

## Crystal and Molecular Structures of Overcrowded Halogenated Compounds. VIII.\* Decachlorophenanthrene

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Decachlorophenanthrene,  $C_{14}Cl_{10}$ , is orthorhombic,  $a=5.065$  (3),  $b=17.946$  (6),  $c=18.554$  (5) Å, space group  $Pbcn$ ,  $Z=4$ , molecular symmetry  $C_2$  (2). The structure was solved by *MULTAN* and refined to  $R=0.119$  (1976 reflexions measured with Mo  $K\alpha$  on a Stoe semi-automatic Weissenberg diffractometer). The molecule is highly distorted from planarity, Cl(4) and Cl(5) being 1.43 Å, respectively, above and below the mean molecular plane;  $d[Cl(4)\cdots Cl(5)]=3.099$  (3) Å. Because of the buttressing effect of the other Cl atoms, the phenanthrene skeleton shows less splaying apart than, for example, in 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline [Herbstein, Kapon & Rabinovich, *Israel J. Chem.* (1972), **10**, 537–558]. The crystal structures of decachlorophenanthrene, in which both enantiomers occur, and of benzo[*c*]phenanthrene [Herbstein & Schmidt, *J. Chem. Soc.* (1954), pp. 3302–3314] in which only one enantiomer occurs, are related in the same way as the crystal structures of DL- and L-alanine, and other such racemate-optically active pairs.

### Introduction

Decachlorophenanthrene (DCP), prepared independently by Ballester (1966), Brooks, Collin & Silberman (1966), Weis (1968) and Ishimori, West, Teo & Dahl (1971), is the most highly overcrowded molecule of the series of perchlorinated aromatic hydrocarbons including hexachlorobenzene (crystal structure reported by Brown & Strydom, 1974), octachloronaphthalene (Gafner & Herbstein, 1963) and decachloropyrene (Hazell & Jagner, 1976). The Cl atoms around the periphery of the C skeleton interact in situations similar to those in 4,5-dichlorophenanthrene (one pair), 1,8-dichloronaphthalene (two pairs) and *o*-dichlorobenzene (seven pairs), thus providing an opportunity, somewhat complicated by buttressing effects, of comparing these various types of interaction in one molecule.

### Experimental

#### *Determination and refinement of the structure*

Yellow needles, elongated along [100] and showing {001}, {010}, {021} faces, were obtained by slow cooling of a xylene solution. Cell dimensions [from back-reflexion Weissenberg and inclined-beam oscillation photographs (Herbstein, 1963)] and other crystallographic information are given in Table 1.

The intensities of 1976 independent, non-zero reflexions ( $0kl$ – $3kl$ ) were measured on a semi-automatic Stoe–Weissenberg diffractometer in the  $\omega/2\theta$  mode, with graphite-monochromated Mo  $K\alpha$  radiation. Background, Lorentz, polarization and absorption (Busing

Table 1. *Crystallographic results and other data for decachlorophenanthrene*

$C_{14}Cl_{10}$ , $M=522.69$ , m.p. 252°C*
Orthorhombic
$a=5.065$ (3), $b=17.946$ (6), $c=18.554$ (5) Å
$U=1686.5$ Å <sup>3</sup>
$D_m=2.02$ , $D_c=2.058$ g cm <sup>-3</sup> for $Z=4$
$\mu=16$ cm <sup>-1</sup> for Mo $K\alpha$ radiation
$F(000)=1016$
Wavelengths Cu $K\alpha_1=1.54050$ Å
$K\alpha_2=1.54434$
Systematic absences: $0kl$ absent for $k$ odd
$h0l$ absent for $l$ odd
$hk0$ absent for $h+k$ odd
Space group $Pbcn$ (No. 60)

\* Weis (1968) gives m.p. 238°C, but our value, measured for Weis's sample recrystallized from *o*-xylene, agrees well with those of the other authors [see Ishimori *et al.* (1971) for comparison of m.p.'s]. We have checked that the Ballester, Ishimori and Weis samples are essentially identical crystallographically (Ballester and Ishimori samples supplied by Professor Robert West).

& Levy, 1957) corrections were made. Crystal dimensions were  $0.60 \times 0.25 \times 0.25$  mm. Structure factors were placed on an approximately absolute scale by Wilson's (1942) method.

