Crystal Structure of *p*-n-Decyloxybenzoic Acid

By **John D. Bunning** and **John E. Lydon**,* Astbury Department of Biophysics, The University, Leeds LS2 9JT

The crystal structure of the mesogenic title compound has been determined by single-crystal *X*-ray diffraction studies from 5 994 reflections. Crystals are triclinic with cell dimensions a = 8.115(1), b = 21.618(2), c = 4.820(1) Å, α = 94.07(1), β = 102.91(2), γ = 80.95(1)°, space group $P\bar{1}$, and Z = 2. The structure was determined by a direct method and refined by a least-squares procedure to R 0.0584.

The molecules are paired by hydrogen bonding between the carboxy-groups, the two halves of the dimer being related by a centre of symmetry. The two benzene rings and the two carboxy-groups of each dimer form a near-planar assembly and the alkyl chains are in the fully extended conformation.

In the crystal the aliphatic chains and the aromatic rings are segregated into alternating sheets. In the aliphatic regions the chains are interleaved and lie at an angle of *ca.* 12° to the sheet normal.

A statistical randomisation of the two possible hydrogen-bonding schemes between the carboxy-groups was found. The bond lengths in the groups were found to be perfectly normal and we suggest that anomalous values reported for the butoxy-compound by previous workers may result from an incomplete structure refinement.

This crystal structure is compared with those of lower homologues and the implications concerning the structure of the higher-temperature crystalline form and of the smectic *C* phase are discussed.

THE mesogenic properties of the *p*-n-alkoxybenzoic acids were first investigated in detail by Jones *et al.*,[1] who found that the way in which the liquid-crystal forming properties change with alkyl chain-length follows a common pattern. The lowest homologues, from C_1—C_3, form no mesophases at all; the next homologues, from C_4—C_7, form only nematic phases. From C_8—C_{13}, both smectic (*C*) and nematic phases occur and beyond C_{14} there are only smectic phases. Homologues with chains longer than eighteen carbon atoms have not yet been studied, but extrapolation of the present data suggests that the temperature of the mesophase→isotropic liquid transition will have approached that of the solid→mesophase transition when there are about thirty carbon atoms in the chain. Liquid-crystal formation is therefore not to be expected beyond this point.

The compound under investigation here, *p*-n-decyloxybenzoic acid (IV) is of interest because it has two crystalline forms in addition to the two mesophases. According to Herbert [2] the scheme of phase transitions is:

$$C_{\mathrm{I}} \xrightarrow{86^\circ} C_{\mathrm{II}} \xrightarrow{97^\circ} S_C \xrightarrow{125^\circ} N \xrightarrow{143^\circ} I$$

Bryan *et al.*[3-6] have determined the crystal structures of the methoxy-, ethoxy-, and butoxy-derivatives (none of which have a C_{II} or an S_C phase). A point of interest in two of these structures was the disorder of the carboxy-groups coupled with unusual values for the C–O bond lengths. One reason for this investigation was to see if this ' anomaly ' recurs in higher homologues. A further reason follows from the suggestion of these workers that for the homologues beyond C_6 the packing of the alkyl chains will be the dominating factor influencing the molecular ordering in the crystal. They argued that if this is the case, the crystal structures which will be found for these higher homologues will all be the same and the alkyl-chain regions will continue the same molecular ordering as in other long-chain derivatives, *e.g.* the long-chain fatty acids.

The influence of the molecular on the crystal structure of the alkoxybenzoic acids has been discussed in some detail by Bryan *et al.* The methoxy- and ethoxy-compounds have extensive aromatic–aromatic interactions in their crystals, which it was suggested are responsible for their high melting points. In the butoxy-compound the alkyl residue is of such a length that the weaker aromatic–aliphatic interactions occur as a steric necessity in the crystal and the melting point is appreciably reduced. The melting of the crystal occurs at a lower temperature than does the breakdown of hydrogen bonding and there is sufficient molecular anisotropy and mobility to cause the formation of a nematic phase. There is a progressive decline in both the melting points and densities for the first six homologues and this was taken to indicate that a similar head-to-tail packing of molecules occurs in all cases, with the aliphatic–aromatic interactions becoming steadily more dominant. Beyond this point in the series there is an abrupt change to a new type of crystal structure when it was assumed that aliphatic–aliphatic interactions would be predominant. This change coincides with the appearance of the smectic phase. On the basis of their unit-cell dimensions Bryan *et al.* predicted that the heptyloxy and subsequent compounds would be found to have crystal structures similar to those adopted by the long-chain alkanoic acids.

