\bar{1}10]$ and is drawn as passing through the centre of the $C_3$–$C_3'$ bond.
$Z_{Tr}$ is parallel to the crystallographic [001] axis.

The translation of the molecule is thus almost isotropic in the plane normal to [001] but has a slightly larger amplitude in the $[\bar{1}10]$ direction in which the molecules in one stack move in between those in the adjacent stack.

The accuracy with which the principal axes of motion can be determined depends on the anisotropy of the motion and the standard deviations of the

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* Assumption of $D_2$ symmetry for the thermal motion of the molecule would have reduced the order of the equations to eight. This would have forced a symmetry on the results which might not have been possessed by the thermal-motion parameters from the L.S. analysis. As this symmetry should be shown, rather than assumed to exist, the twelfth-order calculation was done and the results found to be consistent with $D_2$ symmetry. This is independent proof of the overall correctness of the thermal-motion parameters obtained from the refinement.

elements of the motion tensor. As the translational movement is almost isotropic in the (001) plane ($T_{22}-T_{11} \sim 2\sigma(T_{ij})$) and the non-diagonal terms are of magnitude comparable with their standard deviations, the determined directions of $X_{Tr}$ and $Y_{Tr}$ are not statistically significant. The negative value of $T_{33}$ is anomalous as it leads to an imaginary root-mean-square translational amplitude in the $Z$ direction; $T_{33}$ is only one-half of its standard deviation, however, and can be taken as zero, thus implying no translational movement along $Z$. This result is unexpected but does not appear to be a consequence of the assumption that the atomic vibrations can be explained entirely in terms of rigid-body motions of the molecules. The absence of $Z$-direction translation in the naphthalene ring can be seen qualitatively from the linear dependence of the $b_{33}$ values (Table 3) on the distances of the atoms from the molecular origin. This being so, the thermal motions in the $Z$ direction must result almost exclusively from librations about the $X$ and $Y$ axes, as found from the full tensor analysis. Errors are to be expected in the absolute values of the $b_{33}$ due to the method of scaling, which forced an overall isotropy on the thermal motions. However such errors cannot be held responsible for the unexpectedly small value of $T_{33}$ as they can alter only the scale of the results obtained but not their nature.

The calculated and observed values of $V_{ij}$ (Table 4) agree within the limits of error except for the $V_{11}$ values for $Cl_1$ and $Cl_2$. In particular there are no discrepancies in the $V_{22}$ and $V_{33}$ values of the chlorine atoms, suggesting that there are no large intramolecular vibrations tending to increase the separation of the chlorine atoms. We have not been able to find a physical explanation for the discrepancies (particularly their signs) in the $V_{11}$ terms, and these may result from the weighting scheme used in setting up the normal equations for the vibrational tensors.

The principal axes of the librational tensor deviate from the molecular axes by approximately the same angle as those of the translational tensor, but are rotated in the opposite direction (see Fig. 3). The large $\omega_{11}$ and $w_{22}$ restore a measure of (possibly artificial) isotropy to the individual atomic motions; simultaneous movement of all the atoms in one molecule along the $Z$ axis is the only prohibited movement.

## 5. Correction of the atomic coordinates for the effects of rotational oscillations of the molecule

Cruickshank's revised method (1961) has been used to correct the atomic coordinates for the small apparent shifts resulting from rotational oscillations of the molecule. This method assumes that the shape of the atomic peak is Gaussian and a breadth parameter $q^2$ is needed to describe it. A value for $q^2$ can be obtained from an electron-density map but as this was not available to us, the value of 0·1 Å$^2$, obtained by Cruickshank (1956*c*) for the carbon atoms in anthracene, was used for both carbon and chlorine atoms. This is unlikely to influence the results significantly as they are not sensitively dependent on the choice of $q^2$. The largest correction was found to be 0·01 Å. The rotation-corrected coordinates are given in Table 7.

Table 7. *Final atomic coordinates after correction for effects of molecular rotational oscillations*

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| $Cl_1$ | 0·740 Å | 2·228 Å | 1·246 Å |
| $Cl_2$ | 1·599 | 0·409 | 0·862 |
| $C_1$ | 0·004 | 4·716 | 1·101 |
| $C_2$ | 0·476 | 3·454 | 1·127 |
| $C_3$ | 1·896 | 3·212 | 1·080 |
| $C_4$ | 2·515 | 1·892 | 1·019 |
| $C_5$ | 3·843 | 1·712 | 1·061 |
| $H_1$ | 1·063 | 4·880 | 1·101 |
| $H_2$ | 4·254 | 0·713 | 1·061 |

The hydrogen positions have been calculated on the assumptions that the C–H distance is 1·08 Å and that they lie on the lines between $C_3'$ and $C_1$ and $C_3'$ and $C_5$ respectively and have the same $z$ coordinates as the C atoms to which they are attached.

