An *X*-Ray Study of the *p*-n-Alkoxybenzoic Acids. Part IV.[1] Crystal Structure of *p*-n-Butoxybenzoic Acid

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The crystal structure of the title compound has been determined from 1951 diffractometer data. Crystals are triclinic, $a = 7.744(1)$, $b = 10.676(2)$, $c = 14.278(2)$ Å, $\alpha = 95.54(2)$, $\beta = 108.42(1)$, $\gamma = 102.63(1)^\circ$, space group $P\bar{1}$, $Z = 4$. The structure was solved by Patterson methods, and refined by least-squares methods to R 0.050.

The molecules form hydrogen-bonded dimers (O–H · · · O 2.600 and 2.652(3) Å), but different conformations are found for the two crystallographically independent molecules in the asymmetric unit. Both butyl groups adopt extended near-planar arrangements with the O–C(α)–C(β)–C(γ) side-chain torsion angles 176 and 64°. The carboxy-groups are not coplanar with the phenyl rings, and one is disordered by 180° rotation about the C–C bond linking it to the ring, leading to equivalent C–O bond lengths. The reason that this compound shows liquid-crystalline behaviour, unlike its methoxy- and ethoxy-homologues, is given in terms of molecular packing.

THE liquid-crystalline behaviour of the *p*-n-alkoxybenzoic acids has been described by Jones and his co-workers.[2] The acids from *p*-n-propoxybenzoic acid to *p*-n-cetyloxybenzoic acid, the highest member of the series studied, show a nematic phase in the melt, and from *p*-n-heptyloxybenzoic acid onwards show also a smectic phase. Bennett and Jones [2] linked the failure of *p*-methoxy- and *p*-ethoxy-benzoic acids to show such behaviour to their high m.p.s (184 and 195 °C), which are some 40—50 °C above the observed temperature for the transition in the higher homologues from a nematic phase to an amorphous melt. We are attempting, by *X*-ray studies, to establish a structural basis for these observations. We have shown,[3] from a study of the unit cells of the acids with C(1)—(10) in the alkyl residue, that the adoption of a unit cell characteristic of a long-chain fatty acid structure [4] (indicating that the alkyl chain had then become the determining factor of the crystal packing) occurred first with *p*-n-heptyloxybenzoic acid, coincident with the first appearance of a smectic phase in the melt. The crystal structures of anisic [5] and *p*-ethoxybenzoic acid [1] are each a layer type with a short, *ca.* 4 Å, unit-cell axis leading to extensive overlap of the phenyl rings of molecules separated by translation along this axis. The acids form hydrogen-bonded dimers in the crystal, arranged head-to-tail within the layers, with their long axes parallel. In the crystal structure of *p*-n-butoxybenzoic acid, (I), described here, this parallel head-to-tail alignment of hydrogen-bonded dimers is preserved, but the strong aromatic–aromatic interactions characteristic of the crystal structures of the two lowest acids are replaced by weaker aromatic–aliphatic interactions, and the layer structure gives way to a three-dimensionally interlocked arrangement of dimers. This looser type

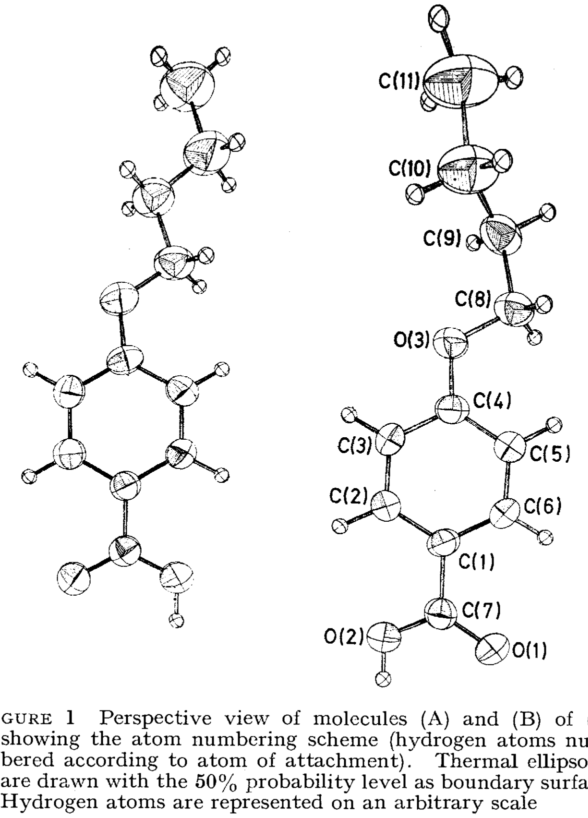

FIGURE 1 Perspective view of molecules (A) and (B) of (I), showing the atom numbering scheme (hydrogen atoms numbered according to atom of attachment). Thermal ellipsoids are drawn with the 50% probability level as boundary surface. Hydrogen atoms are represented on an arbitrary scale

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[1] Part III, R. F. Bryan and J. J. Jenkins, 4/2471, preceding paper.

