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An X-Ray Study of the *p*-n-Alkoxybenzoic Acids. Part VII. Crystal Structures of Related Forms of *p*-n-Hexoxy- and *p*-n-Octoxy-Benzoic Acids

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X-ray structure analyses have been carried out at room temperature for a crystalline modification of *p*-n-hexoxybenzoic acid (6OBAC) which undergoes four solid-solid transitions on heating before yielding a nematic phase, and for a form of *p*-n-octoxybenzoic acid, different from that previously reported, which undergoes a single solid-solid transition before yielding a smectic phase. In both crystals the molecules are present as centrosymmetric hydrogen-bonded dimers. The alkyl chains are in the all-*trans* extended conformation but the dimers have a non-planar conformation arising from a *gauche*-relation of the ether oxygen and C(γ) about the C(α)-C(β) bond of the chain. This molecular conformation is the same as that found in other crystalline modifications of homologous members. The dimers in each structure are arranged in identical stacks along the crystal *b*-axes, and in projection down that axis are arranged in parallel staggered rows in a head-to-tail fashion in 8OBAC, but in an alternating head-to-head and tail-to-tail sequence in 6OBAC. Chains in a given stack interact laterally with the antiparallel chains or dimerized cores in neighboring stacks. $C_{13}H_{18}O_3$ (6OBAC). Monoclinic, $P2_1/c$, $a = 14.689(3)$, $b = 4.957(2)$, $c = 21.888(4)$ Å, $\beta = 128.68(2)°$, $Z = 4$. $C_{15}H_{22}O_3$ (8OBAC). Triclinic, $P\bar{1}$, $a = 13.442(4)$, $b = 4.869(2)$, $c = 12.192(2)$ Å, $\alpha = 88.58(2)$, $\beta = 116.76(2)$, $\gamma = 88.91(2)°$, $Z = 2$.

INTRODUCTION

Solid-state polymorphism is frequently found in materials showing thermal mesomorphism. It is clearly widespread in the *p*-n-alkoxybenzoic acids, although the full range of alternative solid-state organization in the series has not yet been completely worked out. It is therefore reasonable to suppose that the particular features of a molecular crystal structure which favor mesogenicity are akin to those which favor such polymorphism. A knowledge of the solid-state structures of phases intervening between the most stable arrangement and the mesophase would yield useful information on the type of molecular reorganization involved in passing from one phase to the next. Unfortunately, it is often difficult to prepare ordered samples of these higher temperature polymorphs so that for molecules of any complexity little is known of the processes involved.

The two crystal structures reported here fall into a somewhat different but nonetheless useful and more accessible category which is also of importance in the study of solid phase—mesophase relationships. This category comprises materials which at ambient temperature and pressure yield different crystal forms from different solvents. A comparison of structures of this kind, which is more easily made than in the former case, sheds light on energetically equivalent (or very nearly equivalent) packing modes for the molecules.

The structure reported here for *p*-n-hexoxybenzoic acid (6OBAC) is that for a crystal modification prepared from solution in tetrahydrofuran. This particular form undergoes no fewer than four solid-solid transitions on heating before yielding a nematic phase, emphasizing the delicate balance of packing energies for these molecules which stand immediately before the emergence of smectic properties in the series. A second crystal form, of triclinic symmetry,[1] may be crystallized from glacial acetic acid, but the crystals are of poor quality and a complete analysis of it has not yet been possible. The crystal structure reported here has some features in common with those found in crystals of the smectogenic acids, particularly an antiparallel lateral juxtaposition of alkyl chains in neighboring dimers, but it also has an orthogonal crossing of the core axes of adjacent dimers, a feature thus far noted only in the low temperature polymorphic forms of two other nematogens, *p*-[(*p*′-methoxybenzylidene)amino]phenyl acetate[2] and *p*-[(*p*′-methoxybenzylidene)amino]-α-methyl cinnamate,[3,4] and not at all in other crystals so far examined in this series.