As there are four molecules in the unit cell and the space group is  $Pbcn$ , the site group symmetry must be  $C_i$  ( $\bar{1}$ ) or  $C_2$  (2); however the first possibility is excluded on chemical grounds. Thus the molecules lie about the twofold axes along [010] but their positions and orientations are not further restricted by symmetry considerations. After an abortive attempt to solve the structure by the Patterson method (this failure was later ascribed to the high degree of peak overlap), *MULTAN* (Germain, Main & Woolfson, 1971) was applied to the 236 reflexions with  $E > 1.75$ . The first *E* map showed the positions of all the atoms. A struc-

\* Part VII: Herbstein, Kapon & Rabinovich (1972).

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ture-factor calculation gave  $R=0.435$ . Atomic scattering factors for C were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for Cl from Dawson (1960); dispersion corrections were applied for Cl. Standard refinement by least squares converged at  $R=0.119$  (goodness of fit 0.41). The weighting scheme was  $w(F_o)=1/[F_o]$  for  $[F_o]>196$  and  $w(F_o)=\frac{1}{1.58}$  for  $[F_o]\leq 196$ . The rather high value of  $R$  is probably due to systematic errors in the intensity measurements; there are no indications that the structure is disordered. The atomic coordinates appear to be reliable but the  $U_{ij}$  values are not accurate enough to warrant analysis of the molecular thermal vibrations [three C atoms have non-positive definite temperature factors; the absolute values of  $U_{11}$  are in doubt because the interlayer scale factors were not measured independently (Lingafelter & Donohue, 1966)]. Final atomic parameters are given in Table 2.\*

Most of the computing was done with the *CRYM* system (Duchamp, Trus & Westphal, 1969).

## Results

### Molecular dimensions

Details of the molecular structure are shown in Figs. 1 and 2. Average standard deviations are  $\sigma(\text{C-Cl})\sim 0.012$ ,  $\sigma(\text{C-C})\sim 0.016$  Å,  $\sigma(\text{C-C-C})\sim 1.7^\circ$ . Best planes through the molecule as a whole, and through various groups of atoms, were determined by the methods of Schomaker, Waser, Marsh & Bergman (1959) and Waser, Marsh & Cordes (1973). Torsion and fold angles [see Herbstein, Kapon & Rabinovich (1972), especially pp. 554-555] were calculated at the C atoms of the ring system. These results are summarized in Table 3 and Figs. 3 and 4, and are compared here with the analogous values for 1,10-dichloro-3,8-dimethyl-

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31669 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

4,7-phenanthroline (DCDMP) (Herbstein *et al.*, 1972, where other comparisons are made).

Table 3. Equations of best planes through various parts of the decachlorophenanthrene molecule

Form of equation is  $AX+BY+CZ=D$  (Å), where  $X, Y, Z$ , are in Å and  $A, B, C$  are direction cosines with respect to the unit-cell axes.

Region	A	B	C	D
Whole molecule	0.8346	0	0.5509	2.555
Ring B	0.7776	0	0.6288	2.917
Ring C	0.7568	-0.3178	0.5712	1.397

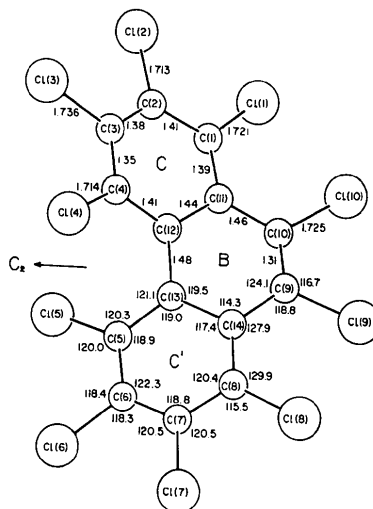


Fig. 1. Numbering scheme, bond lengths and bond angles in DCP. The numbering scheme, based on *Chemical Abstracts*, is the same as that used by Kay, Okaya & Cox (1971) for phenanthrene; chlorines are numbered according to numbering of the carbon skeleton. The nomenclature of the rings is that of Smith & Barrett (1971). Distances between adjacent chlorine atoms are: Cl(4)-Cl(5) 3.099 Å (4,5-dichlorophenanthrene type); Cl(1)-Cl(10) 2.982 Å (1,8-dichloronaphthalene type); Cl(1)-Cl(2) 3.023, Cl(2)-Cl(3) 3.078, Cl(3)-Cl(4) 3.084, Cl(9)-Cl(10) 2.933 Å (*o*-dichlorobenzene type).

Table 2. Decachlorophenanthrene: fractional coordinates ( $\times 10^4$ ) and anisotropic Debye-Waller factors (units of  $10^{-4}$  Å<sup>2</sup>)

Standard deviations in brackets. Anisotropic Debye-Waller factors have the form  $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$ . For atomic numbering see Fig. 1.

