Fig. 4. Molecular packing along the *b* axis. Dashed lines indicate the hydrogen bonds.

C(3')–C(4')–C(5')–O(5') = –173·2°; Table 5], introducing no short contacts between O(5') and the base atoms in contrast to the 2,2'-(O)-cyclocytidine derivatives (Brennan & Sundaralingam, 1973; Yamagata, Koshibe, Tokuoka, Fujii, Fujiwara, Kanai & Tomita, 1979; Yamagata, Suzuki, Fujii, Fujiwara & Tomita, 1979) where the C(5')–O(5') bond relative to the sugar ring is *gauche–gauche*.

(c) *Molecular packing*

The molecular packing along the *b* axis is shown in Fig. 4.

The base plane is nearly parallel to (010), but no base stacking is observed. There are two kinds of hydrogen bond, as shown in Fig. 4, *i.e.* O(3')–H···

O(4) (2·819 Å) and O(5')–H···O(4) (2·790 Å), where O(4) participates in hydrogen bonding as a unique acceptor.

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The Structures of 5-Phenyl-2,4-pentadienoic Acid (PPA) and 1,5-Diphenyl-2,4-pentadien-1-one (DPO)

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Abstract

The crystal structures of PPA and DPO have been determined from visually estimated Cu $K\alpha$ data, and refined to R values of 0·096 and 0·098 for 1973 and 804 non-zero reflexions, respectively. The unit cells are:

Pcab, $a = 10·49$ (1), $b = 37·47$ (6), $c = 9·50$ (2) Å, $Z = 16$ for PPA; and *Pcab*, $a = 15·49$ (2), $b = 16·51$ (3), $c = 10·34$ (2) Å, $Z = 8$ for DPO. The molecules take *trans-trans-s-cis* conformations in both crystals. Two molecules in PPA form a noncentrosymmetric hydrogen-bonded dimer, which takes a propeller-like

conformation, while the molecule in DPO is planar. The molecules are arranged in a herring-bone manner in these crystals as observed generally in those of polyene-type compounds in *Pbca*. The morphotropism of the crystals of the polyenes is discussed in connexion with crystal design for photoreactivity. It is also shown that the structures of representative monocarboxylic acids can be morphotropically derived from that of PPA, acrylic acid (*Ibam*) or formic acid (*Pna2₁*) for the respective hydrogen-bond type.

Introduction

The present work forms part of topochemical studies on olefinic compounds containing a benzene ring or a carboxyl group (Ohkura, Kashino & Haisa, 1973; Shimizu, Kekka, Kashino & Haisa, 1974). The early studies are mainly concerned with centrosymmetric molecules (Nakanishi, Ueno & Sasada, 1978a,b), but the general principle including noncentrosymmetric molecules is applicable. The crystal structures of PPA and DPO have been determined for comparison with a series of polyene-type compounds, and for examination of the mechanism of the topochemical formation of the photoproducts of PPA (Green, Lahav & Schmidt, 1971). A systematization of the crystal structures of monocarboxylic acids is discussed on the basis of morphotropism (Haisa, 1978); this leads to a better understanding of the packing modes of carboxylic acids by Leiserowitz (1976).

Table 1. *Crystal data and experimental details*

	PPA*	DPO*
M_r	174·2	234·3
m.p. (K)	442–444 (in a sealed glass capillary) (sublimes)	376–378
Morphology	Colourless plates, (010) developed and elongated along c	Yellow plates, (001) developed and bounded by {120}
Systematic absences	0kl, l odd; h0l, h odd; hk0, k odd	0kl, l odd; h0l, h odd; hk0, k odd
Space group	$Pcab\ (D_{2h}^{15})$	$Pcab\ (D_{2h}^{15})$
a (Å)	10·49 (1)	15·49 (2)
b (Å)	37·47 (6)	16·51 (3)
c (Å)	9·50 (2)	10·34 (2)
$V\ (Å^3)$	3734 (10)	2644 (6)
Z	16	8
$D_x\ (Mg\ m^{-3})$	1·239	1·177
$D_m\ (Mg\ m^{-3})$	1·22	1·18
Flotation mixture	KBr–H₂O	KI–H₂O
$\mu\ (mm^{-1})$ for Cu $K\alpha$	0·70	0·57
F(000)	1472	992
Dimensions of specimens used (mm)	0·40 × 0·22 × 0·68 0·35 × 0·22 × 0·65	0·40 × 0·38 × 0·15 0·60 × 0·38 × 0·06
Layers photographed	hk0 to hk7; 0kl to 7kl	hk0 to hk8; 0kl to 8kl
Non-zero reflexions	1973	804
Percentage accessible	46	27
B from Wilson's plot	6·7 Å²	7·4 Å²

* PPA: C₆H₅CH=CHCH=CHCOOH. DPO: C₆H₅CH=CHCH=CHCOC₆H₅.

Experimental

Crystals of PPA and DPO were grown from ethanol solutions by slow evaporation. Intensities were estimated visually on equi-inclination Weissenberg photographs and were corrected for Lorentz and polarization factors and for spot shape. Crystal data and experimental details are summarized in Table 1.