The structure reported for *p*-n-octoxybenzoic acid (8OBAC) is for a crystal modification produced from ethanol solution. The packing mode is similar in certain respects to that reported here for 6OBAC, but it is substantially different from that found for the crystal modification prepared from propanol solution and described in Part VI.[5] Presumably at room temperature and pressure one of these two forms is metastable with respect to the other, but at this time we cannot say which as both crystal forms undergo a solid-solid transition at indistinguishable temperatures (74 ± 0.5°C). The form described here has a somewhat smaller molecular volume and is presumably favored at higher pressures. It is possible to visualize a conservative mechanism by which the two crystal forms might interconvert, but it is not known under what circumstances, if any, such a transformation occurs; nor is it known at this time what relation either form bears to the solid phases formed on cooling from the melt.

EXPERIMENTAL

Samples of the two acids were prepared by reaction of equimolar amounts of *p*-hydroxybenzoic acid with the alkyl iodide in alcoholic KOH.[6] Each acid was purified by repeated crystallization from ethanol or glacial acetic acid. Large well-formed lathe-like single crystals of 6OBAC were grown by controlled cooling of a saturated solution of the acid in tetrahydrofuran. The crystal used in the X-ray study was cut from a larger crystal. Crystals of 8OBAC were grown by controlled cooling of a saturated solution of the acid in ethanol under conditions which had previously yielded, in other places, crystals of the isotypic variety reported in Part VI. Despite repeated efforts we have been unable to grow the isotypic crystal form from ethanol solution in Charlottesville, though it grows readily enough from propanol solution.

Transition temperatures

These were determined for the two acids by differential scanning calorimetry using a Perkin Elmer DSC-II instrument calibrated against indium as a standard.[7] The temperatures given in Table I are for the onset of endothermic activity for the initial heating of the two materials as crystals of known type as checked by their X-ray diffraction patterns. The transition temperatures were reproducible on reheating the cooled samples, but for 6OBAC the magnitude (but not the positions) of the endotherms varied depending on the cooling history of the sample. The transition $K_{III} \rightarrow K_{II}$ is normally of much lower enthalpy than the others, and is occasionally missing on heating. Some or all of the solid-solid exotherms may also be missing on cooling. Transition temperatures for heating only have been given for 6OBAC by Herbert,[8] who records only one solid-solid transition taking place at 75°. This may correspond to our $K_{IV} \rightarrow K_{III}$ transition,

TABLE I

Transition temperatures (deg. C)

Compound	$K_V \rightarrow$	$K_{IV} \rightarrow$	$K_{III} \rightarrow$	$K_{II} \rightarrow$	$K_I \rightarrow$	$S \rightarrow$	$N \rightarrow I$
6OBAC	58	71	87	99	→	101	145
8OBAC				74	97	104	146

with $K_{III} \rightarrow K_{II}$ very weak and $K_{II} \rightarrow K_I$ coalesced with $K_I \rightarrow N$. Bennett and Jones[9] and Gray and Jones,[10] who studied the phase transitions for this acid microscopically, do not report any solid-solid transitions.

Crystal data

Crystallographic data for the two acids are summarized in Table II. The space group for 6OBAC was established from the conditions governing reflection: *h*0*l* with *l* even only, and 0*k*0 with *k* even only. Crystal symmetry was established from 25° precession photographs taken using Mo Kα radiation. Unit cell dimensions were obtained by a least-squares fit to the observed diffractometer values of $\pm 2\theta$ for 24 strong general reflections in each case. Crystal densities were measured by flotation in aqueous KI solution.

TABLE II

Crystallographic data

	6OBAC	8OBAC
Crystal symmetry	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	14.689(3)	13.442(4)
b	4.957(2)	4.869(2)
c	21.888(4)	12.192(2)
α (deg.)	90.00(–)	88.58(2)
β	128.68(2)	116.76(2)
γ	90.00(–)	88.91(2)
Cell vol. (Å^3)	1244.1	711.9
Mol. wt.	222.27	250.33
D_{obs} (g cm^{-3})	1.18(1)	1.17(1)
Z	4	2
D_{cal} (g cm^{-3})	1.187	1.167
Molecular vol. (Å^3)	311.0	355.9
Points scanned	1842	2003
Significant Fs	1294	1662
Scan range (2θ)	4	4
R (significant data)	0.039	0.051
R_w	0.037	0.058

Intensity data

These were measured using the methods described in detail in Parts V and VI. A single quadrant of reciprocal space was surveyed for 6OBAC and a hemisphere for 8OBAC. Crystal alignment was checked by measurement of the intensities of reflections in symmetry equivalent zones, and the stability of the experimental conditions was monitored by periodic measurement of the intensities of two reference reflections. In neither case was any significant variation in intensity recorded for these reflections over the course of the experiment.