[2] 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.

[3] Part I, R. F. Bryan, *J. Chem. Soc.*, 1960, 2517.

[4] E. von Sydow, *Arkiv Kemi*, 1956, **9**, 231.

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

of packing is taken to explain the lower m.p. and, on the assumption that it is also characteristic of the crystal structures of the higher homologues, allows an explanation of their liquid-crystalline behaviour.

TABLE 1

Positional parameters as fractions of the unit-cell edge, (C and O × 10^4, H × 10^3), and thermal parameters * with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule (A)									
O(1)	387(3)	1 623(2)	459(2)	270(7)	112(3)	89(2)	56(4)	−37(3)	−9(2)
O(2)	2 027(3)	210(2)	985(2)	300(7)	88(3)	92(2)	50(4)	−17(3)	0(2)
O(3)	6925(3)	5 105(2)	4 305(2)	257(6)	123(3)	57(2)	33(4)	2(3)	−6(2)
C(1)	3 116(4)	2 358(3)	1 894(2)	176(8)	80(3)	49(2)	21(4)	24(3)	15(2)
C(2)	4 578(5)	2 064(3)	2 612(2)	237(9)	85(4)	57(2)	28(5)	16(4)	17(2)
C(3)	5 823(5)	2 998(3)	3 403(2)	234(9)	98(4)	59(2)	44(5)	14(4)	23(2)
C(4)	5 632(4)	4 254(3)	3 489(2)	180(8)	112(4)	38(2)	14(5)	21(3)	5(2)
C(5)	4 197(5)	4 581(3)	2 768(2)	219(9)	82(4)	64(2)	44(5)	22(4)	−4(2)
C(6)	2 957(4)	3 623(3)	1 979(2)	178(8)	98(4)	58(2)	50(5)	11(4)	5(2)
C(7)	1 773(5)	1 335(3)	1 068(2)	196(8)	92(4)	58(2)	31(4)	21(4)	13(2)
C(8)	6 819(5)	6 413(3)	4 464(2)	256(10)	116(5)	61(2)	19(5)	21(4)	−9(3)
C(9)	8 437(5)	7 120(4)	5 428(3)	271(10)	130(5)	70(3)	33(6)	35(4)	−9(4)
C(10)	8 565(6)	8 526(4)	5 636(3)	343(12)	144(6)	100(3)	27(7)	9(5)	−18(4)
C(11)	10 173(6)	9 429(4)	6 583(3)	391(14)	167(6)	99(4)	−6(7)	7(6)	−4(4)
H(O1) †	−51(7)	95(5)	−106(4)	15.5(17)					
H(2)	472(4)	115(3)	255(2)	4.9(7)					
H(3)	680(4)	278(3)	394(2)	5.8(8)					
H(5)	405(3)	547(2)	281(2)	3.6(6)					
H(6)	194(4)	387(3)	148(2)	5.0(7)					
H(8′)	552(4)	650(3)	449(2)	5.6(8)					
H(8″)	697(4)	685(3)	387(2)	4.8(7)					
H(9′)	825(5)	673(4)	605(3)	10.2(12)					
H(9″)	964(5)	705(3)	532(3)	8.5(10)					
H(10′)	729(6)	856(4)	561(3)	12.0(13)					
H(10″)	868(6)	882(4)	500(3)	11.1(13)					
H(11)	1 008(6)	888(4)	714(3)	10.5(12)					
H(11′)	1 028(5)	1 018(5)	670(3)	10.5(12)					
H(11″)	1 131(7)	905(4)	648(3)	13.5(15)					
Molecule (B)									
O(1)	6 789(3)	1 327(2)	5 188(1)	334(7)	114(3)	36(1)	−8(4)	37(2)	1(2)
O(2)	5 518(3)	597(2)	6 287(2)	314(7)	102(3)	52(1)	−33(3)	37(3)	0(2)
O(3)	11 600(3)	5 552(2)	9 115(1)	203(5)	104(3)	47(1)	−15(3)	32(2)	−6(2)
C(1)	8 019(4)	2 515(3)	6 852(2)	184(8)	77(3)	36(2)	26(4)	19(3)	2(2)
C(2)	8 148(4)	2 523(3)	7 846(2)	206(8)	83(4)	46(2)	4(4)	33(3)	14(2)
C(3)	9 366(4)	3 548(3)	8 583(2)	208(8)	101(4)	36(2)	15(5)	33(3)	12(2)
C(4)	10 459(4)	4 585(3)	8 334(2)	143(7)	84(4)	45(2)	18(4)	22(3)	0(2)
C(5)	10 337(4)	4 586(3)	7 342(2)	192(8)	95(4)	47(2)	−2(5)	34(3)	6(2)
C(6)	9 112(4)	3 549(3)	6 615(2)	216(8)	104(4)	34(2)	17(5)	34(3)	6(2)
C(7)	6 718(4)	1 427(3)	6 044(2)	202(8)	77(3)	46(2)	23(4)	19(3)	15(2)
C(8)	12 799(5)	6 635(3)	8 900(2)	211(9)	104(4)	64(2)	−12(5)	31(4)	−9(3)
C(9)	14 085(5)	7 550(3)	9 878(3)	217(9)	112(4)	73(3)	−9(5)	51(4)	−18(3)
C(10)	15 352(5)	6 980(4)	10 602(3)	252(10)	174(6)	80(3)	57(6)	15(5)	−25(3)
C(11)	16 658(6)	7 970(5)	11 533(3)	286(12)	265(8)	92(3)	−16(5)	−16(5)	−54(4)
H(O2)	480(6)	−7(4)	581(3)	13.3(15)					
H(2)	735(3)	179(2)	805(2)	3.5(6)					
H(3)	939(4)	354(2)	927(2)	4.2(7)					
H(5)	1 110(4)	535(3)	717(2)	4.7(7)					
H(6)	907(3)	356(2)	594(2)	2.8(6)					
H(8′)	1 199(5)	709(3)	841(2)	7.2(9)					
H(8″)	1 366(4)	622(3)	862(2)	4.9(7)					
H(9′)	1 320(4)	787(3)	1 020(2)	4.7(7)					
H(9″)	1 479(4)	840(3)	971(2)	4.7(7)					
H(10′)	1 457(5)	618(3)	1 079(3)	9.3(11)					
H(10″)	1 606(5)	660(3)	1 022(2)	7.6(10)					
H(11)	1 709(6)	884(4)	1 124(3)	11.8(13)					
H(11′)	1 586(6)	829(4)	1 191(3)	10.3(12)					
H(11″)	1 761(6)	767(4)	1 200(3)	13.6(15)					