## 6. Comparison of present results with those of Davydova & Struchkov (1961)

Davydova & Struchkov based their determination of this crystal structure on 350 non-zero intensities obtained with Mo $K\alpha$ radiation. The structure was refined by three-dimensional Fourier methods, using an overall isotropic temperature factor ($\langle B\rangle = 3{\cdot}7$ Å$^2$). The final value of $R$ was 15%. The atomic coordinates from the two analyses agree within their combined errors, except for the $x$ coordinates of $C_4$ (nomenclature of this paper) which differ by 0·075 Å. Consequently the molecular dimensions are in close, although not exact, agreement. The most important difference is that Davydova & Struchkov found their molecular parameters to be in accordance with molecular symmetry $D_2$ whereas we find small, but significant, deviations from this symmetry. As our refinement was carried further than theirs, and as our estimated standard deviations are somewhat smaller, the following discussion of molecular geometry will be entirely in terms of our results given in Fig. 4.

## 7. Molecular geometry

The bond lengths and angles, atomic nomenclature and distances of the atoms from the mean carbon plane are given in Fig. 4, together with the relevant standard deviations.

The overcrowding of the chlorine atoms is relieved by out-of-plane displacements of approximately 0·2 Å, and in-plane bending apart of the C–Cl bonds by 4° each. Analogous but larger out-of-plane displacements of 0·73 Å have been reported by Donaldson & Robert-

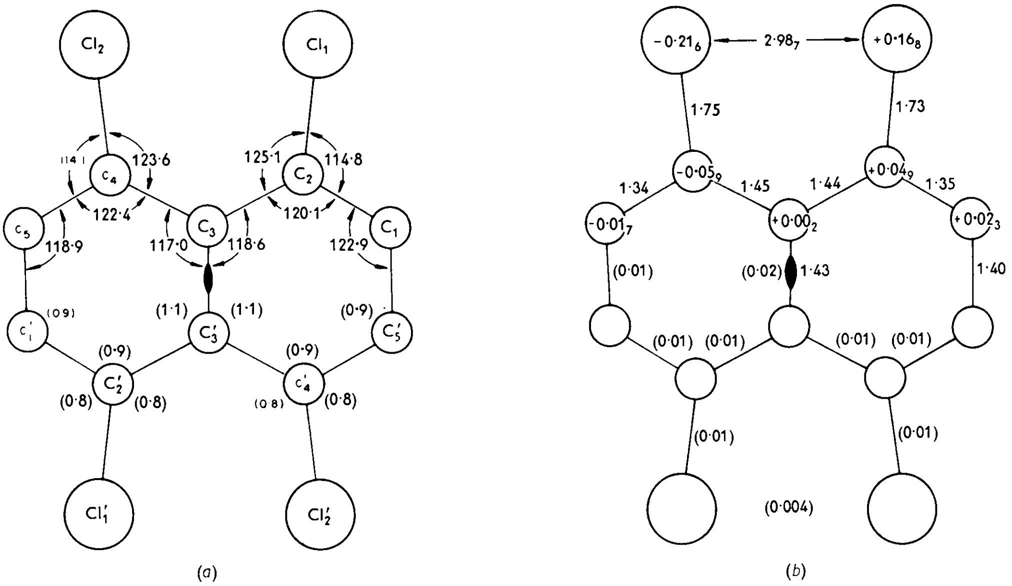

Fig. 4. (*a*) Atomic nomenclature, bond angles and their standard deviations in degrees, (*b*) distances of the atoms above the mean carbon plane, interatomic distances and their standard deviations in Å.

son (1953) for the α-methyl groups in octamethylnaphthalene. $d(\mathrm{Cl}\cdots\mathrm{Cl})$ is 2·99 Å, which is the shortest value yet reported for the intramolecular distance between non-bonded chlorine atoms. In 4 : 4′-dichloroacenaphthene (Avoyan & Struchkov, 1961), where the overcrowding is formally similar to that in 1:4:5:8-tetrachloronaphthalene, $d(\mathrm{Cl}\cdots\mathrm{Cl})=$ 3·12 Å; the distortion of the acenaphthene nucleus itself leads to an increased distance between chlorine atoms and to reduced out-of-plane displacements. Other comparable values are $d(\alpha\text{-CH}_3\cdots\alpha\text{-CH}_3)$ = 2·98 Å in octamethylnaphthalene and $d(\mathrm{Cl}\cdots\mathrm{O})$ = 2·79 Å in 1:5-dichloroanthraquinone (Bailey, 1958).