No absorption corrections were made and structure amplitudes were derived in the usual way. The statistical distribution of intensities for 8OBAC indicated the choice of the centrosymmetric space group, $P\bar{1}$, rather than the non-centrosymmetric $P1$.

Structure determination and refinement

In each case the structure was solved from a consideration of the sharpened three-dimensional Patterson function, by identification of the vector plane for a centrosymmetric dimer of "oxobenzoic acid." This was very straightforward for 8OBAC and the mirror related planes for 6OBAC were fairly readily distinguished and resolved. The remaining atoms of the alkyl chains were found from three-dimensional electron-density syntheses in the usual way.

Refinement by the block-diagonal least-squares method (3 × 3 and 6 × 6 blocks) proceeded smoothly to convergence in each case with the maximum shift-to-error ratio in the final cycle being 0.10 for 6OBAC and 0.14 for 8OBAC, the average ratios being <0.025 in each case. Anisotropic thermal parameters were adopted for C and O atoms. Hydrogen atoms were located from difference electron-density maps and their positional and isotropic thermal parameters included in the refinement.

Final electron-density maps calculated at the conclusion of the refinement showed residual density around the mid-points of ring bonds, etc., but no structurally significant peaks.

Scattering functions and the weighting scheme adopted were the same as those described in Part V.[11] All calculations described were carried out on an XDS Sigma 2 computer using programs written in this laboratory.

RESULTS

Molecular geometry and conformation

Atomic parameters defining the crystal structures of the two acids are given with their standard deviations in Tables III and IV. The numbering scheme adopted is that described in Part V with hydrogen atoms numbered to correspond to the atom of attachment. Bond lengths and angles are given in Table V. Within the limits of accuracy of the determinations there are no significant differences in the values for corresponding bond lengths and

TABLE III

Atomic parameters defining the crystal structure of 6OBAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	34(1)	2467(3)	537(1)	4.6	200	230	287
O(2)	1388(1)	1388(3)	419(1)	4.6	206	236	280
O(3)	4167(1)	10306(3)	3023(1)	4.0	193	225	253
C(1)	1821(2)	4838(4)	1308(1)	3.3	197	199	220
C(2)	2939(2)	5175(5)	1543(1)	3.7	203	220	228
C(3)	3690(2)	7015(5)	2107(1)	3.7	194	223	229
C(4)	3337(2)	8585(4)	2451(1)	3.3	193	198	223
C(5)	2218(2)	8324(5)	2214(1)	3.8	198	217	239
C(6)	1475(2)	6455(5)	1642(1)	3.8	187	220	246
C(7)	1018(2)	2803(4)	721(1)	3.7	201	219	227
C(8)	3878(2)	12014(5)	3409(1)	4.2	211	233	248
C(9)	4931(2)	13695(5)	3995(1)	4.7	208	256	264
C(10)	5956(2)	12125(5)	4671(1)	5.0	217	239	290
C(11)	6990(2)	13918(6)	5272(1)	5.8	227	268	312
C(12)	8017(2)	12404(7)	5949(2)	7.7	233	283	399
C(13)	8994(2)	14232(8)	6577(2)	8.9	229	341	411
H(2)	321(2)	407(4)	131(1)	3.8(4)			
H(3)	443(1)	719(4)	225(1)	4.4(5)			
H(5)	196(1)	942(4)	246(1)	4.6(5)			
H(6)	75(1)	630(4)	149(1)	3.4(4)			
H(8a)	367(1)	1092(4)	366(1)	4.6(5)			
H(8b)	317(1)	1304(4)	300(1)	5.6(5)			
H(9a)	470(2)	1505(5)	423(1)	7.0(6)			
H(9b)	521(2)	1458(4)	371(1)	6.0(5)			
H(10a)	570(2)	1109(5)	493(1)	7.7(6)			
H(10b)	620(2)	1076(5)	445(1)	7.6(6)			
H(11a)	676(2)	1537(6)	550(1)	9.7(7)			
H(11b)	713(2)	1488(6)	493(1)	10.0(8)			
H(12a)	780(2)	1128(6)	623(1)	12.6(9)			
H(12b)	827(3)	1108(7)	566(2)	18.1(12)			
H(13a)	882(2)	1537(7)	690(2)	13.7(10)			
H(13b)	971(2)	1319(7)	707(1)	13.6(10)			
H(13c)	915(2)	1551(7)	629(2)	14.0(10)			
H(O)	67(2)	−36(7)	0(2)	13.5(9)			