* Anisotropic, in the form $-[h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}]$.
† Isotropic thermal parameters for H atoms, B/Å^2.

RESULTS AND DISCUSSION

Final positional and thermal parameters are listed in Table 1, and a view of the two crystallographically independent molecules in the asymmetric unit is shown in Figure 1. Table 2 lists bond lengths and angles, Table 3 details of least-squares mean planes, Table 4, non-bonded contacts, and Figure 2 shows a view of the molecular packing.

The two molecules, (A) and (B), in the asymmetric unit have different conformations. The principal difference is in the disposition of the alkyl chain with respect to the ring planes. In each case the butyl residue adopts an

Table 2

Bond lengths (Å) and angles (deg.). Standard deviations, in parentheses, include contributions from the errors in the unit-cell parameters and the effects of correlation between the parameters of an individual atom, but not correlations between the parameters of different atoms. The thermally corrected values, in square brackets, are based on a riding model

(*a*) Bonds

	Molecule (A)	Molecule (B)
O(1)–C(7)	1.268(4) [1.302]	1.236(3) [1.262]
O(2)–C(7)	1.259(3) [1.290]	1.293(3) [1.315]
C(1)–C(7)	1.465(4) [1.471]	1.480(4) [1.483]
C(1)–C(2)	1.384(4) [1.393]	1.389(3) [1.394]
C(2)–C(3)	1.369(4) [1.369]	1.377(4) [1.378]
C(3)–C(4)	1.379(4) [1.392]	1.388(4) [1.395]
C(4)–C(5)	1.390(4) [1.395]	1.389(3) [1.397]
C(5)–C(6)	1.379(4) [1.383]	1.378(4) [1.380]
C(6)–C(1)	1.380(4) [1.387]	1.377(4) [1.384]
C(4)–O(3)	1.358(3) [1.377]	1.360(3) [1.373]
C(8)–O(3)	1.417(4) [1.418]	1.440(3) [1.444]
C(8)–C(9)	1.526(5) [1.528]	1.513(4) [1.515]
C(9)–C(10)	1.477(5) [1.498]	1.498(4) [1.519]
C(10)–C(11)	1.513(6) [1.527]	1.523(5) [1.552]
O–H	0.98(5) [1.08]	0.88(5) [0.98]
C(2)–H(2)	1.00(3) [1.00]	1.02(2) [1.02]
C(3)–H(3)	0.98(3) [0.99]	0.98(3) [0.98]
C(5)–H(5)	0.98(2) [0.99]	1.00(3) [1.00]
C(6)–H(6)	0.99(3) [0.99]	0.96(2) [0.98]
C(8)–H(8′)	1.04(3) [1.05]	1.02(3) [1.05]
C(8)–H(8″)	1.03(3) [1.03]	1.03(3) [1.04]
C(9)–H(9′)	1.06(4) [1.12]	0.97(3) [0.98]
C(9)–H(9″)	1.01(4) [1.05]	1.08(3) [1.08]
C(10)–H(10′)	0.99(4) [1.05]	1.05(4) [1.10]
C(10)–H(10″)	1.01(4) [1.07]	1.00(3) [1.01]
C(11)–H(11)	0.94(4) [0.98]	1.08(4) [1.15]
C(11)–H(11′)	0.97(4) [0.99]	1.03(4) [1.04]
C(11)–H(11″)	1.00(5) [1.07]	0.96(5) [1.02]