RESULTS AND DISCUSSION

Molecular Structure.—The molecules are paired by hydrogen bonding between carboxy-groups making obliquely Z-shaped dimers: two hydrogen-bonding schemes are possible (Figure 1). It appears that dimers of both kinds occur in equal numbers and are randomly distributed throughout the crystal.

The refined atom co-ordinates are listed in Table 1. Bond lengths, bond angles, and torsional angles are listed in Tables 2—4.† The bond lengths and angles were, on the whole, as expected [7] and these values have a

---

† Final structural factors and thermal parameters are listed in Supplementary Publication No. SUP 22594 (19 pp.). See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

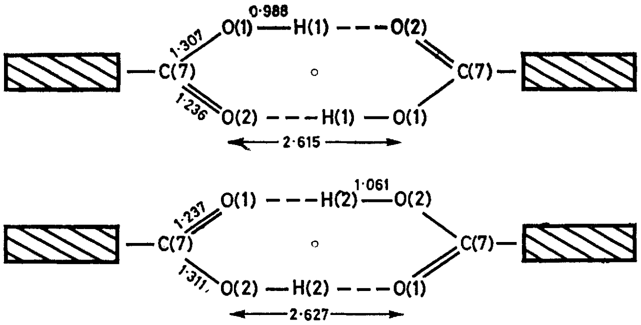

FIGURE 1 The two hydrogen bonding schemes by which the molecules of (IV) form dimers. Shaded rectangles represent the decyloxyphenyl groups and small open circles the centre of symmetry (which is also the origin of the unit cell)

close correspondence to those found in the three lower homologues for which data are available. These are the methoxy- (I), ethoxy- (II), and butoxy- (III) compounds, studied by Bryan *et al.* The last case is of especial interest because it contains two crystallographically independent molecules (*A* and *B* in Bryan's notation). There are significant differences between these two molecules and these give some indication of the extent to which the intermolecular forces modify the molecular parameters.

TABLE 1

Atom co-ordinates, with estimated standard deviations in parentheses

(*a*) Non-hydrogen atoms ($\times 10^5$)

Atom	*x/a*	*y/b*	*z/c*
C(1)	21 115(22)	07 926(10)	64 119(31)
C(2)	38 601(23)	06 358(10)	66 313(31)
C(3)	47 311(22)	09 673(11)	52 426(30)
C(4)	38 618(22)	14 687(10)	36 235(32)
C(5)	21 007(23)	16 249(11)	33 543(32)
C(6)	12 442(23)	12 924(11)	47 403(31)
C(7)	11 929(23)	04 426(11)	79 430(32)
C(8)	63 811(23)	16 884(12)	22 876(31)
C(9)	68 756(24)	22 165(12)	09 012(32)
C(10)	68 322(25)	28 210(12)	26 729(32)
C(11)	72 814(25)	33 680(12)	13 123(32)
C(12)	71 547(25)	39 782(13)	30 373(32)
C(13)	75 555(25)	45 291(12)	16 484(32)
C(14)	74 179(25)	51 408(13)	33 639(32)
C(15)	78 076(26)	56 918(12)	19 593(32)
C(16)	76 657(28)	63 053(14)	36 313(33)
C(17)	80 731(30)	68 415(14)	21 610(35)
O(1)	20 317(18)	−00 108(08)	94 374(27)
O(2)	−04 088(17)	06 057(08)	77 178(27)
O(3)	45 844(17)	18 413(08)	22 313(27)

(*b*) Hydrogen atoms ($\times 10^4$) *

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
H(21)	4 476	0 254	7 606	H(122)	7 934	3 929	5 023
H(31)	5 942	0 825	5 297	H(131)	8 722	4 415	1 210
H(51)	1 474	1 995	2 108	H(132)	6 706	4 587	9 669
H(61)	9 955	1 441	4 511	H(141)	6 222	5 247	3 703
H(81)	6 614	1 262	1 332	H(142)	8 383	5 062	5 325
H(82)	7 091	1 640	4 418	H(151)	9 068	5 588	1 666
H(91)	8 051	2 056	0 416	H(152)	6 986	5 735	9 927
H(92)	6 035	2 294	8 983	H(161)	6 280	6 421	3 770
H(101)	5 555	2 954	2 971	H(162)	8 508	6 233	5 653
H(102)	7 644	2 750	4 629	H(171)	7 963	7 223	3 413
H(111)	8 532	3 236	1 023	H(172)	9 417	6 764	2 498
H(112)	6 558	3 407	9 300	H(173)	7 309	6 923	0 398
H(121)	5 962	4 087	3 545	H(1)	1 411	9 765	0 863

* Numbered (except for those in the carboxy-groups) according to the carbon atom to which they are attached; estimated standard deviations *ca.* 4×10^{-4}, 2×10^{-4}, and 6×10^{-4} for *x/a*, *y/b*, and *z/c*.