Positional parameters are given as fractions of the unit cell edges, $\times 10^4$ for C and O, $\times 10^3$ for H. Thermal parameters are given as equivalent isotropic B values (Å^2) for C and O, together with the root-mean-square amplitudes of thermal vibration (Å $\times$ 10^3) along the principal axes of the ellipsoids; and as observed B values for H.

angles in the two compounds and the dimensions found agree well with those found in Parts V and VI with the exception of the carboxy group geometry.

By contrast with the other acids in this series, the C—O bond lengths of the carboxy groups are significantly different and close to the values expected for ordered hydroxy and carbonyl distances. The molecules are present in the crystal as centrosymmetric hydrogen-bonded dimers with the O ... O separations being 2.632 Å for 6OBAC and 2.628 Å for 8OBAC,

TABLE IV

Atomic parameters defining the crystal structure of 8OBAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	920(2)	2401(4)	221(2)	4.41	177	244	277
O(2)	−566(2)	1483(4)	−1527(2)	4.73	188	240	295
O(3)	1595(2)	10325(4)	−3578(2)	3.86	166	230	257
C(1)	640(2)	4878(6)	−1591(3)	3.48	182	210	234
C(2)	49(3)	5195(7)	−2869(3)	4.04	200	224	252
C(3)	382(2)	7061(7)	−3500(3)	3.79	188	221	245
C(4)	1316(2)	8584(6)	−2872(3)	3.36	172	207	235
C(5)	1904(3)	8325(6)	−1597(3)	3.73	187	221	241
C(6)	1553(2)	6466(6)	−977(3)	3.70	186	226	235
C(7)	337(2)	2813(6)	−903(3)	3.66	193	212	236
C(8)	2594(3)	11850(6)	−2990(3)	3.92	186	234	244
C(9)	2760(3)	13420(7)	−3969(3)	4.33	190	249	257
C(10)	2940(3)	11631(7)	−4863(3)	4.59	198	252	268
C(11)	3263(3)	13246(7)	−5733(3)	4.74	198	263	268
C(12)	3472(3)	11491(7)	−6616(3)	4.90	216	255	273
C(13)	3852(3)	13109(8)	−7434(3)	4.94	205	261	278
C(14)	4039(3)	11369(8)	−8344(3)	5.80	233	282	294
C(15)	4479(3)	13040(10)	−9105(4)	6.50	226	294	333
H(2)	−68(2)	413(6)	−335(3)	5.5(7)			
H(3)	−2(2)	729(6)	−437(2)	4.1(6)			
H(5)	261(2)	955(6)	−110(3)	5.2(7)			
H(6)	193(2)	629(6)	−9(2)	4.2(6)			
H(8a)	323(2)	1061(6)	−254(2)	4.0(6)			
H(8b)	253(2)	1308(6)	−239(2)	4.5(7)			
H(9a)	340(2)	1473(6)	−353(3)	5.3(7)			
H(9b)	212(3)	1475(7)	−441(3)	6.1(8)			
H(10a)	350(2)	1036(6)	−443(3)	5.6(8)			
H(10b)	229(3)	1065(7)	−535(3)	6.2(8)			
H(11a)	396(3)	1448(7)	−524(3)	6.5(8)			
H(11b)	272(3)	1472(7)	−615(3)	6.3(8)			
H(12a)	402(3)	1004(7)	−615(3)	7.6(9)			
H(12b)	282(2)	1034(7)	−713(3)	6.1(8)			
H(13a)	460(3)	1417(7)	−688(3)	6.5(8)			
H(13b)	327(3)	1485(7)	−787(3)	8.2(10)			
H(14a)	461(3)	985(7)	−789(3)	7.0(9)			
H(14b)	323(3)	1049(8)	−889(3)	8.1(10)			
H(15a)	401(4)	1484(10)	−960(4)	12.1(14)			
H(15b)	467(3)	1151(7)	−973(3)	7.3(9)			
H(15c)	530(3)	1386(8)	−866(4)	10.0(12)			
H(O)	−71(4)	−6(9)	−89(4)	11.4(13)			

Positional parameters are given as fractions of the unit cell edges, $\times 10^4$ for C and O, $\times 10^3$ for H. Thermal parameters are given as equivalent isotropic B values (Å^2) for C and O, together with the root-mean-square amplitudes of thermal vibration (Å $\times 10^3$) along the principal axes of the ellipsoids; and as observed B values for H. Estimated standard deviations are given in parentheses and are applicable to the least significant figures quoted.