Structure determination and refinement

The structures of PPA and DPO were solved by the symbolic addition procedure and by the Patterson

Table 2. *The final positional parameters* $(\times 10^4)$ *of the non-hydrogen atoms with standard deviations in parentheses*

	x	y	z
(a) PPA			
O(1A)	2168 (3)	839 (1)	4498 (3)
O(2A)	251 (3)	600 (1)	4263 (3)
C(1A)	1125 (4)	822 (1)	3902 (4)
C(2A)	808 (4)	1052 (1)	2704 (4)
C(3A)	1478 (4)	1339 (1)	2357 (4)
C(4A)	1161 (4)	1572 (1)	1191 (4)
C(5A)	1770 (4)	1874 (1)	913 (4)
C(6A)	1463 (4)	2134 (1)	−180 (4)
C(7A)	2164 (4)	2444 (1)	−272 (4)
C(8A)	1865 (5)	2702 (1)	−1260 (5)
C(9A)	867 (5)	2658 (1)	−2168 (5)
C(10A)	179 (5)	2346 (1)	−2111 (6)
C(11A)	462 (4)	2086 (1)	−1126 (5)
O(1B)	826 (3)	207 (1)	6473 (3)
O(2B)	2867 (3)	363 (1)	6391 (3)
C(1B)	1937 (4)	173 (1)	6896 (4)
C(2B)	2286 (4)	−83 (1)	7983 (4)
C(3B)	1427 (4)	−261 (1)	8721 (4)
C(4B)	1704 (4)	−520 (1)	9801 (4)
C(5B)	822 (4)	−684 (1)	10557 (4)
C(6B)	1008 (4)	−958 (1)	11634 (4)
C(7B)	−19 (4)	−1074 (1)	12426 (5)
C(8B)	113 (5)	−1335 (1)	13443 (5)
C(9B)	1290 (5)	−1483 (1)	13693 (5)
C(10B)	2335 (5)	−1369 (1)	12926 (6)
C(11B)	2196 (4)	−1107 (1)	11904 (5)
(b) DPO			
O	708 (4)	2524 (4)	404 (4)
C(1)	663 (4)	2594 (4)	1597 (6)
C(2)	207 (5)	1990 (4)	2379 (6)
C(3)	33 (5)	1244 (4)	1930 (7)
C(4)	−381 (4)	610 (4)	2668 (7)
C(5)	−585 (4)	−114 (4)	2194 (6)
C(6)	−1039 (4)	−772 (4)	2860 (6)
C(7)	−1405 (5)	−1406 (4)	2137 (7)
C(8)	−1875 (6)	−2009 (5)	2746 (8)
C(9)	−1981 (5)	−2005 (5)	4065 (8)
C(10)	−1604 (5)	−1410 (5)	4789 (9)
C(11)	−1134 (5)	−785 (4)	4225 (7)
C(12)	1084 (4)	3303 (4)	2235 (6)
C(13)	1069 (5)	3412 (4)	3589 (9)
C(14)	1502 (5)	4062 (5)	4137 (8)
C(15)	1921 (5)	4623 (5)	3410 (9)
C(16)	1939 (6)	4538 (5)	2057 (8)
C(17)	1527 (5)	3871 (4)	1484 (7)

method respectively. The locations of the H atoms were determined from the difference syntheses. The refinements were made by block-diagonal least-squares calculations. The weighting scheme at the later stages was: $w = 1 \cdot 0$ for $0 < |F_o| \leq F_{max}$, and $w = (|F_{max}|/|F_o|)^2$ for $|F_o| > F_{max}$, F_{max} being $8 \cdot 0$ for both PPA and DPO. The final R values were $0 \cdot 096$ and $0 \cdot 098$ for 1973 and 804 non-zero reflexions for PPA and DPO respectively.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The computations were carried out at the Okayama University Computer Center. The programs used were *SIGM*, *TANG*, *HBLS*-5 and *DAPH* (Ashida, 1973). The final atomic parameters are listed in Tables 2 and 3.*

Results

The projections of the crystal structure and the numbering of the atoms of PPA are shown in Fig. 1, and those of DPO in Fig. 2. Bond lengths and angles are listed in Table 4. The torsion angles about the exocyclic bonds are given in Table 5. Molecular overlapping and short distances between the ethylenic double bonds are shown in Fig. 3.

Discussion

Molecular structures

The asymmetric unit of PPA consists of two molecules, A and B, which form a noncentrosymmetric hydrogen-bonded dimer $[O(1A)\cdots O(2B)$ $2 \cdot 637$ (4) Å, $O(1A)\cdots H(OB)-O(2B)$ 168 (6)°; $O(1B)\cdots O(2A)$ $2 \cdot 633$ (4) Å, $O(1B)\cdots H(OA)-O(2A)$ 171 (5)°]. The hydrogen-bond system forms a plane within $0 \cdot 12$ Å. The corresponding bond lengths and angles of molecules A and B are approximately identical, and similar to those of DPO. In both PPA and DPO the inner
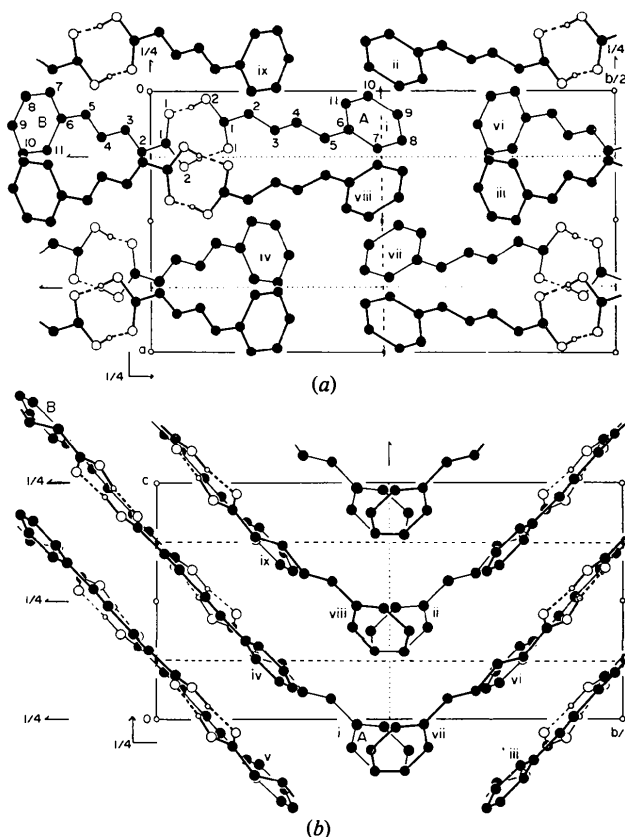
Table 3. *The final parameters* $(\times 10^3$, *except B*) *of the hydrogen atoms*