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)†	3646 (30)	2451 (6)	1315 (5)	-143 (116)	403 (51)	298 (44)	-180 (58)	-79 (51)	97 (38)
C(2)†	3905 (30)	1774 (7)	936 (6)	-176 (114)	481 (60)	277 (43)	-35 (61)	-50 (52)	43 (41)
C(3)	2216 (31)	1193 (5)	1100 (5)	68 (118)	271 (41)	287 (42)	125 (54)	-35 (53)	-15 (33)
C(4)	655 (29)	1199 (5)	1693 (5)	25 (110)	201 (34)	242 (38)	56 (46)	22 (48)	-21 (30)
C(10)	907 (33)	3183 (5)	2234 (6)	146 (133)	226 (40)	386 (52)	97 (54)	-42 (62)	50 (36)
C(11)†	1907 (29)	2506 (5)	1893 (5)	-109 (111)	255 (38)	281 (40)	85 (48)	-67 (49)	59 (32)
C(12)	706 (30)	1828 (5)	2150 (5)	131 (114)	164 (31)	231 (36)	116 (45)	-45 (49)	26 (27)
Cl(1)	5781 (11)	3149 (2)	1059 (2)	317 (41)	591 (20)	467 (17)	-238 (22)	-58 (20)	212 (15)
Cl(2)	6140 (10)	1691 (2)	248 (2)	299 (40)	692 (22)	336 (13)	127 (23)	145 (18)	153 (14)
Cl(3)	2214 (10)	417 (2)	541 (2)	501 (41)	417 (14)	343 (13)	154 (19)	32 (19)	-130 (11)
Cl(4)	-1720 (9)	519 (1)	1808 (1)	117 (30)	233 (9)	342 (11)	-63 (13)	-37 (14)	-36 (8)
Cl(10)	1837 (12)	4036 (2)	1889 (2)	819 (53)	232 (12)	857 (28)	-194 (20)	162 (31)	90 (15)

† Debye-Waller factor not positive-definite.