TABLE 2

Bond lengths (Å) with estimated standard deviations in parentheses

C(1)–C(2)	1.388(2)	C(8)–C(9)	1.511(3)
C(1)–C(6)	1.394(3)	C(8)–O(3)	1.438(2)
C(1)–C(7)	1.475(3)	C(9)–C(10)	1.510(3)
C(2)–C(3)	1.378(3)	C(10)–C(11)	1.521(3)
C(3)–C(4)	1.395(2)	C(11)–C(12)	1.511(3)
C(4)–C(5)	1.395(2)	C(12)–C(13)	1.518(3)
C(4)–O(3)	1.358(2)	C(13)–C(14)	1.512(3)
C(5)–C(6)	1.373(3)	C(14)–C(15)	1.518(3)
C(7)–O(1)	1.271(2)	C(15)–C(16)	1.504(3)
C(7)–O(2)	1.274(2)	C(16)–C(17)	1.516(4)

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses

C(1)–C(2)–C(3)	121.0(2)	C(8)–C(9)–C(10)	113.1(1)
C(1)–C(6)–C(5)	120.7(2)	C(8)–O(3)–C(4)	118.2(2)
C(1)–C(7)–O(1)	118.6(2)	C(9)–C(10)–C(11)	114.6(1)
C(1)–C(7)–O(2)	118.9(2)	C(9)–C(8)–O(3)	106.8(2)
C(2)–C(1)–C(6)	118.6(2)	C(10)–C(11)–C(12)	114.2(2)
C(2)–C(1)–C(7)	120.7(2)	C(11)–C(12)–C(13)	114.4(2)
C(2)–C(3)–C(4)	119.9(2)	C(12)–C(13)–C(14)	114.4(2)
C(3)–C(4)–C(5)	119.6(2)	C(13)–C(14)–C(15)	114.3(2)
C(3)–C(4)–O(3)	125.3(2)	C(14)–C(15)–C(16)	114.9(2)
C(4)–C(5)–C(6)	120.1(2)	C(15)–C(16)–C(17)	113.2(2)
C(5)–C(4)–O(3)	115.1(2)	O(1)–C(7)–O(2)	122.5(2)
C(6)–C(1)–C(7)	120.7(2)		

TABLE 4

Torsion angles (°)

O(1)–C(7)–C(1)–C(2)	−0.9
O(2)–C(7)–C(1)–C(2)	179.1
O(1)–C(7)–C(1)–C(6)	179.8
O(2)–C(7)–C(1)–C(6)	−0.2
C(7)–C(1)–C(2)–C(3)	−179.0
C(7)–C(1)–C(6)–C(5)	178.9
C(1)–C(2)–C(3)–C(4)	0.6
C(1)–C(6)–C(5)–C(4)	−0.5
C(2)–C(3)–C(4)–O(3)	177.9
C(6)–C(5)–C(4)–O(3)	−178.0
C(3)–C(4)–O(3)–C(8)	3.7
C(5)–C(4)–O(3)–C(8)	−176.8
C(4)–O(3)–C(8)–C(9)	−173.3
O(3)–C(8)–C(9)–C(10)	69.7
C(8)–C(9)–C(10)–C(11)	−178.6
C(9)–C(10)–C(11)–C(12)	177.3
C(10)–C(11)–C(12)–C(13)	−178.4
C(11)–C(12)–C(13)–C(14)	179.6
C(12)–C(13)–C(14)–C(15)	−179.6
C(13)–C(14)–C(15)–C(16)	179.6
C(14)–C(15)–C(16)–C(17)	179.7

Each monomer of *p*-n-decyloxybenzoic acid (IV) is made up of two approximately planar parts: the alkyl chain, and the benzene ring together with the carboxy-group. The torsion angle between these two parts [O(3)–C(8)–C(9)–C(10) in Figure 2] is 69.7°. A similar geometry occurs in molecule *B* of (III) where the corresponding angle is 64° but in molecule *A* the atoms O(3) and C(10) are *trans* and the angle is 176°.