(*b*) Bond angles not involving H

	Molecule (A)	Molecule (B)
O(1)–C(7)–O(2)	122.4(3)	122.5(3)
O(1)–C(7)–C(1)	118.1(3)	121.3(3)
O(2)–C(7)–C(1)	119.4(3)	116.2(3)
C(7)–C(1)–C(6)	121.4(3)	119.4(3)
C(7)–C(1)–C(2)	120.0(3)	121.4(3)
C(6)–C(1)–C(2)	118.6(3)	119.1(3)
C(1)–C(2)–C(3)	121.0(3)	120.3(3)
C(2)–C(3)–C(4)	119.9(3)	119.9(3)
C(3)–C(4)–C(5)	120.2(3)	120.1(3)
C(4)–C(5)–C(6)	118.8(3)	119.0(3)
C(5)–C(6)–C(1)	121.5(3)	121.5(3)
C(3)–C(4)–O(3)	115.4(3)	115.3(3)
C(5)–C(4)–O(3)	124.3(3)	124.6(3)
C(4)–O(3)–C(8)	119.4(3)	117.5(2)
O(3)–C(8)–C(9)	107.2(3)	108.4(3)
C(8)–C(9)–C(10)	112.4(3)	114.6(3)
C(9)–C(10)–C(11)	113.3(4)	112.8(3)

(*c*) Bond angles involving H

C(7)–O–H	119(3) 115(3)	C(8)–C(9)–H(9′)	107(2) 108(2)
C(1)–C(2)–H(2)	119(2) 122(2)	C(10)–C(9)–H(9′)	107(2) 110(2)
C(3)–C(2)–H(2)	120(2) 118(2)	C(10)–C(9)–H(9″)	107(2) 109(2)
C(2)–C(3)–H(3)	121(2) 118(2)	H(9′)–C(9)–H(9″)	114(3) 105(2)
C(4)–C(3)–H(3)	119(2) 122(2)	C(9)–C(10)–H(10′)	104(2) 108(2)
C(4)–C(5)–H(5)	122(2) 119(2)	C(9)–C(10)–H(10″)	102(2) 107(2)
C(6)–C(5)–H(5)	119(2) 122(2)	C(11)–C(10)–H(10′)	116(2) 111(2)
C(5)–C(6)–H(6)	118(2) 118(2)	C(11)–C(10)–H(10″)	114(2) 113(2)
C(1)–C(6)–H(6)	121(2) 121(2)	H(10′)–C(10)–H(10″)	105(3) 105(3)

Table 2 (*Continued*)

O(3)–C(8)–H(8′)	114(2) 109(2)	C(10)–C(11)–H(11)	111(2) 104(2)
O(3)–C(8)–H(8′)	109(2) 104(2)	C(10)–C(11)–H(11′)	113(2) 109(2)
C(9)–C(8)–H(8′)	112(2) 112(2)	C(10)–C(11)–H(11″)	104(3) 116(3)
C(9)–C(8)–H(8″)	110(2) 109(2)	H(11)–C(11)–H(11′)	111(3) 100(3)
H(8′)–C(8)–H(8″)	105(2) 114(2)	H(11)–C(11)–H(11″)	105(4) 119(3)
C(8)–C(9)–H(9′)	111(2) 110(2)	H(11′)–C(11)–H(11″)	113(3) 108(3)

Table 3

Equations of least-squares mean planes in the form $aX + bY + cZ = d$, where X, Y, and Z are in Å with respect to a Cartesian axial system having its origin coincident with the space-group centre of symmetry. The matrix relating the fractional co-ordinates to co-ordinates in this system is:

$$\begin{bmatrix} 7.7440 & 0.0000 & 0.0000 \\ -2.3334 & 10.4179 & 0.0000 \\ -4.5115 & -2.4227 & 13.3281 \end{bmatrix}$$