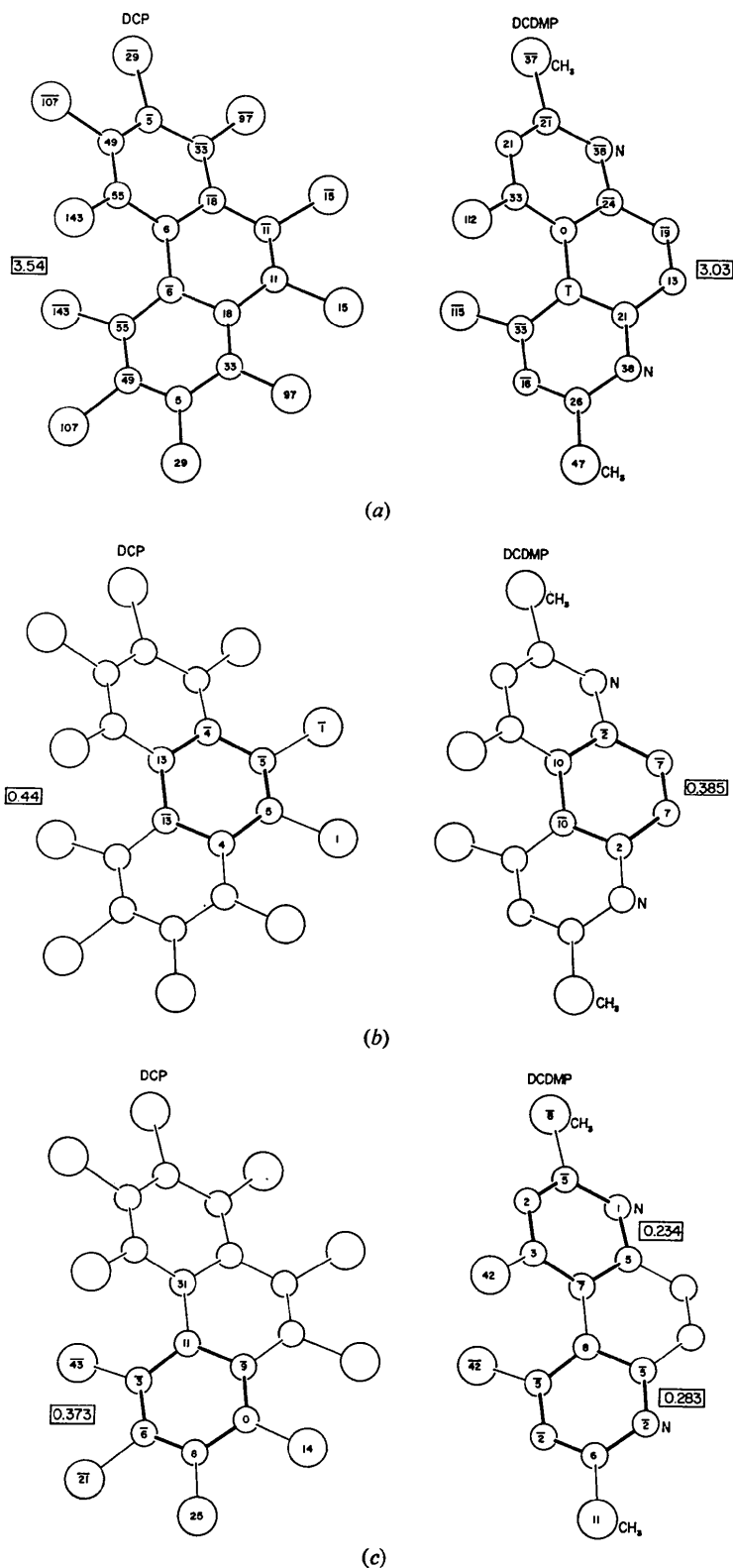


Fig. 2. Deviations ( $10^{-2}\text{\AA}$ ) from planarity in decachlorophenanthrene: (a) the molecule as a whole; (b) ring B; (c) ring C. These values are compared with the analogous quantities in 1,10-dichloro-3,8-dimethyl-4,7-phenanthroline (DCDMP) (Herbstein *et al.*, 1972). The boxed figures give the values for  $\sum |d_j|$  (Å) calculated for ring atoms of each molecule as a whole, and for the individual rings.

### Molecular arrangement

An ORTEP stereo view of the crystal structure is shown in Fig. 5. The molecular symmetry is  $C_2$  (2) and the molecule can therefore exist in two non-superimposable mirror-image forms. Both enantiomers occur in the centrosymmetric crystals, which are therefore racemic. The molecules are arranged in stacks along [100], a particular stack containing molecules of one chirality only.\* It is convenient for later discussion to consider the crystal as made up of infinite slices parallel to (010); these slices contain stacks related by  $2_1$  axes parallel to [100]. Thus each slice contains molecules of one chirality only. The parallel slices along [010] are related by  $a$  glide planes and thus the chirality of the slices alternates along the [010] direction. It is to be emphasized that this is a formal description only and that the intermolecular bonding appears to be reasonably isotropic; the shortest Cl...Cl distance of 3.36 Å (appreciably but not unprecedentedly shorter than the standard van der Waals distance of 3.60 Å) is between Cl(3) in the reference molecule and Cl(3) in the molecule related by the centre of symmetry at the origin.

### Discussion

#### Molecular dimensions

The DCP molecule is distorted similarly to the DCDMP (Herbstein *et al.*, 1972) and 2,7-dibromo-4,5-bis(2-pyridyl)phenanthrene-2,6-diol (DPPD) (Smith & Barrett, 1971) molecules, but the amount of distortion, as judged from the torsion angles, fold angles and deviations from planarity (see boxed sums in Fig. 2) is greatest in DCP. The bond lengths in the phenanthrene ring system do not differ significantly from those in phenanthrene itself (Kay, Okaya & Cox, 1971). There are, however, significant differences in some of the skeletal bond angles between the three molecules DCP, DPPD, and DCDMP (Fig. 4) which derive from the buttressing effects of the additional Cl atoms in DCP. In DCP the component of the displacement of the 4,5 Cl atoms normal to the mean molecular plane is larger than in DCDMP (2.86 Å as against 2.27 Å) whereas the component of in-plane splaying apart is much less (1.10 Å as against 2.075 Å).

The C-Cl lengths (mean 1.724 Å, range 1.713-1.736 Å) are similar to those found in decachloropyrene [mean 1.719 Å, range 1.710-1.732 Å, Hazell *et al.* (1976)]. The mean values straddle the C-Cl length found in hexachlorobenzene [1.722 (2) Å; Brown & Strydom, 1974] which shows only very small (0.01-0.02 Å) deviations from planarity. Rudman (1971) has suggested that, for aromatic compounds, each of two adjacent C-Cl bonds is shorter (average 1.709 Å) than a single C-Cl bond (average 1.737 Å). DCP has seven

\* If the DCP molecule is considered as a member of the helicene family, with the helical axis along the normal to the mean molecular plane, then the enantiomer described by the coordinates of Table 1 and shown in Figs. 1 and 2, is in the *P* (plus) configuration (Cahn, Ingold & Prelog, 1966, p. 391).