The crystal structures of three naphthalene compounds which are overcrowded due to the presence of bulky substituents have been determined: these are octamethylnaphthalene, 1:4:5:8-tetrachloronaphthalene and tetrabenzonaphthalene (Herbstein & Schmidt, 1954). None of these molecules is centrosymmetric, while the first two have (at least) two-fold axes normal to the mean plane of the naphthalene ring system. On the other hand the only substituted benzene derivative reported to show deviations from planarity is chloranil (Ueda, 1962; Chu, Jeffrey & Sakurai, 1962), which is centrosymmetric. This difference can be explained by considering the buttressing effects of adjacent atoms and the following general rule can be proposed for free molecules whose chemical constitution would permit them to have either $C_i$–$\bar{1}$ or $D_2$–222 symmetry, and where there are sufficient large substituents to cause some buttressing between all the adjacent peripheral atoms: those molecules with an even number of pairs of possible substituent positions will have $D_2$ symmetry and those with an odd number $C_i$ symmetry. Packing of such molecules in crystals may result in loss of exact symmetry; this happens for 1:4:5:8-tetrachloronaphthalene (molecular symmetry in crystal $C_2$) but not for octamethylnaphthalene ($D_2$). Only the buttressing effect has been considered in formulating this rule but (as Dr Hirshfeld has pointed out to us) skeletal strain must also play a role in determining molecular conformation. The difficulty of making predictions is illustrated by 1:5-dichloroanthraquinone (Bailey, 1958); here the molecular symmetry is $C_i$, in agreement with the rule but the overcrowding is relieved by a mechanism rather different from that in 1:4:5:8-tetrachloronaphthalene. In 1:5-dichloroanthraquinone, the quinoid ring-system is chair-shaped while the two benzenoid rings, and the substituted chlorines, are in one plane. The oxygen atoms project 0·29 Å above and below this plane, and the quinoid carbons 0·14 Å in the same directions. The bond angles are changed so that the chlorine atoms are splayed outwards.

None of the three substituted naphthalene molecules mentioned above possesses a centre or mirror plane of symmetry: therefore these molecules must occur as optical enantiomorphs. However, all three crystallize in centrosymmetric crystals, which must therefore contain both mirror-image forms. There is no spontaneous resolution on crystallization such as is found with a number of asymmetric molecules.

The naphthalene nucleus is significantly non-planar with the $C_2$ and $C_4$ atoms displaced in the same directions as the chlorine atoms bonded to them. Table 8 allows comparison of the C–C bond lengths with those in the naphthalene molecule which are the weighted mean of three analyses as reported by Cruickshank & Sparks (1960). The maximum difference between equivalent bonds in tetrachloronaph-

Table 8. *Comparison of* C–C *bond lengths in* 1:4:5:8-*tetrachloronaphthalene and naphthalene*

The mean standard deviation of the first set of results is 0·010 Å, and of the second set 0·005 Å. The standard deviation ($\sigma$) of differences between the two sets is 0·011 Å

| Atom pair | Bond lengths in $C_{10}Cl_4H_4$ ($l_{TCN}$) | $C_{10}H_8$ ($l_N$) | $l_{TCN}-l_N$ | $\lvert l_{TCN}-l_N\rvert/\sigma$ |
|---|---|---|---|---|
| $C_1$–$C_2$ | 1·348 Å | 1·364 Å | −0·016 Å | 1·45 |
| $C_2$–$C_3$ | 1·441 | 1·421 | 0·020 | 1·82 |
| $C_3$–$C_4$ | 1·455 | 1·421 | 0·034 | 3·09 |
| $C_4$–$C_5$ | 1·340 | 1·364 | −0·024 | 2·19 |
| $C_5$–$C_1'$ | 1·398 | 1·415 | −0·017 | 1·55 |
| $C_3$–$C_3'$ | 1·434 | 1·418 | 0·016 | 1·45 |
| Mean | 1·403 Å | 1·402 Å | | |

thalene and naphthalene is 0·034 Å and the mean values agree to the last significant figure. Although the differences are not statistically significant (except perhaps for $C_3$–$C_4$), it is interesting to note that they do form a pattern which is consistent with the effect that the overcrowding would be expected to have on an elastic naphthalene nucleus, i.e. $C_2$–$C_3$, $C_3$–$C_4$ and $C_3$–$C_3'$ are longer, whereas $C_1$–$C_2$ and $C_1$–$C_5'$ are shorter than in naphthalene.