	x	y	z	B (Å^2)
(a) PPA				
H(OA)	58 (4)	45 (1)	520 (5)	6·7 (12)
H(2A)	5 (4)	100 (1)	224 (4)	4·2 (9)
H(3A)	219 (3)	140 (1)	301 (4)	4·0 (9)
H(4A)	31 (3)	153 (1)	60 (4)	3·3 (8)
H(5A)	241 (4)	195 (1)	156 (5)	6·1 (11)
H(7A)	294 (3)	247 (1)	46 (4)	3·3 (8)
H(8A)	234 (5)	294 (1)	−137 (6)	7·0 (12)
H(9A)	65 (5)	285 (1)	−288 (6)	7·5 (13)
H(10A)	−58 (6)	231 (2)	−273 (7)	10·3 (18)
H(11A)	−9 (4)	188 (1)	−112 (5)	5·6 (11)
H(OB)	248 (5)	54 (2)	556 (7)	9·4 (16)
H(2B)	316 (3)	−9 (1)	821 (4)	4·4 (10)
H(3B)	53 (3)	−22 (1)	858 (4)	2·4 (7)
H(4B)	257 (3)	−57 (1)	992 (4)	3·0 (7)
H(5B)	−13 (3)	−62 (1)	1037 (4)	3·2 (8)
H(7B)	−87 (5)	−96 (1)	1215 (6)	7·7 (14)
H(8B)	−61 (4)	−140 (1)	1401 (5)	6·6 (12)
H(9B)	125 (4)	−169 (1)	1438 (4)	4·6 (9)
H(10B)	319 (4)	−147 (1)	1303 (5)	6·4 (12)
H(11B)	298 (3)	−102 (1)	1134 (4)	3·9 (8)
(b) DPO				
H(2)	11 (4)	214 (4)	329 (6)	5·9 (17)
H(3)	13 (4)	110 (4)	84 (6)	5·5 (16)
H(4)	−50 (5)	75 (5)	356 (8)	8·2 (22)
H(5)	−50 (4)	−21 (4)	102 (7)	6·2 (18)
H(7)	−133 (5)	−138 (4)	102 (8)	7·6 (20)
H(8)	−216 (4)	−239 (4)	229 (6)	5·5 (16)
H(9)	−233 (6)	−251 (5)	442 (8)	8·7 (21)
H(10)	−164 (4)	−143 (4)	581 (7)	6·1 (18)
H(11)	−80 (5)	−35 (4)	471 (7)	6·8 (19)
H(13)	71 (5)	298 (4)	423 (7)	6·9 (20)
H(14)	141 (5)	415 (4)	507 (8)	7·5 (21)
H(15)	226 (5)	515 (5)	379 (8)	8·2 (21)
H(16)	228 (5)	487 (5)	155 (7)	8·1 (21)
H(17)	163 (4)	375 (4)	51 (6)	5·5 (17)

(a)

(b)