When allowance had been made for the random distribution of the two hydrogen-bonding schemes throughout the crystal, the structure of the carboxy-group was found to be perfectly normal. The O–C–O angle was in close agreement with that of other homologues and the C–O bond lengths are 1.31 Å (single bond) and 1.24 Å (double bond). Bryan *et al.* have reported that a similar disorder occurs in the crystals of the ethoxy-compound (II) and for the *B* molecules in the crystals of the butoxy-compound (III) (but in these cases the two types of dimers are probably not present in equal abundance). We suggest that the anomalous bond lengths for the carboxy-groups reported in these cases result from an incomplete structure refinement. If a treatment involving refinement of the site occupancies were to be carried out, it may well transpire that the bond lengths will be found to be perfectly normal.

The length of the C(1)–C(7) carboxy to phenyl bond (1.475 Å) is closely similar to those of corresponding bonds in the other homologues. The C–C bond lengths of the aromatic ring vary from 1.371 to 1.395 Å and are similar to those found previously. As expected, the shortest bonds are C(2)–C(3) and C(5)–C(6) because of the combined $-M$ effect of the carboxy-group, and $+M$ effect of the alkoxy-oxygen and (to a lesser extent) the $+I$ effect of the alkyl chains.

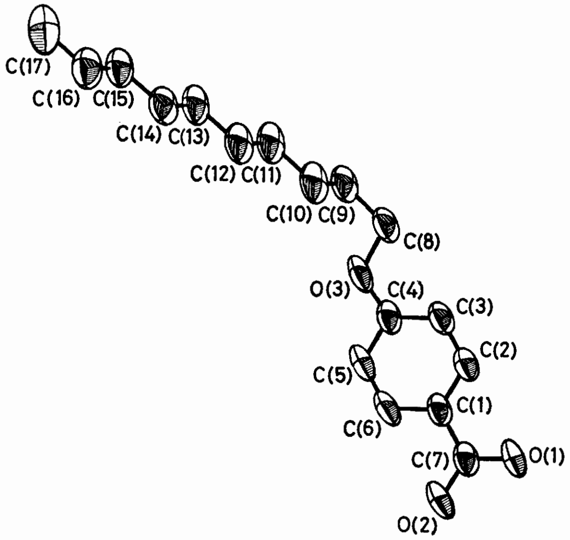

FIGURE 2 A view of half of the dimer (*i.e.* one asymmetric unit) of (IV) showing the thermal vibration ellipsoids of the non-hydrogen atoms as drawn by the ORTEP program (Oak Ridge National Laboratory Report ORNL 3794)

An idea of the planarity of the various parts of the molecule can be gained from Tables 4 and 5 of torsion angles and best planes. If deviations of $<3\sigma$ in the atom co-ordinates from the plane are considered to indicate planarity, then atoms of the carboxy- and phenyl groups cannot be regarded as being strictly coplanar. The mean displacement is 0.005 4 Å and atoms C(1), C(4), C(6), and O(2) lie significant distances from the best plane. We are forced therefore to consider the carboxy- and aromatic groups separately. The carboxy-group, including C(1), is rigorously coplanar, the mean deviation being only 0.000 05 Å. With the exception of C(4) which is out-of-plane by 3.5σ, the atoms of the benzene ring are also coplanar. The dihedral angle between the aromatic and carboxy-planes is 1.21° [as compared with 3.8, 4.3, and 10.6 for compound (II), and compound (III) molecules *A* and *B*].

TABLE 5

Equations of some least-squares mean planes through the carbon and oxygen atoms, and in square brackets, deviations (Å × 10^5) of atoms from the planes

Plane (1): Phenyl ring

$$0.68473X + 12.97287Y + 3.56052Z - 3.45118 = 0$$

[C(1) 460, C(2) −96, C(3) −572, C(4) 873, C(5) − 507, C(6), −158, C(7) 3 280, C(8) −940, O(1) 3 413, O(2) 5 453, O(3) 4 588]

Plane (2): Carboxy group and C(1)

$$0.84501X + 13.13881Y + 3.51118Z - 3.47117 = 0$$

[C(1) −3, C(7) 9, O(1) −3, O(2) −3]