The mean C–Cl distance is found to be 1·740 ± 0·007 Å and is in agreement with values found for 9:10-dichloroanthracene (1·74 ± 0·015 Å; Trotter, 1959), 4-4′ dichlorodiphenylsulphone (1·736 ± 0·007 Å; Sime & Abrahams, 1960), *p*-dichlorobenzene at −140 °C. (1·74 ± 0·01 Å; Frasson, Garbuglio & Bezzi, 1959), tetrachloro-hydroquinone (1·733 ± 0·011 Å; Sakurai, 1962, 4:4′-dichloroacenaphthene (1·75 ± 0·01 Å; Avoyan & Struchkov, 1961) and *o*-chlorobenzoic acid (1·737 ± 0·007 Å; Ferguson & Sim, 1961). There are, however, some other aromatic compounds in which the C–Cl distances have been found to be closer to 1·70 Å. One recent example is 1:3:5-trichlorobenzene (1·71 ± 0·01 Å, Milledge & Pant, 1960) while the value given for the aromatic C–Cl bond length in the *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1958) is 1·70 ± 0·01 Å. For chloranil two different values have been given for *d*(C–Cl): 1·714 ± 0·008 Å by Chu *et al.* (1962) and 1·749 ± 0·012 Å by Ueda (1961). The shorter value is in agreement with the nuclear quadrupole resonance data (Chu *et al.*, 1962). The accuracy of these bond-length determinations is not quite high enough for an unequivocal discussion of the apparent differences.

The mean plane of the carbon atoms is through $z = 1{\cdot}078$ Å and the standard deviation of this parameter is 0·002 Å. This, together with the fact that the standard deviation of the *z* coordinates of the chlorine atoms is 0·003 Å leads to the conclusion that the asymmetry of the chlorine atoms, which are 0·17 Å above and 0·22 Å below the carbon plane, is highly significant.

The asymmetry of the chlorine atoms cannot be readily explained but some asymmetry is to be expected as the molecules are unsymmetrically disposed with respect to one another within the stacks and this must result in an asymmetry in the packing forces. A consequence of this is that the molecular symmetry is not higher than that required by the space group i.e. $C_2$–2. The departure of the chlorine atoms from $D_2$–222, the symmetry that the molecule would be expected to possess in the gas phase, is highly significant.

## 8. Packing of the molecules

The molecules are arranged in stacks along [001]. These stacks are very nearly hexagonally packed (see Fig. 5). For an exact hexagonal arrangement $b/a = \sqrt{3}$, whereas here $b/a = 1{\cdot}614$. The angle between [100] and [110] is 58° 13′ and that between [110] and $[\bar{1}10]$ is 63° 34′. The closest contacts between stacks in which the molecules are at the same mean *z* coor-