Fig 1. Projections of the crystal structure of PPA (a) along c, and (b) along a. Symmetry code: (i) x,y,z; (ii) $-x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (iv) $\frac{1}{2} + x, -y, \frac{3}{2} - z$; (v) $-x, -y, 1 - z$; (vi) $x, \frac{1}{2} + y, \frac{3}{2} - z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (viii) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (ix) $-x, -y, 2 - z$.
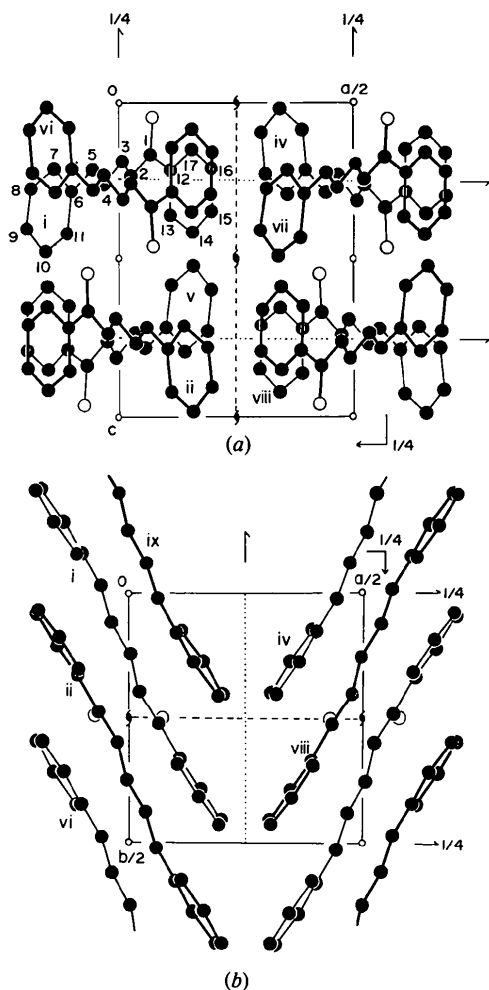
Fig. 2. Projections of the crystal structure of DPO (a) along b, and (b) along c. Symmetry code: (i) x,y,z; (ii) −x, ½ − y, ½ + z; (iii) −½ − x, y, ½ + z; (iv) ½ + x, −y, ½ − z; (v) −x, −y, 1 − z; (vi) x, ½ + y, ½ − z; (vii) ½ + x, ½ − y, z; (viii) ½ − x, y, ½ + z; (ix) −x, −y, −z.

angles at C(6) are smaller than the sp^2 angle, as is characteristic for benzene rings with a −CH=CHR substituent (Sasada, Shimanouchi, Nakanishi & Hasegawa, 1971). The C(4)—C(5)—C(6) angles are enlarged as in chalcone and its derivatives (Ohkura et al., 1973; Rabinovich & Shakked, 1974). In the conjugate diene systems, the shortest of all the single bonds is C(3)—C(4) and the lengths of the other bonds are similar to those of the chalcones. The C=O bond in DPO is slightly longer than the average value of 1·225 (10) Å for the chalcones.

The molecules of PPA and DPO take the *trans-trans-s-cis* conformation. The C=O bond in the *s-cis* conformation has also been observed for DPO in benzene solution (Bramley & Le Fèvre, 1962), and for the 4'-bromo derivative of DPO (BPBB) in crystals (Vorontsova & Kazaryan, 1973), as expected from the

Table 4. *Bond lengths (Å) and angles (°) with standard deviations in parentheses*

(a) PPA

	Molecule A	Molecule B
O(1)—C(1)	1·234 (5)	1·240 (5)
O(2)—C(1)	1·286 (5)	1·300 (5)
C(1)—C(2)	1·464 (6)	1·454 (6)
C(2)—C(3)	1·326 (6)	1·322 (6)
C(3)—C(4)	1·451 (6)	1·444 (6)
C(4)—C(5)	1·327 (6)	1·322 (6)
C(5)—C(6)	1·459 (6)	1·463 (6)
C(6)—C(7)	1·377 (6)	1·384 (6)
C(7)—C(8)	1·383 (7)	1·381 (7)
C(8)—C(9)	1·367 (7)	1·375 (8)
C(9)—C(10)	1·375 (7)	1·385 (8)
C(10)—C(11)	1·383 (7)	1·388 (7)
C(11)—C(6)	1·394 (6)	1·389 (6)
O(2)—H(O)	1·12 (5)	1·11 (6)
O(1)—C(1)—O(2)	122·9 (4)	121·9 (4)
O(1)—C(1)—C(2)	121·8 (4)	122·4 (4)
O(2)—C(1)—C(2)	115·2 (3)	115·8 (4)
C(1)—C(2)—C(3)	123·3 (4)	122·5 (4)
C(2)—C(3)—C(4)	123·9 (4)	125·4 (4)
C(3)—C(4)—C(5)	123·8 (4)	123·9 (4)
C(4)—C(5)—C(6)	127·2 (4)	127·8 (4)
C(5)—C(6)—C(7)	119·3 (4)	119·8 (4)
C(5)—C(6)—C(11)	122·6 (4)	122·0 (4)
C(11)—C(6)—C(7)	118·0 (4)	118·2 (4)
C(6)—C(7)—C(8)	120·8 (4)	121·6 (4)
C(7)—C(8)—C(9)	121·2 (5)	119·8 (5)
C(8)—C(9)—C(10)	118·7 (5)	119·7 (5)
C(9)—C(10)—C(11)	120·8 (5)	120·3 (5)
C(10)—C(11)—C(6)	120·5 (4)	120·4 (4)
C(1)—O(2)—H(O)	109 (3)	108 (3)