Plane (3): Phenyl ring and carboxy group

$$0.75622X + 13.07963Y + 3.53317Z - 3.47367 = 0$$

[C(1) −1 187, C(2) −721, C(3) 160, C(4) 1 962, C(5) −437, C(6) −1 434, C(7) 184, C(8) 2 550, O(1) 24, O(2) 1 448, O(3) 6 972]

Plane (4): Alkyl chain [C(8) to C(17)]

$$6.94363X - 2.18517Y + 1.27621Z - 4.43471 = 0$$

[C(8) −8 091, C(9) −2 988, C(10) 3 399, C(11) 5 273, C(12) 5 156, C(13) 2 223, C(14) 2 195, C(15) −711, C(16) −2 632, C(17) −4 825]

Plane (5): Alkyl chain [C(9) to C(17)]

$$7.04667X - 2.06184Y + 1.15653Z - 4.54856 = 0$$

[C(8) −13 556, C(9) −5 633, C(10) −664, C(11) 3 975, C(12) 2 416, C(13) 3 237, C(14) 769, C(15) 625, C(16) −2 687, C(17) −2 039]

The alkyl chain has a more-or-less fully extended conformation but the atoms are not rigorously coplanar. The mean deviation of the 10 carbon atoms from the best plane is 0.038 5 Å and the greatest displacement is that of C(8) (0.080 9 Å). If this atom is omitted and the best plane drawn through the remainder, the mean deviation is 0.024 5 Å and the ' worst ' atom is now C(9) with a displacement of 0.056 4 Å.

The only region of any appreciable distortion in the molecule appears to be where the alkoxy-chain is attached to the aromatic ring. Here there is a close contact (2.22 Å) between H(3) and one of the hydrogen atoms on C(8), and this apparently causes the displacement of C(4) [and more noticeably of O(3)] from the aromatic plane and of C(8) from the best plane drawn through the alkyl chain. Furthermore the bond angles at C(4) show a considerable distortion from trigonal symmetry and we conclude that there is an appreciable departure from sp^2 hybridisation of this atom.

Crystal Structure.—The pattern of molecular packing in the crystal is shown in Figure 3. It is apparent that there is a segregation of aliphatic and aromatic parts of the molecules and that the structure consists of layers of alkyl chains sandwiched between phenyl–carboxy-layers. The alkyl chains are tilted at an angle of *ca.* 12° to the layer normal and the aromatic groups at *ca.* 50°.

The prediction of Bryan *et al.* concerning the packing of the alkyl chains apparently does not hold true for *p*-n-decyloxybenzoic acid (IV). The alkyl chains are packed in a rather unusual pattern, which is not found in any of the crystal structures of the long-chain alkanoic acids, and the chains lie in pairs (Figure 3). On either side of each chain, one neighbour lies approximately ' in-' and the other ' out-of-phase.'

The crystal structure of this lower temperature form (C_{I}) of (IV) does not immediately suggest a model for the structure of the higher temperature form (C_{II}). It is possible that an alternative scheme of hydrogen bonding is adopted where the molecules are ' laced ' together in infinite sheets as [Figure 4 (b)] and it has been suggested [8] that cybotactic groups containing this structure exist in the nematic phase of the nonyloxy-derivative and may also occur in the higher-temperature forms. We consider it more likely, however, that the dimers remain intact throughout the sequence $C_{\mathrm{I}} \rightarrow C_{\mathrm{II}} \rightarrow S_C \rightarrow N$ and that the C_{I} to C_{II} phase-change involves an internal readjustment of the molecule (probably in the region where the alkoxy-chain is attached to the aromatic group) which allows a greater degree of thermal motion of the alkyl chains in the crystal.

Implications concerning the Structure of the Smectic C *Mesophase*.—This crystal structure determination throws a new light on the structure of the S_C mesophase of the alkoxybenzoic acids (and possibly of related compounds also) and calls into question the model proposed by Vainshtein and Chistyakov [9] and by Chistyakov *et al.*[10] They studied the nonyloxy-compound and on the basis of the *X*-ray diffraction pattern of the mesophase, proposed a model of what might be termed the classic S_C type where the dimeric molecules are fully extended forming straight rods and are tilted at an angle of 54° to the layer normal. This angle was presumably calculated by comparing the estimated dimer length (43.6 Å quoted in ref. 9) with the layer spacing (for which no value was given, but which we have found to be 24.8 Å). The corresponding values for (IV) are: length of fully extended molecule 45.9 Å, and S_C layer thickness 26.5 Å, giving a similar value for the tilt angle. In addition to the measurement of smectic-layer thickness, Chistyakov *et al.* attempted a more detailed appraisal of the *X*-ray diffraction pattern by comparing it with the analogous optical diffraction pattern obtained for a mask corresponding to a two-dimensional projection of the smectic structure (normal to the layer surfaces). They obtained an apparently convincing degree of agreement for the salient features of the pattern and took this as proof of the correctness of the simple tilted model.