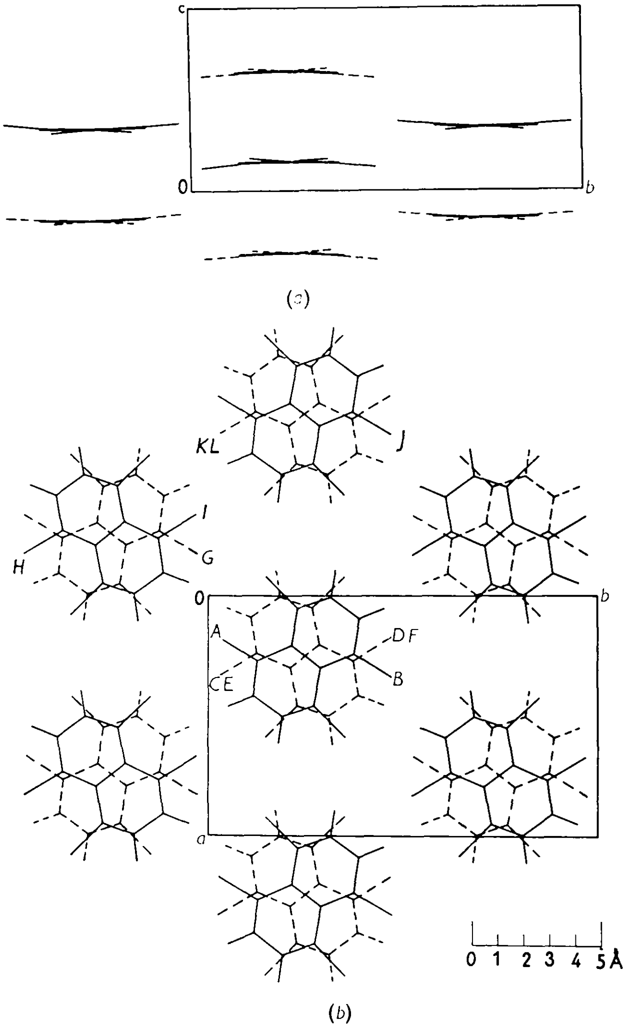

Fig. 5. Arrangement of molecules in the crystal in projection down (*a*) [100] and (*b*) [001].

dinates (i.e. the row of stacks along [100]) are between chlorine and hydrogen atoms. As an example one may take the contacts between asymmetric units *A* and *J*, where $d(\mathrm{Cl}\cdots\mathrm{H}) = 2{\cdot}91$ Å. In contrast, the close contacts between stacks in which the molecules are staggered with respect to those in the adjacent stack (i.e. [110] and [$\bar{1}$10] rows), are through chlorine–chlorine approaches with only one close hydrogen–chlorine contact. The close Cl ··· Cl distances are between *A* and *G* (3·49 Å) and *A* and *I* (3·80 Å). The close Cl ··· H distance is also between *A* and *I* (2·82 Å) and is somewhat less than the sum of the van der Waals radii of chlorine (1·8 Å) and hydrogen (1·2 Å). All types of atom interact fairly closely within the molecular stacks i.e. in the [001] direction, but C ··· C and C ··· Cl contacts appear to be more important than Cl ··· Cl (3·83 Å). Table 9 lists the pairs of atoms which are separated by less than 1·1 times the sum of their van der Waals radii. The designations of the neighbouring asymmetric units is shown in Fig. 5(*b*), the designating letters being inserted at the $Cl_2$ position of each asymmetric unit.

Table 9. *Intermolecular distances*

Only those values have been listed which are less than 1·1 times the sum of the van der Waals radii

| Atom in the parent (*A*) asymmetric unit | Neighbouring asymmetric unit (see Fig. 5) | Atom in the neighbouring asymmetric unit | Interatomic distance |
|---|---|---|---|
| $Cl_1$ | *C* | $C_5$ | 3·74 Å |
| $Cl_2$ | | $Cl_2$ | 3·83 |
| $C_3$ | | $C_3$ | 3·65 |
| $C_4$ | | $Cl_2$ | 3·73 |
| | | $C_4$ | 3·55 |
| $C_5$ | | $Cl_2$ | 3·65 |
| $Cl_1$ | *D* | $C_1$ | 3·52 |
| $C_1$ | | $Cl_1$ | 3·80 |
| | | $C_2$ | 3·65 |
| $C_2$ | | $C_1$ | 3·60 |
| | | $C_2$ | 3·59 |
| $C_3$ | | $C_3$ | 3·71 |
| $Cl_2$ | *E* | $Cl_2$ | 3·83 |
| | | $C_4$ | 3·73 |
| | | $C_5$ | 3·66 |
| $C_3$ | | $C_3$ | 3·65 |
| $C_4$ | | $C_4$ | 3·55 |
| $C_5$ | | $Cl_1$ | 3·74 |
| $Cl_1$ | *F* | $C_1$ | 3·80 |
| $C_1$ | | $Cl_1$ | 3·52 |
| | | $C_2$ | 3·60 |
| $C_2$ | | $C_1$ | 3·65 |
| | | $C_2$ | 3·59 |
| $C_3$ | | $C_3$ | 3·71 |
| $Cl_1$ | *G* | $Cl_2$ | 3·49 |
| $Cl_2$ | | $Cl_1$ | 3·49 |
| | | $Cl_2$ | 3·73 |
| $Cl_1$ | *I* | $Cl_2$ | 3·80 |
| $Cl_2$ | | $C_5$ | 3·61 |
| | | $H_2$ | 2·82 |
| $Cl_1$ | *J* | $H_1$ | 2·91 |
| $H_1$ | | $Cl_1$ | 2·91 |