In each case data for molecule (A) precedes that for molecule (B)

Plane	*a*	*b*	*c*	*d*
(1) Butyl group	−0.8017	−0.2856	0.5251	0.1095
	0.8243	−0.3692	0.4292	−0.2175
(2) Carboxy-group	−0.7296	−0.3695	0.5755	−0.0224
	0.7565	−0.6030	0.2530	3.6457
(3) Phenyl ring	−0.7785	−0.3299	0.5339	−0.1047
	0.8548	−0.5011	0.1350	2.9137

Deviations (Å) from plane (3)

C(7) 0.04, O(1) 0.13, O(2) −0.03, O(3) 0.02; C(7) −0.006, O(1) 0.18, O(2) −0.22, O(3) −0.01

Table 4

Shorter intermolecular contacts (Å). Contacts are from the first atom at *x*, *y*, *z* to the second at the position indicated by the Roman superscript. The reverse contacts from the second atom at *x*, *y*, *z* are also made. Atoms of molecule (B) are italicised

(i) C ··· C < 3.8			
C(1) ··· *C*(8$^{\mathrm{I}}$)	3.67	C(5) ··· *C*(5$^{\mathrm{I}}$)	3.77
C(2) ··· *C*(8$^{\mathrm{I}}$)	3.58	C(6) ··· *C*(4$^{\mathrm{I}}$)	3.54
C(3) ··· *C*(8$^{\mathrm{I}}$)	3.79	C(10) ··· *C*(7$^{\mathrm{II}}$)	3.75 †
C(4) ··· *C*(5$^{\mathrm{I}}$)	3.69	C(11) ··· *C*(11$^{\mathrm{V}}$)	3.63
C(5) ··· *C*(4$^{\mathrm{I}}$)	3.79		
(ii) C ··· O < 3.3			
C(2) ··· *O*(2$^{\mathrm{I}}$)	3.37	C(3) ··· *O*(1$^{\mathrm{I}}$)	3.24
(iii) O ··· O < 2.9			
O(1) ··· O(2$^{\mathrm{III}}$)	2.60	*O*(1) ··· *O*(2$^{\mathrm{IV}}$)	2.65
(iv) C ··· H < 3.0			
C(7) ··· H(O1$^{\mathrm{III}}$)	2.50	*C*(7) ··· *H*(O2$^{\mathrm{IV}}$)	2.65
C(1) ··· *H*(8″$^{\mathrm{I}}$)	2.97	*C*(7) ··· *H*(O2)	1.85
C(6) ··· H(8″$^{\mathrm{I}}$)	2.98	*C*(4) ··· H(6$^{\mathrm{VI}}$)	2.80
(v) O ··· H < 2.7			
O(2) ··· H(O1$^{\mathrm{III}}$)	1.62	*O*(1) ··· H(3$^{\mathrm{VIII}}$)	2.48
O(2) ··· *H*(2$^{\mathrm{III}}$)	2.70	*O*(2) ··· H(2)	2.63
O(1) ··· *H*(*O*2$^{\mathrm{IV}}$)	1.78		
(vi) H ··· H < 2.6			
H(O1) ··· H(O1$^{\mathrm{III}}$)	2.34	H(3) ··· H(9″$^{\mathrm{I}}$)	2.58
H(O2) ··· *H*(*O*2$^{\mathrm{IV}}$)	2.45	H(9″) ··· *H*(6$^{\mathrm{I}}$)	2.42
H(3) ··· *H*(9′$^{\mathrm{VII}}$)	2.59	*H*(2) ··· *H*(11″$^{\mathrm{VII}}$)	2.49

† The reverse contact is to the first atom at $x, y - 1, z$.

I $2 - x, 1 - y, 1 - z$; II $x, 1 + y, z$; III $\bar{x}, \bar{y}, \bar{z}$; IV $1 - x, \bar{y}, 1 - z$; V $3 - x, 2 - y, 2 - z$; VI $1 - x, 1 - y, 1 - z$; VII $2 - x, 1 - y, 2 - z$; VIII x, y, z.

extended near-planar form, but with O(3) and C(10) *trans* in (A) and *cisoid* in (B) with the torsion angle O(3)–C(8)–C(9)–C(10) 176 in (A) and 64° in (B).