(b) DPO

O—C(1)	1·241 (9)	C(12)—C(1)—O	119·1 (6)
C(1)—C(2)	1·465 (10)	O—C(1)—C(2)	120·8 (7)
C(2)—C(3)	1·344 (10)	C(12)—C(1)—C(2)	120·1 (6)
C(3)—C(4)	1·446 (10)	C(1)—C(2)—C(3)	122·0 (7)
C(4)—C(5)	1·330 (10)	C(2)—C(3)—C(4)	124·7 (7)
C(5)—C(6)	1·466 (9)	C(3)—C(4)—C(5)	124·2 (7)
C(6)—C(7)	1·407 (11)	C(4)—C(5)—C(6)	127·3 (6)
C(7)—C(8)	1·383 (13)	C(5)—C(6)—C(7)	119·7 (7)
C(8)—C(9)	1·374 (13)	C(5)—C(6)—C(11)	121·9 (6)
C(9)—C(10)	1·366 (13)	C(11)—C(6)—C(7)	118·4 (7)
C(10)—C(11)	1·391 (12)	C(6)—C(7)—C(8)	120·4 (8)
C(11)—C(6)	1·419 (10)	C(7)—C(8)—C(9)	120·8 (8)
C(1)—C(12)	1·494 (10)	C(8)—C(9)—C(10)	119·7 (8)
C(12)—C(13)	1·412 (10)	C(9)—C(10)—C(11)	121·8 (8)
C(13)—C(14)	1·386 (11)	C(10)—C(11)—C(6)	118·9 (7)
C(14)—C(15)	1·358 (12)	C(1)—C(12)—C(13)	122·0 (6)
C(15)—C(16)	1·406 (12)	C(1)—C(12)—C(17)	119·7 (6)
C(16)—C(17)	1·404 (12)	C(17)—C(12)—C(13)	118·3 (6)
C(17)—C(12)	1·397 (10)	C(12)—C(13)—C(14)	119·7 (7)
		C(13)—C(14)—C(15)	122·2 (8)
		C(14)—C(15)—C(16)	119·5 (8)
		C(15)—C(16)—C(17)	119·3 (8)
		C(16)—C(17)—C(12)	121·0 (7)

intramolecular steric effects (Rabinovich & Shakked, 1974).

As can be seen from Table 5, in PPA all the torsions about the single bonds in the same sense give rise to a dihedral angle of 50·4° between the phenyl rings at both ends of the dimer, which takes a propeller-like con-
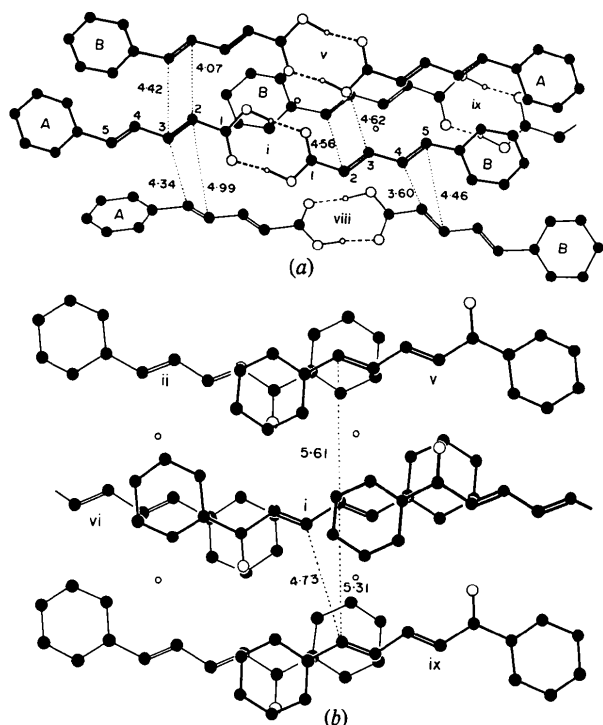
Fig. 3. Molecular overlapping and short distances (Å) between the ethylenic double bonds for (a) PPA and (b) DPO. See Figs. 1 and 2 for the symmetry codes.

Table 5. Torsion angles (°)

	PPA		
	Molecule A	Molecule B	DPO
O(1)—C(1)—C(2)—C(3)	−14·6 (6)	−9·0 (6)	19·2 (11)
C(1)—C(2)—C(3)—C(4)	181·3 (4)	179·2 (4)	177·3 (7)
C(2)—C(3)—C(4)—C(5)	174·4 (4)	177·4 (4)	176·9 (7)
C(3)—C(4)—C(5)—C(6)	184·0 (4)	177·3 (4)	183·1 (7)
C(4)—C(5)—C(6)—C(7)	176·6 (4)	173·2 (4)	163·0 (8)

formation. In DPO the torsion about the C(5)—C(6) bond is nearly equal to but opposite in sense to that about the C(1)—C(2) bond, and those about the other bonds are very small. Thus the two phenyl rings are nearly coplanar with a dihedral angle of 0·9°, in contrast to those in BPBB (dihedral angle 50·9°) and PPA.

Crystal structures

PPA. The long axis of the dimer is nearly parallel to $\langle 0\bar{1}4 \rangle$. The dimers related by a c glide are held together to form a broad ribbon. The ribbons are held together by side-by-side contact to form a sheet in the ac plane. The sheets are stacked along b, resulting in a herringbone arrangement of dimers.

As can be seen from Fig. 3(a), the short distance and near parallelism between the bonds $C(2A^i)=C(3A^i)$ and $C(4B^v)=C(5B^v)$ explain the formation of photoproduct (I) (Green et al., 1971). The angle between the bonds is 28°, but the parallelism required for the reaction would be attainable by thermal motion. The molecules B^i and B^{ix} related by $\bar{1}$ are in a favourable arrangement for the topochemical formation of (II) (Green et al., 1971). The distances between the double bonds are slightly larger than those found in photopolymerizable crystals (Cohen, Schmidt & Sonntag, 1964; Bryan & Freyberg, 1975; Sasada et al., 1971). The shortest distance between the double bonds is found between $C(4B^i)=C(51B^i)$ and $C(2B^{viii})=C(3B^{viii})$, but the angle between the bonds is 87°. Thus the reaction between these bonds is disadvantageous.
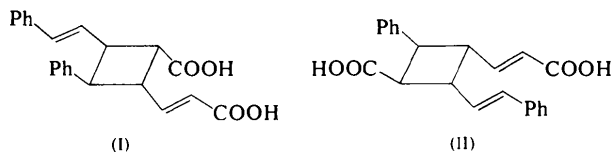

(I)   (II)

Table 6. Characteristic features of polyene crystals in Pbca

See text for definitions of δ_1, δ_2, ΔL, n, D and R.