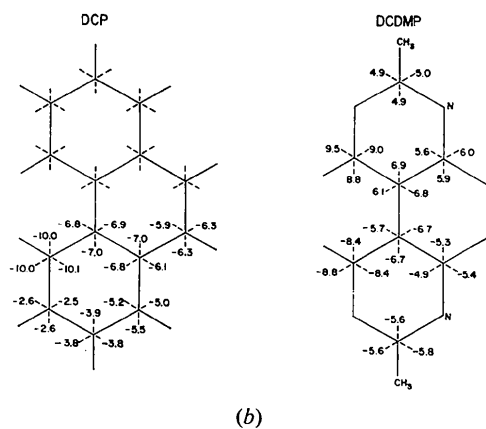
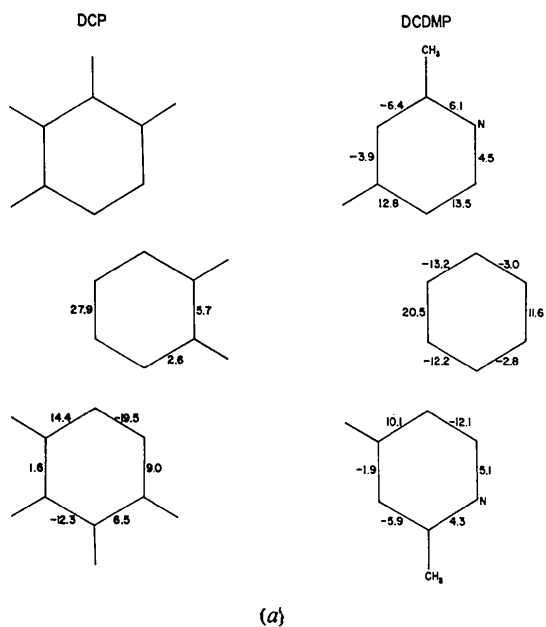


Fig. 3. Comparison of (a) torsion angles and (b) fold angles in DCP and in DCDMP.

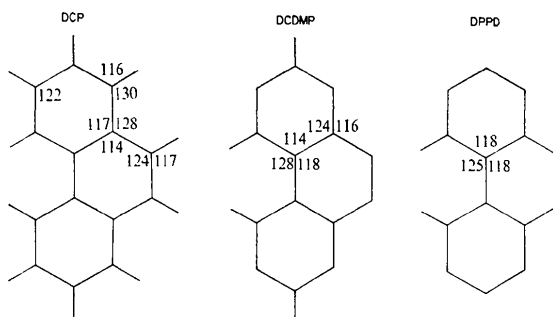


Fig. 4. Comparison of skeletal bond angles in DCP, DCDMP and DPPD. Only those bond angles are shown which deviate by at least 1.5° from 120°; bond angles are rounded off to the nearest degree.

pairs of *ortho* C–Cl bonds, while perchloropyrene has six. Deviations of the C–Cl bond from the mean plane of the C skeleton would tend to increase the bond length (increase of  $sp^3$  character); thus the present results and those for decachloropyrene support Rudman's conclusion, although the results for hexachlorobenzene suggest that the difference is perhaps smaller than he had supposed.

The distance between the Cl atoms in the 4 and 5 positions is 3.099 (5) Å, close to that found in DCDMP [3.082 (3) Å]. The distance between *peri* Cl atoms [Cl(1)···Cl(10)] is 2.982 (5) Å, close to the analogous values found in 1,4,5,8-tetrachloronaphthalene (2.99 Å, Gafner & Herbstein, 1962) and in octachloronaphthalene (3.00 Å, Gafner & Herbstein, 1963); in decachloropyrene the analogous values are 2.996, 2.960, 3.062 and 3.014 Å. Two of the distances between *ortho* Cl atoms in DCP (3.078, 3.084 Å) are only a little shorter than the average of 3.14 Å found for isolated pairs of *ortho* Cl atoms (Rudman, 1971) or the value of 3.11 (1) Å found in hexachlorobenzene (Brown & Strydom, 1974). However, two of these distances (3.023, 2.933 Å) are appreciably shorter; a similar situation is found in decachloropyrene and, to a somewhat lesser extent, in octachloronaphthalene.