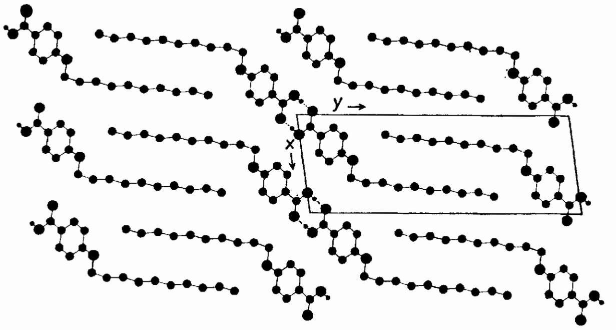

FIGURE 3 The packing of the molecules in the crystal of acid (IV). The direction of viewing has been chosen to avoid any overlap of the atoms and lies close to the *c* axis

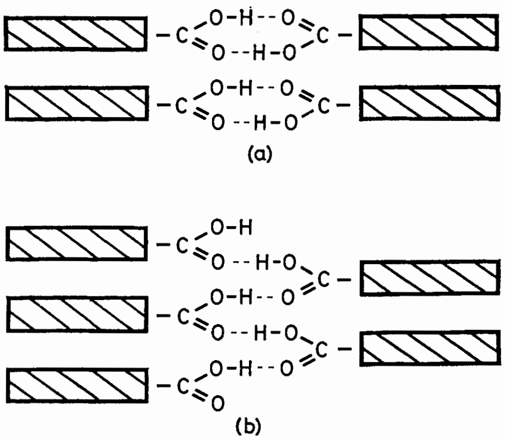

FIGURE 4 The two ways in which molecules of the alkoxybenzoic acids can be linked by hydrogen bonding. The dimerisation shown in (a) has been found in all the crystal structures so far examined.

There are however two features of the crystal structure of (V), one intra- and the other inter-molecular, which demand a reappraisal of the classic model for the S_C mesophase of this family of compounds. Firstly, Chistyakov *et al.* assumed that the molecules are fully extended with a linear conformation. This may be so but we are not aware of any direct evidence on the matter and it seems more likely that the molecules will have more or less the same oblique Z-shape as in the crystal. If this is the case, the length of the dimer (measured as the line between one terminal methyl group and the other) is *ca.* 35 Å and the tilt angle is reduced to 45°. The second feature concerns the interpenetration of the alkyl chains of molecules in adjacent layers. Chistyakov *et al.* appear to have assumed that this did not occur, and again they may be correct, but we consider it more likely that the situation in the mesophase is similar to that in the crystal. We suggest that the major distinction between the smectic mesophase and the crystalline solid forms lie in the thermal motion of the alkyl chains which allows the smectic layers to slide over one another, in spite of the interdigitation.

We visualise this mesophase as consisting of layers of highly mobile alkyl chains (lying either normal to the layers or inclined at a small angle to the normal) alternating with layers of hydrogen-bonded benzoic acid groups tilted at an appreciable angle (say 50°) to the normal, the latter giving rise to the birefringence of this phase as viewed normal to the layers. The smectic layer thickness for (IV) is some 5.5 Å greater than the perpendicular separation of the corresponding layers of the C_{I} form. We interpret this in terms of a minor alteration in the molecular geometry, probably of the angle subtended at the alkoxy-oxygen atom by the two halves of the molecule, but in the absence of structural information about the C_{II} phase we cannot say whether this represents a change occurring at the $C_{\mathrm{I}} \rightarrow C_{\mathrm{II}}$ or the $C_{\mathrm{II}} \rightarrow S_C$ transition, or changes occurring at both.

EXPERIMENTAL

Crystal Data.—$C_{17}H_{26}O_3$, $M = 278.4$. Triclinic, $a = 8.115(1)$, $b = 21.618(2)$, $c = 4.820(1)$ Å, $\alpha = 94.07(1)°$, $\beta = 102.91(2):$, $\gamma = 80.95(1)°$, $U = 406.67$ Å, $D_m = 1.08$, $Z = 2$, $D_c = 1.137$ g cm^{-3}. Space group $P\bar{1}$. (These values are in close agreement with those found by Bryan [3] but the cell has been re-indexed.) Ni-filtered Cu-K_α radiation, $\lambda = 1.541\ 8$ Å; $\mu(\text{Cu-}K_\alpha) = 6.153\ cm^{-1}$.