Compound	Molecular symmetry	Cell constants (Å) a'	b'	c'	Z	δ_1 (°)	δ_2 (°)*	ΔL (Å)	n	D (Å)*	R (Å)
(a) DPDP	$\bar{1}$	10·06	22·03	7·57	4	26	56	5·0	4·1	2·4	2·1
(b) DPOT	$\bar{1}$	10·20	19·58	7·50	4	26	56	5·1	4·1	2·4	2·1
(c) P2VB	$\bar{1}$	7·311	21·06	9·567	4	–	–	–	–	–	–
(d) DSP	$\bar{1}$	7·655	20·639	9·599	4	32	24	3·3	–	3·5	2·1
(e) HGDB	$\bar{1}$	8·727	19·676	10·551	4	26	0	3·9	3·2	3·6	1·8
(f) DPO	1	16·51	15·49	10·34	8	28	0	3·7	3·0	3·6	1·8
(g) BPBB	1	10·16	25·62	11·02	8	45	0	3·6	2·9	3·6	3·6
(h) PPA	1	9·50	37·47	10·49	16	45	0	3·4	2·8	3·4	3·4

References: (a) 1,10-Diphenyl-1,3,5,7,9-decapentaene (Drenth & Wiebenga, 1954). (b) 1,8-Diphenyl-1,3,5,7-octatetraene (Drenth & Wiebenga, 1955). (c) 1,4-Bis[(β-pyridyl)-2-vinyl]benzene (Nakanishi, Ueno, Hasegawa & Sasada, 1972). (d) 2,5-Distyrylpyrazine (Sasada, Shimanouchi, Nakanishi & Hasegawa, 1971). (e) Hexamethylene glycol dibenzoate (Pérez & Brisse, 1977). (f) 1,5-Diphenyl-2,4-pentadien-1-one (this work). (g) 1-(p-Bromophenyl)-4-benzoyl-1,3-butadiene (Vorontsova & Kazaryan, 1973). (h) 5-Phenyl-2,4-pentadienoic acid (this work).

* The values cannot strictly be defined for the propeller-like molecules.
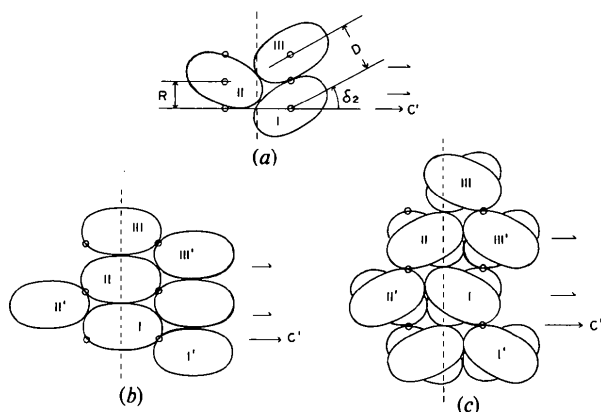
Fig. 4. Schematic view along the long molecular axis of the molecular packing in the $a'c'$ plane for (a) the planar centrosymmetric polyenes, (b) the planar noncentrosymmetric polyene (DPO), and (c) the noncentrosymmetric polyenes with propeller-like conformations (BPBB and PPA). The a' axis makes an angle of $(90 - \delta_1)°$ with the plane of the paper. A small circle shows the location of $\bar{1}$.

DPO. The long axis of the molecule is nearly parallel to $\langle 120 \rangle$. A sheet is formed in the bc plane by van der Waals interactions between the molecules related by a b glide and those related by $\bar{1}$. The sheets are stacked along **a**, resulting in a herring-bone arrangement of molecules as in PPA.

The planes of $C_6H_5COC-^i$ and $C_6H_5CH=CH-^{vi}$ overlap as shown in Fig. 3(b), the dihedral angle being $10\cdot4°$. The ethylenic double bonds of the overlapping molecules are not close to each other and are not parallel, differing from the bonds in photopolymerizable crystals of *trans*-cinnamic acid (Cohen *et al.*, 1964; Bryan & Freyberg, 1975) and of *p*-phenylenediacrylic acid diphenyl ester (Nakanishi *et al.*, 1978a). The distance between the nearest parallel bonds is $5\cdot31$ Å for $C(4^i)\cdots C(5^{ix})$, being much larger than the 4 Å requisite for dimerization (Cohen *et al.*, 1964).

Morphotropism

Polyenes. A series of polyenes, including a saturated chain compound (HGDB), belong to the *Pbca* family (Haisa, 1978); the characteristic features of these crystal structures are given in Table 6, where the crystallographic axes a', b' and c' are referred to those of DPDP for ready comparison.

In these crystals the molecules are held together by an a' glide and by $\bar{1}$ to form a sheet in the $a'c'$ plane. The long axes of the molecules related by the a' glide are nearly parallel to each other. Consequently, all the molecules in the sheet are aligned nearly in parallel.