#### Molecular arrangement

Some, but not all, of the overcrowded molecules with (exact or approximate)  $C_2$  (2) molecular symmetry crystallize in stacks of superimposed, translationally equivalent molecules. Benzo[*c*]phenanthrene (Herbstein & Schmidt, 1954), 1,12-dimethylbenzo[*c*]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963), hexahelicene (DeRango, Tsoucaris, Declercq, Germain & Putzeys, 1973), 2-bromohexahelicene (Lightner, Hefelfinger, Powers, Frank & Trueblood, 1972), 2-methylhexahelicene (Frank, Hefelfinger & Lightner, 1973; isomorphous with 2-bromohexahelicene), octachlorofulvalene (Wheatley, 1961; Ammon, Wheeler & Agrat, 1973) and DCP belong to this crystal-structure type. DCDMP does not, as the translation unit along the stack axis in the crystal contains two centrosymmetrically related molecules.

A further distinction can be made between those crystals where spontaneous resolution of enantiomers has occurred on crystallization and those where it has not. The first group contains benzo[*c*]phenanthrene (space group  $P2_12_12_1$ ) and the unsubstituted and substituted hexahelicenes ( $P2_12_12_1$ ) as members, and the second group 1,12-dimethylbenzo[*c*]phenanthrene [ $Pbcn$ ,  $a=7.234$ ,  $b=15.120$ ,  $c=12.165$  Å (at  $-80$  K),  $Z=4$ , isostructural with DCP], octachlorofulvalene [ $C2/c$ ,  $Z=4$ , molecular symmetry  $C_2(2)$ ] and DCP. Examination of the crystal structures of these compounds shows a common structural principle: the crystals can all be dissected into parallel slices containing molecules of one chirality only, the molecules being arranged in stacks of superimposed translationally equivalent molecules. In the first group adjacent parallel slices are related by a twofold screw axis, and hence all slices are optically equivalent, the crystal containing one type of enantiomer. In the second group adjacent slices are related by glide planes (and centres of symmetry) and hence the chirality of the molecules alternates from one slice to the next. {The  $C2/c$  polymorph of dibenzo[*c,g*]phenanthrene (McIntosh, Robertson & Vand, 1954) crystallizes in stacks of superimposed, translationally equivalent molecules but represents an intermediate situation as some slices parallel to (100) are segregated with respect to molecular chirality whereas other slices contain both enantiomers (see Fig. 2 of McIntosh *et al.*, 1954).}

This situation is a variation on a theme already developed in the amino acid field. Ickert (1962) pointed out that DL-alanine has (100) planes occupied exclusively by D or L-enantiomers and predicted the crystal structure of L-alanine on this basis. Simpson & Marsh (1966) confirmed Ickert's prediction in their determination of the crystal structure of L-alanine, and further generalizations to other racemate-optically active pairs have been made by Pedone & Benedetti (1972) and Benedetti, Pedone & Sirigu (1973). For the amino (and other) acids, enantiomers and racemates are separately available for the *same* chemical species, whereas for the overcrowded molecules the comparisons have to be made between different chemical species. However the

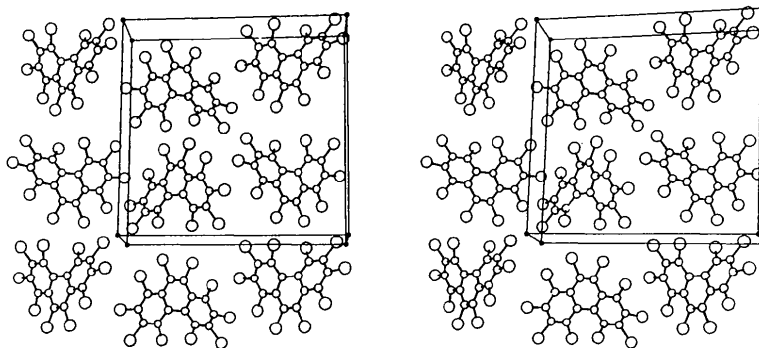


Fig. 5. ORTEP (Johnson, 1965) stereo view of molecular arrangement viewed along [100]. The reference molecule (coordinates in Table 2) is at the lower left hand corner of the unit cell.

same principle applies in both: the existence in a pair of optically active and racemic structures, of a conservative plane of close-packed congruent molecules, whose repetitions by the appropriate symmetry elements generate the two structures [statement adapted from Pedone & Benedetti (1972)].

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