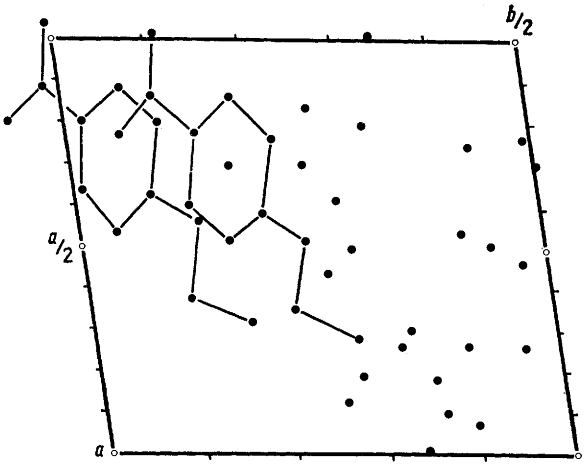

FIGURE 5 Part of the first Fourier synthesis, with signs predicted by the MULTAN program, and showing the positions of the 24 highest peaks

Data Collection.—The intensity data for 5994 reflections were collected by use of an Enraf-Nonius CAD 4 diffractometer and measured by the moving crystal–moving counter technique for $2° \leqslant \theta \leqslant 70°$. 486 very weak reflections were omitted from the analysis. Merging of Friedel pairs gave 2967 unique reflections used for the structure determination and refinement.

The crystal used was blade-like rather than equidimensional and to determine whether any absorption correction was necessary a full azimuthal scan was made of a reflection with low θ angle. This showed a variation of $<10\%$ and it was therefore decided that an absorption correction was not needed.

Structure Solution and Refinement.—The structure was solved by a direct method using the MULTAN suite of programs,[11] and the SHELX 76 programs [12] were used in the subsequent refinement.

Preliminary analysis of the E distributions indicated the structure to be centrosymmetric. It was therefore tackled with the MULTAN centrosymmetric program and six reflections were used in the starting set. The E map with the smallest ψ_0 value showed a pattern of peaks recognisable as the aromatic part of the molecule plus the first three atoms of the alkoxy-chain. A second Fourier synthesis, obtained by use of phases derived from these co-ordinates showed in addition a complete set of ghost peaks. As shown in Figure 5 the vector separating equivalent atoms in these two sets is *ca.* 2.5 Å and lies approximately parallel to the y axis. It seemed likely therefore that the MULTAN program had been only partly successful. A significant number of the sign relationships must have been correctly evaluated in order to give a recognisable portion of the molecule, but in spite of this, many of the signs of reflections with non-zero values for k were actually incorrect. This would have the effect of creating two images of the molecule equally displaced on either side of the correct position. (In this context it is of interest to note that Bryan *et al.* were unsuccessful in their attempts to solve the structure of the butoxy-compound by either the FAME–MAGIC [13] or the MULTAN direct-method programs.) A structure-factor calculation was performed taking the atom co-ordinates as the midpoints of the two images. The signs thus obtained were used for a Fourier synthesis which revealed the positions of all the non-hydrogen atoms in the molecule. After three cycles of least-squares structure-factor refinement, a difference Fourier was produced and this showed all of the hydrogen atom positions.

At this stage the two carbon–oxygen bond lengths of each carboxy-group appeared to be similar, with values of 1.26 and 1.27 Å, whereas it was expected that the bonding scheme would correspond to one or other of the two alternatives, (a) and (b) in Figure 6, and that there would be a clear distinction between the single and the double bonds, the expected values being 1.31 and 1.23 Å. This ' anomaly ' was similar to that encountered by Bryan *et al.* for molecule *B* of (III) and we were prompted to examine more closely the refinement of the co-ordinates of the atoms concerned in the hydrogen bonding scheme. There appeared to be two possible explanations for the anomaly. (i) The C–O bonds of each carboxy-group are indeed equal in length and hence in bond order, presumably owing to resonance. If both oxygen atoms are then considered to be in identical environments, then structure (d) of Figure 6 seems to be the only possibility. (ii) The bond lengths are perfectly normal but the molecules are disordered in the crystal with structures (a) and (b) (Figure 6) occurring in more or less equal numbers. The apparently anomalous bond lengths would then arise because the refinement program had attempted to fit the atom co-ordinates not to their true positions but to a pattern of electron density corresponding to the superposition of each alternative.