The molecular packing in the sheet viewed down the long molecular axis is shown schematically in Fig. 4. (a) In the centrosymmetric compounds the planar

molecules (I) and (II) related by the a' glide make a side-by-side contact, and molecules (I) and (III) are related by $\bar{1}$ overlap in parallel. The angle δ_2 between the molecular plane and **c**′ determines the mode of contact between the overlapping molecules. In DPDP and DPOT with a large δ_2 the contact is $C\cdots H$, the interplanar distance D being $2\cdot4$ Å, while in the others with a smaller δ_2 the contact is $C\cdots C$, D being $3\cdot5$–$3\cdot6$ Å. (b) In DPO two noncentrosymmetric molecules (I) and (I′) related by $\bar{1}$ behave as the centrosymmetric molecule, and hence the packing mode is the same as that in (a). (c) In noncentrosymmetric BPBB and PPA the propeller-like conformation of the asymmetric units causes molecular packing differing from that in (a) and (b). The asymmetric units (I) and (II′) related by 2_1 along **c**′ overlap when viewed along **c**′ in contrast to those (I and II′) in DPO.

Let ΔL be the displacement along the long axes of the molecules in side-by-side contact, and R be the component distance between the long axes projected along **c**′, then the angle δ_1 between the long axis and a' is given by

$$\cos \delta_1 = \Delta L/(\Delta L^2 + R^2)^{1/2}. \tag{1}$$

If all the C—C bond lengths in the zigzag chains are $1\cdot42$ Å, and the C—C—C angles are $120°$, then ΔL satisfying the condition for intimate packing of the chains may be given by

$$\Delta L = 1\cdot42n \sin(120°/2), \tag{2}$$

where n is expected to be even or odd, according to whether the dihedral angle $[\simeq(180 - 2\delta_2)°]$ between the planes of the chains is smaller or larger than $90°$ respectively. In fact, the value of n calculated from the observed ΔL is close to 4 for DPDP and DPOT, and to 3 for the others.

It can be seen from Fig. 4 that R in (1) is expressed by

$$R = D/(m \cos \delta_2), \tag{3}$$

where $m = 1$ for BPBB and PPA or 2 for the others, according to whether the molecules related by 2_1 along **c**′ overlap or not when viewed along **c**′. The ΔL and R explain the observed values near 30 and $45°$ of δ_1. The cell dimension a' is given by $2k(\Delta L^2 + R^2)^{1/2}$, where $k = 2$ when $m = 2$ and molecular symmetry $= 1$, and $k = 1$ when $m = 2$ and molecular symmetry $= \bar{1}$, or when $m = 1$ and molecular symmetry $= 1$. The factors determining δ_2 would play an important role in crystal design.

Monocarboxylic acids. The two types of hydrogen-bond systems are centrosymmetric or noncentrosymmetric dimer, and infinite chain. The centrosymmetric dimers are most frequently found in the crystals, as will be discussed below. The noncentrosymmetric dimers have been found in only six crystals, as listed in Table 7. The crystals of PPA may be con-

Table 7. *Noncentrosymmetric hydrogen-bonded dimers of monocarboxylic acids*

Compound	Space group	Z	Correspondence of the axes to those of PPA
(a) PPA	*Pbca*	16	$a' = 9.50, b' = 37.47, c' = 10.49$ Å
(b) Laevopimaric acid	$P2_12_12_1$	8	
(c) 3-Butynoic acid	$Pca2_1$	8	$a = 8.060, c = 25.433, b = 4.195$ Å
(d) 2-Tellurophenecarboxylic acid	$P2_1/c$	8	$a = 7.144, b = 16.384, c = 10.951$ Å, $\beta = 91.9°$
(e) m-Nitrobenzoic acid, stable form	$P2_1/c$	8	$c = 10.37, a = 13.22, b = 10.67$ Å, $\beta = 91.2°$
(f) m-Nitrobenzoic acid, unstable form	$P2_1/c$	8	

References: (a) This work. (b) Karle (1972). (c) Benghiat & Leiserowitz (1972a). (d) Fanfani, Nunzi, Zanazzi & Zanzari (1972). (e) Dhaneshwar, Tavale & Pant (1974). (f) Dhaneshwar, Kulkarni, Tavale & Pant (1975).

Table 8. *Crystallographic pedigree of representative monocarboxylic acids whose crystals consist of centrosymmetric hydrogen-bonded dimers*