In molecule (A) the two carboxy C–O distances [1.259(4) and 1.268(3) Å], are not significantly different, whereas in (B) there is the expected distinction between them [1.236(3) and 1.293(3) Å]. Although a model for (A) with the carboxy-hydrogen atom attached to O(1) refined satisfactorily to yield O–H 0.98 Å, the equivalence of the C–O distances in (A) suggests rotational disorder in the carboxy-group. Difference electron-density maps were therefore calculated, excluding the contributions of the carboxy-hydrogen atoms, in the planes of the carboxy-groups of (A) and (B). These show (Figure 3) that in (B) the hydrogen atom is localized and attached to O(2), but in (A) the electron density is significantly extended along the O $\cdots$ O line, an arrangement compatible with the suggested disorder. A similar situation is found for the carboxy-group in *p*-ethoxybenzoic acid.[1] No attempt was made to determine the partial occupancies of each site for the disordered molecule.

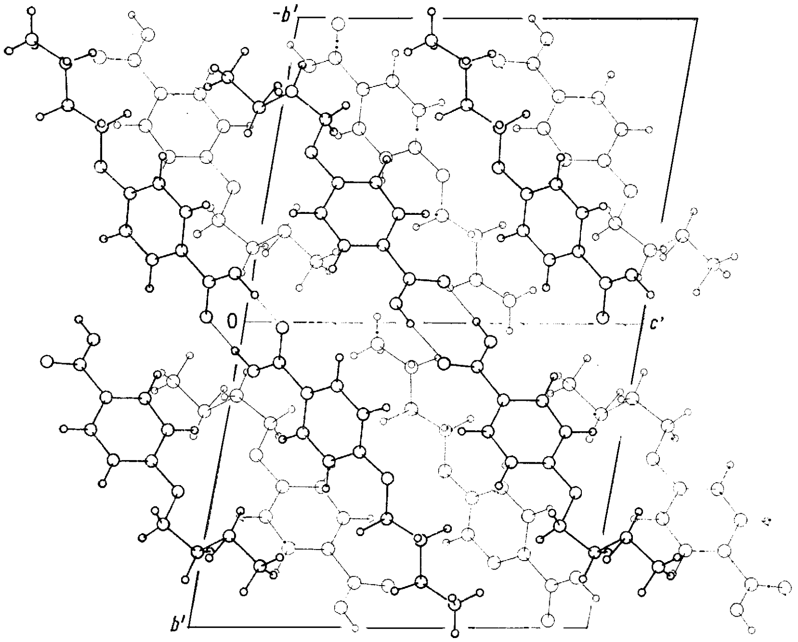

FIGURE 2 Molecular packing in the crystal structure of (I), seen in projection down *a*. Note the interlocking arrangement formed by interleaving the alkyl termini with hydrogen-bonded carboxy-groups of neighbouring dimers

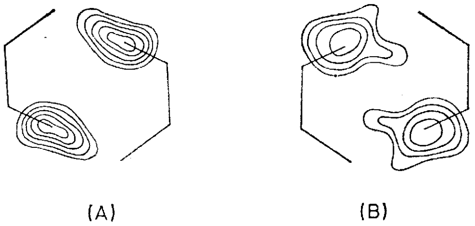

FIGURE 3 Residual electron density in the planes of the carboxy-groups, excluding the contribution of the carboxy-hydrogen atoms to the calculated structure factors. Contour levels are at 0.05 eÅ^{-3} increments from zero. Note the extension of density along the internuclear line in molecule (A)

Apart from the anomalies associated with the carboxy-group of (A), other bond lengths and angles in (A) and (B) were as expected, and corresponding values were in good agreement with each other, and those for anisic acid (II) and *p*-ethoxybenzoic acid (III). In the carboxy-groups of (I; molecule A) and (II), the thermally-uncorrected C=O bond distances are 1.236(3) and 1.233(8) C–O 1.293(3) and 1.290(8), and included O–C–O– angles 122.5(3) and 123.4(6)°. Agreement among the O–C–C angles is less good, but these are undoubtedly affected by the differing displacements of the carboxy-planes from the planes of the phenyl rings in each molecule (see later).

The C–C distances from the carboxy-groups to the rings are: 1.465(4) molecule (A), 1.480(4) molecule (B), 1.502(9) (II), and 1.467(4) Å (III), somewhat shorter in the two presumably disordered structures than in (I), molecule (B) and (III).

Variations in C–C distances in the phenyl rings exceed the formal σ value, but are most probably due to the effects of anisotropic thermal vibration of the atoms which are clearly not adequately corrected by the riding model adopted in Table 2.

The phenyl C–O distances in the three compounds [(I); molecules (A) and (B), (II), and (III)] are in excellent accord. The O–C aliphatic distance in molecule (A) is shorter [1.417(4)] than in molecule (B) [1.440(3)] and, in (II) [1.443(8) Å] and (III) [1.450(4) Å]. C–C distances in the side-chains of (I) and (IV) range from 1.477—1.526(6) Å, and are clearly subject to substantial errors resulting from the neglect of thermal motion corrections.