Each of these possibilities was tested by placing the oxygen and hydrogen atoms at the postulated sites and proceeding with further cycles of structure refinement. For the first case the oxygen atoms were placed at a distance from the carboxy-carbon atoms corresponding to a bond order of 1.5 and the hydrogen atoms were placed centrally [Figure 6 (d)]. As ' refinement ' proceeded the value of R rose appreciably and the hydrogen atoms reverted to

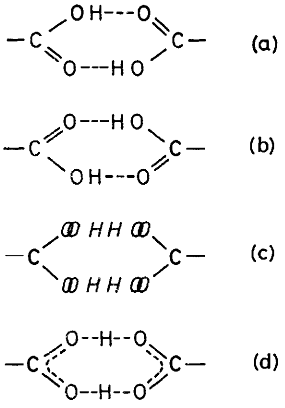

FIGURE 6 Possible hydrogen-bonding schemes in the dimer. Half-weight atoms in structure (c) are represented in italic type. Structure (d) shows an alternative symmetrical possibility, which is essentially two protons sandwiched between carboxylate ions

asymmetric positions *ca.* 1.0 Å from one oxygen atom and 1.6 Å from the other. This clearly did not look promising.

The second case was tested similarly. Half-weight atoms were placed at the oxygen and hydrogen sites [Figure 6 (c)] and both the co-ordinates and the site-occupancy values were allowed to refine. The atom co-ordinates changed very little, the site occupancy remained at 0.5, and the R fell from 0.059 5 to 0.584, an improvement which has a 99.5% significance level according to Hamilton's significance criterion.[14]

In the final stages of the structure refinement, all non-hydrogen atom co-ordinates and anisotropic thermal vibration parameters were allowed to refine. The thermal vibration parameters of the hydrogen atoms were not refined; each atom was assigned a value for an isotropic thermal vibration parameter corresponding to the mean of the anisotropic thermal vibration parameters of the atom to which it was bonded. Unobserved reflections were omitted from the refinement as were five reflections with inconsistent equivalents. The final value for R was 0.058 4.

We thank Dr. G. W. Gray (University of Hull) for the sample of (IV) used for this study, Dr. D. W. Banner for helpful discussions on diffractometer technique, D. Akrigg for assistance with the computing, and W. D. Brain for photographic assistance with the illustrations. We also thank the S.R.C. for a research studentship (to J. D. B.).

[8/1567 *Received, 30th August,* 1978]

REFERENCES

[1] A. E. Bradfield and B. Jones, *J. Chem. Soc.*, 1929, 2660; B. Jones, *ibid.*, 1935, 1874; G. M. Bennett and B. Jones, *ibid.*, 1939, 420.

[2] A. J. Herbert, *Trans. Faraday Soc.*, 1967, **63**, 555.

[3] R. F. Bryan, *J. Chem. Soc.* (*B*), 1967, 1311.

[4] R. F. Bryan and J. J. Jenkins, *J.C.S. Perkin II*, 1975, 1171.

[5] R. F. Bryan and L. Fallon, III, *J.C.S. Perkin II*, 1975, 1175.

[6] R. F. Bryan, *J. Chem. Soc.*, 1960, 2517.

[7] *Chem. Soc. Special Publ.*, No. 18, 1965.

[8] L. S. Chou and E. F. Carr, in ' Liquid Crystals and Ordered Fluids,' Plenum, New York, 1974, vol. 2, p. 39.

[9] B. K. Vainshtein and I. G. Chistyakov, Liquid Crystals: Proc. Internat. Conf., Raman Res. Inst., Bangalore, Dec. 1973. Pramana Suppl., Indian Acad. Sci., ed. S. Chandrasekhar.

[10] I. G. Chistyakov, L. S. Schabischev, R. I. Jarenov, and L. A. Gvsakov, *Mol. Crystals Liquid Crystals*, 1969, **7**, 279.

[11] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

[12] G. M. Sheldrick, Program for Crystal Structure Determination, personal communication.

[13] E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abs. Amer. Cryst. Assocn., Atlanta, Georgia, 1967, p. 20.

[14] W. C. Hamilton, *Acta Cryst.*, 1965, **18** 502.