The various asymmetric units, designated *A*, *B*, etc., are listed below together with the distances of the mean carbon planes from (001), given as fractions of *c*.

| | | | |
|---|---|---|---|
| *A*, *B*, *J* | 0·15 | *C*, *D*, *K* | 0·65 |
| *E*, *F*, *L* | −0·35 | *G* | −0·15 |
| *H*, *I* | 0·35 | | |

An anomaly of the packing is that the relative positions of molecules in adjacent staggered stacks are such that the origins of the molecules in one stack are approximately 0·35 Å off the mean *z* coordinates of the two nearest molecules in the adjacent stacks. The closest intermolecular approaches in the crystal are $Cl_1(A)\cdots Cl_2(G)$ (3·49 Å), $Cl_2(G)\cdots Cl_1(G)$ (3·49 Å), $Cl_2(A)\cdots Cl_1(G)$ (3·49 Å) and $Cl_2(A)\cdots H_2(I)$ (2·82 Å) and the asymmetric position of the carbon plane is probably mainly due to a balancing of the interactions between these pairs of atoms.

We are indebted to Dr E. Clar for providing the crystals used in this analysis, to Dr J. S. Rollett and Mrs G. E. Peters for the least-squares programme and carrying out the Deuce computations respectively, to Dr D. W. Smits, Dr J. C. Schoone, Dr D. Rogers and Dr J. D. Neethling for various Zebra programmes, to the referee and Dr F. L. Hirshfeld (Weizmann Institute) for helpful criticisms of the manuscript and to Dr J. N. van Niekerk for his interest in this work.

*Note added in proof.*—Improved co-ordinate values were reported by Davydova & Struchkov (1962) after this paper had been submitted for publication. These co-ordinates were in all cases closer to those given in Table 3 than their 1961 values; in particular the discrepancy in the *x* co-ordinates of C4 has been reduced to 0·015 Å. Davydova & Struckhov compare the results of the two analyses in some detail. The good agreement of atomic co-ordinates leads to good agreement of molecular dimensions derived from these two independent investigations.

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# The Crystal Structure of Triphenyl Phosphate

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The space group of triphenyl phosphate is $P2_1/a$ and the unit-cell dimensions

$$a = 17{\cdot}24,\ b = 5{\cdot}86,\ c = 17{\cdot}24\ \text{Å};\ \beta = 104°.$$

The structure was solved by direct methods using visually estimated intensities. The three P–O bonds where the oxygen is joined to a phenyl group are found to be 1·63 Å and the remaining P–O bond is only 1·43 Å. The P–O–C angle is 122°.

## Introduction

Of the phosphates examined in the past there appears to be no example of the phosphate group, $PO_4$, joined to three identical organic groups leaving the fourth oxygen bonded only to the phosphorus atom. Triphenyl phosphate is of this type and although the melting point is low (50 °C.) the crystals were suitable for X-ray examination.

## Experimental

The sample of triphenyl phosphate was prepared using the methods described by Heim (1883) and the German Patent (1923). The material was recrystallized by slowly cooling a solution in alcohol. The crystals were colourless transparent laths.

Oscillation and Weissenberg photographs were taken about the principal axes. The Laue symmetry is $2/m$ and the unit cell dimensions are:

$$a = 17{\cdot}24 \pm 0{\cdot}15,\ b = 5{\cdot}86 \pm 0{\cdot}05,\ c = 17{\cdot}24 \pm 0{\cdot}15\ \text{Å};$$
$$\beta = 104° \pm 30'.$$

The $h0l$ reflexions are absent when $h$ is odd and the $0k0$ reflexions are absent when $k$ is odd. This defines the space group uniquely as $P2_1/a$. The observed density is 1·240 g.cm.$^{-3}$ (Sugden, Reed & Wilkins, 1925) and the density calculated assuming 4 molecules in the unit cell is 1·26 g.cm.$^{-3}$.

The intensities of the reflexions recorded on Weissenberg photographs were estimated visually, Lorentz and polarization corrections applied and placed on an absolute scale by the method of Wilson (1942). The crystals used were small and no correction was made for absorption.

## Analysis of the structure

### [010] *projection*

The Patterson synthesis is shown in Fig. 1. The highest peak is close to $\frac{1}{4}$, $\frac{1}{2}$ and related points. This is likely to be the position of the end of the phos-

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