A feature common to all three compounds is the distortion of the exocyclic bond angles at the *para*-carbon atom of the phenyl ring. Because of repulsions between the methylene hydrogen atoms of the α-carbon atom of the side-chain and a phenyl hydrogen atom, the included C–C–O angle is significantly opened over the expected trigonal value, while the adjacent angle is correspondingly reduced. For molecules (A) and (B) these angles are 124.3, 124.6, 115.4, and 115.3(3)°, *cf.* 124.0 and 115.6(3)° in (III), 125.6 and 114.0(6)° in (II). In all four cases the H ··· H separations leading to the distortion are in the range 2.24—2.35(5) Å.

The C–O–C angles in molecules (A) and (B) are 119.4 and 117.5(3)°, comparable to the values of 116.8(6) and 118.0(3)° in (II) and (III). In (I) and (IV) the O–C–C side-chain angle is significantly less than the tetrahedral value [107.2(3) (A), 108.4(3) (B), and 106.6(3)°: (IV)], whereas the C–C–C angles are all significantly greater, lending weight to the argument that bond angles in such systems are dictated by non-bonded interactions.[6]

As with (II) and (III), there are significant deviations from coplanarity between the atoms of the phenyl ring and carboxy-group of each molecule. In molecule (A) the atoms of the ring are rigorously planar, mean deviation 0.005 Å, but this plane does not include the atoms of the carboxy-group or O(3). The atoms of the carboxy-group and C(1) are also rigorously coplanar, mean deviation 0.0002 Å, and this plane is inclined to the ring plane at 4.3°. As in the other acids this tilt of the two planes is not a rotation about C(1)–C(7), but is an inclination of two planes sharing only a common point, C(1). Also in (I), O(3) lies 0.02 Å from the plane of the phenyl ring and 0.11 Å from the mean plane through the four atoms of the butyl residue (mean deviation 0.003 Å). This latter plane makes an angle of 2.9° with the plane of the phenyl ring and of 7° with the carboxy-group plane. Whereas molecule (A) closely resembles anisic and *p*-ethoxybenzoic acid in the pattern of these small distortions, in molecule (B) the deviations from planarity are much more pronounced. The carboxy-carbon atom, C(7), lies only 0.006 Å from an exact plane through the atoms of the phenyl ring (mean deviation 0.001 Å) and O(3) is but 0.01 Å from this same plane. Thus, in this case, the four-atom carboxy-plane is inclined to the ring plane by rotation about the C(1)–C(7) axis with the dihedral angle 10.6°. The mean plane through the four atoms of the butyl residue (mean deviation 0.004 Å) makes an angle of 62.5° with the phenyl ring plane and of 73° with the carboxy-plane. The planes of the phenyl rings of adjacent molecules are mutually inclined at 115°. The different pattern of, distortions in molecules (A) and (B) confirms that the deviations from planarity have their origin in inter- rather than intra-molecular interactions.

Molecular Packing and Liquid-crystalline Behaviour.— An acceptable explanation of the liquid-crystalline behaviour of this compound and the absence of such in the melts of (II) and (III) is provided by the differences in molecular packing in the crystal. All three acids form centrosymmetric hydrogen-bonded dimers in the crystal with O–H ··· O separations in the range 2.60—2.65 Å so that the molecular anisotropy associated with nematic behaviour is present in each case. In each crystal the dimers are arranged in a parallel head-to-tail fashion with the alkyl terminus of one molecule next to the carboxy-group of a second. Of prime importance in dictating the overall packing mode is the difference in steric bulk of the aromatic (*r* 1.7 Å) and aliphatic (*r* 2.0 Å) parts of the molecule. In the crystal structures of the two lowest acids the alkyl groups are of relatively small proportions, and a layer structure is adopted with a stacking of layers which allows extensive overlap from layer to layer between the phenyl rings of translationally adjacent molecules. This tight packing is reflected in the crystal densities of these two acids compared with those of the higher homologues: 1.39 and 1.33 *vs.* 1.21 g cm^{-3} for the *p*-butoxy acid. These strong aromatic–aromatic interactions, with ring separations of 3.4 Å, are also responsible, presumably, for the high m.p.s of the two lowest members. By contrast, in (I) the alkyl residue is of greater steric importance, and a layer structure is no longer possible. However, the parallel head-to-tail arrangement of neighbouring molecules is maintained with the alkyl termini of pairs of dimers packed between the hydrogen-bonded carboxy-groups of neighbours. This produces a three-dimensionally interlocked arrangement of dimers characterised by an absence of aromatic–aromatic interactions and a preponderance of looser aromatic–aliphatic contacts, consistent with the lower crystal density and m.p. The steady drop in D_m and m.p. in the first six members of the series may thus be interpreted by assuming that all have this same parallel head-to-tail packing arrangement, but that as the size of the side-chain increases, the nature of the intermolecular interactions alters, aromatic–aromatic giving way progressively to aromatic–aliphatic and aliphatic–aliphatic. Ultimately,[3] where the alkyl residue contains seven or more carbon atoms, the crystal structure becomes characteristic of that adopted by a long-chain fatty acid with aliphatic–aliphatic interactions predominant.