	a (Å)	b (Å)	c (Å)	β (°)
Ibam (Z = 8), prototype				
(a) Acrylic acid	9.966	11.747	6.306	
Space group Minimal supergroup	The corresponding axes			
Pccn (Z = 8) *Ibam*	2b	c	a/2	
(b) Bromoacetic acid, form (II)	23.635	6.891	5.009	
C2/m (Z = 4) *Ibam*	l110l	c/2	b	
(c) Butyric acid	8.01	6.82	10.14	111.5
C2/c (Z = 8) *Ibam*	b	c/2	2a	
(d) trans-β-2-Furylacrylic acid	18.975	3.843	20.132	113.9
(e) o-Chlorobenzoic acid	14.73	3.90	25.50	112.7
(f) Crotonic acid	15.30	4.06	16.18	107.4
(g) β-Chloro-trans-cinnamic acid	16.683	5.374	19.588	103.62
(h) 3-Thenoic acid	13.601	5.447	15.054	99.1
$P2_1/c$ (Z = 4) (I) *Pccn*	b/2	a	c	
(i) Angelic acid	6.67	11.60	7.66	100.0
(j) trans-Cinnamic acid	5.644	18.011	9.019	121.47
(k) β-Chloro-cis-cinnamic acid	5.797	24.247	7.240	121.56
(l) 4-Formylbenzoic acid, form (I)	3.74	29.21	7.28	121.5
(II) C2/m	c	b	a	
(m) trans-β-2-Thienylacrylic acid (y)	11.412	4.040	13.005	98.2
(n) Bromoacetic acid, form (I)	12.642	4.340	8.007	109.88
(III) C2/c	a/2	b	c	
(o) o-Fluorobenzoic acid	6.553	3.813	24.754	100.71
(p) 1-Naphthoic acid	6.92	3.87	31.12	92.2
(q) p-Chloro-trans-cinnamic acid	6.538	3.890	32.813	95.94
(r) 2-Thenoic acid	5.67	5.03	19.57	98.2
(s) Benzoic acid	5.52	5.14	21.90	97
(IV) *Pbcn*	c/2	a	b	
(t) Monofluoroacetic acid	4.30	7.55	9.98	85.2
(u) Propionic acid	4.04	9.06	11.00	91.3
(v) Valeric acid	5.55	9.664	11.341	101.8
P2/c (Z = 4) C2/c	a/2	b	c	
(w) trans-β-2-Thienylacrylic acid (β)	9.585	3.911	20.192	109.51
P1̄, the cell constants are omitted				
(x) 4-Formylbenzoic acid, form (II)				
(y) α-Furoic acid				
(z) p-Methoxy-trans-cinnamic acid				

References: (a) Higgs & Sass (1963); Chatani, Sakata & Nitta (1963). (b) Leiserowitz & vor der Bruck (1975). (c) Strieter & Templeton (1962). (d) Filippakis & Schmidt (1967). (e) Ferguson & Sim (1961). (f) Shimizu, Kekka, Kashino & Haisa (1974). (g) Filippakis, Leiserowitz, Rabinovich & Schmidt (1972). (h) Hudson & Robertson (1964). (i) Porte & Robertson (1959). (j) Bryan & Freyberg (1975). (k) Filippakis *et al.* (1972). (l) Haisa, Kashino, Ikejiri, Ohno & Teranishi (1976). (m) Block, Filippakis & Schmidt (1967). (n) Leiserowitz & vor der Bruck (1975). (o) Ferguson & Islam (1975). (p) Trotter (1960). (q) Glusker, Zacharias & Carrell (1975). (r) Hudson & Robertson (1962); Nardelli, Fava & Giraldi (1962). (s) Sim, Robertson & Goodwin (1955). (t) Kanters & Kroon (1972). (u) Strieter, Templeton, Scheuerman & Sass (1962). (v) Scheuerman & Sass (1962). (w) Block *et al.* (1967). (x) Haisa *et al.* (1976). (y) Hudson (1962). (z) Bryan & Freyberg (1975).

sidered as a prototype of these, since the others belong to the subgroups. Laevopimaric acid chooses the route of descent in symmetry to the enantiomorphic subgroup $P2_12_12_1$, since the molecule contains an asymmetric C atom. The crystal structures consisting of long dimers with a pseudo centre of symmetry can be derived from that of PPA. Elimination of the 2_1 axis along c' of PPA leads to the structure of 3-butynoic acid $(Pca2_1)$, the long molecular axis remaining nearly parallel to the a glide plane. The structure of the stable form of m-nitrobenzoic acid and 2-tellurophene-carboxylic acid $(P2_1/c)$ can be obtained by elimination of two respective 2_1 axes in PPA, as shown in Table 7. The crystal structure of the stable form of m-nitrobenzoic acid projected along c is similar to that of PPA projected along a'. On the other hand, the unstable form consists of dimers having the nitro groups at the same side (cis), but belongs also to $P2_1/c$.

Such a crystallographic pedigree is also found for the centrosymmetric dimers. Representatives of every space group are enumerated in Table 8. Acrylic acid (*Ibam*, Z= 8) may be considered to be the prototype of this series. Bromoacetic acid (form II) belongs to *Pccn*, Z = 8, the *klassengleichen* maximal subgroup of *Ibam*. Some acids belong to the *zellengleichen* maximal subgroups C2/m and C2/c. There is a clear correspondence in molecular arrangements between the crystals of *Ibam* and of its maximal subgroups as seen from the similarity in the corresponding axes.

A number of structures of monocarboxylic acids belonging to $P2_1/c$ can be derived from those of its minimal supergroup, *Pccn*, C2/m or C2/c. Some structures are derived from *Pbcn* which is a maximal subgroup of *Ibam* and minimal supergroup of $P2_1/c$, but the crystals of the dimer belonging to *Pbcn* have not been found so far. In this case the corresponding axes of *Ibam* are given in Table 8.

Formic acid and acetic acid $(Pna2_1)$, and tetrolic acid (β form) ($P2_1$, maximal subgroup of $Pna2_1$) form infinite chains of hydrogen bonds. The hydrogen-bonding patterns and molecular arrangements exhibited by these acids are similar (Benghiat & Leiserowitz, 1972b).

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