Such a model allows explanation of the link between m.p. and liquid-crystallinity noted by Bennett and Jones,[2] who showed that the formation of hydrogen-bonded dimers was a necessary condition for liquid-crystallinity in *p*-n-propoxybenzoic acid, noting that its methyl ester showed no evidence of mesomorphism despite its low m.p. (15 °C). We may, then, with reasonable confidence assume that hydrogen bonding persists in the nematic phase and identify the transition from that phase to an amorphous melt with the disruption of the hydrogen bonds between the monomers. In the crystal structure of (I), as long as the hydrogen bonds remain intact, then an interlocked arrangement of dimers will persist. The generally weaker intermolecular interactions in this crystal allow some freedom of

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[6] L. Leiserowitz and D. Rabinovich, *J. Chem. Soc.* (*B*), 1969, 2367.

movement in the alkyl side-chain, or indeed in the dimer as a whole, at a temperature where the hydrogen bonds remain intact. With the two lowest acids, however, the strong intermolecular forces operating between neighbouring phenyl rings in the layer structure do not allow melting until 25—35° above the transition temperature associated with the nematic–amorphous change, so that at the melting point the hydrogen bonds needed to maintain the necessary molecular anisotropy are no longer viable.

By a simple linear extrapolation of the data of ref. 2 we deduce that increasing m.p. may inhibit liquid-crystallinity when a side-chain length of *ca.* **30** carbon atoms is reached.

EXPERIMENTAL

Crystal Data.—$C_{11}H_{14}O_3$, $M = 194.2$. Triclinic, $a = 7.744(1)$, $b = 10.676(2)$, $c = 14.278(2)$ Å, $\alpha = 95.54(2)$, $\beta = 108.42(1)$, $\gamma = 102.63(1)°$, $U = 1\,075$ Å^3, D_m (flotation) = 1.20, $Z = 4$, $D_c = 1.200$, $F(000) = 416$. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 1 cm^{-1}. Single-crystal diffractometry.

Although similar crystallisation conditions were used, the crystals used here had a unit cell different from that reported in ref. **3**. The unit-cell symmetry is the same and the lengths of two of the axes similar, but the earlier modification had a volume only half that of this form, and therefore only one molecule in the asymmetric unit. The third axis, halved in the smaller cell, corresponds to the *c* axis of the present cell along which molecules (A) and (B) alternate. It seems likely that the earlier modification had a crystal structure very similar to the present form, but with an ordered arrangement of molecules along this direction. The observed transition point for this modification (147 °C) corresponds to that reported in ref. 2.

Intensity Measurements.—These were made from a crystal 0.4 × 0.4 × 0.2 mm mounted with c^* parallel to the ϕ axis of a Picker four-circle diffractometer, by standard methods described in ref. 1. Monochromatic Mo-K_α radiation was used, and a hemisphere of reciprocal space was surveyed to $\sin\theta/\lambda$ 0.59. Scattered intensity significantly above background was recorded at 1 951 locations and structure amplitudes derived in the usual way. No correction was made for absorption.

Structure Determination and Refinement.—We were unable to solve the structure by direct methods (MULTAN, FAME-MAGIC).[7] However, the orientation of the molecular planes was readily determined from the three-dimensional Patterson function and an acceptable trial structure derived assuming planar centrosymmetric dimers of '*p*-oxobenzoic acid' centred about 0,0,0 and $\frac{1}{2},0,\frac{1}{2}$. The atoms of the alkyl residues were located by difference Fourier methods.

Refinement was by block-diagonal least-squares methods as described in ref. **5**. Hydrogen atoms were located by difference-Fourier methods and included with isotropic B values. With anisotropic thermal parameters assumed for carbon and oxygen atoms, refinement converged at R 0.050 for 1 951 observed reflections. There were no structurally significant features in a final difference electron-density map.

Scattering functions were taken from ref. 8. All calculations were carried out on an XDS Sigma 2 computer, also used to control the diffractometer, with local programs.

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