TABLE V

Bond lengths (Å) and bond angles (deg.)

Bond	6OBAC	8OBAC
O(1)—C(7)	1.246(2)	1.243(3)
O(2)—C(7)	1.294(2)	1.302(3)
O(3)—C(4)	1.369(2)	1.367(3)
O(3)—C(8)	1.437(2)	1.437(3)
C(1)—C(2)	1.391(2)	1.397(4)
C(2)—C(3)	1.373(3)	1.382(4)
C(3)—C(4)	1.389(2)	1.382(4)
C(4)—C(5)	1.385(2)	1.392(4)
C(5)—C(6)	1.381(3)	1.384(2)
C(6)—C(1)	1.378(2)	1.379(4)
C(7)—C(1)	1.471(3)	1.470(4)
C(8)—C(9)	1.501(3)	1.504(4)
C(9)—C(10)	1.509(3)	1.511(4)
C(10)—C(11)	1.527(3)	1.521(4)
C(11)—C(12)	1.497(4)	1.509(4)
C(12)—C(13)	1.518(4)	1.520(4)
C(13)—C(14)	—	1.517(5)
C(14)—C(15)	—	1.532(5)

Angle	6OBAC	8OBAC
O(1)—C(7)—O(2)	122.3(2)	122.5(3)
O(1)—C(7)—C(1)	120.6(2)	120.8(3)
O(2)—C(7)—C(1)	117.1(2)	116.7(3)
C(2)—C(1)—C(7)	121.1(2)	121.4(3)
C(6)—C(1)—C(7)	120.2(2)	119.8(3)
C(2)—C(1)—C(6)	118.7(2)	118.3(3)
C(1)—C(2)—C(3)	120.5(2)	120.3(3)
C(2)—C(3)—C(4)	120.1(2)	120.1(3)
C(3)—C(4)—C(5)	120.1(2)	120.4(3)
C(4)—C(5)—C(6)	118.9(2)	118.8(3)
C(5)—C(6)—C(1)	121.7(2)	121.7(3)
C(3)—C(4)—O(3)	115.1(2)	115.8(3)
C(5)—C(4)—O(3)	124.8(2)	123.8(3)
C(4)—O(3)—C(8)	118.9(1)	118.7(2)
O(3)—C(8)—C(9)	107.7(2)	108.2(3)
C(8)—C(9)—C(10)	114.5(2)	114.3(3)
C(9)—C(10)—C(11)	113.0(2)	113.1(3)
C(10)—C(11)—C(12)	113.9(3)	114.0(3)
C(11)—C(12)—C(13)	113.2(3)	113.5(3)
C(12)—C(13)—C(14)	—	113.8(3)
C(13)—C(14)—C(15)	—	112.3(3)

about 0.1 Å longer than in the isotypic series. The O—H bond lengths are 1.22(3) Å in 6OBAC and 1.15(4) Å in 8OBAC, not significantly different from one another but markedly closer to one oxygen atom than the other.

The *gauche*-relation of the ether oxygen with respect to C(γ) about the C(α)—C(β) bond of the chain, characteristic of the crystal structures of members of this homologous series, gives torsion angles O(3)—C(8)—C(9)—C(10) of 67.3° in 6OBAC and 62.9° in 8OBAC.

TABLE VI

Equations of selected least-squares mean planes

Plane	*n*	*a*	*b*	*c*	*d*	Δ_{ave}	Δ_{max}
Carboxy group	6	−0.10124	−0.67983	0.72635	−0.09726	0.018	0.037
	8	−0.68357	0.70635	0.18387	0.09734	0.001	0.003
Phenyl ring	6	−0.14075	−0.69295	0.70711	−0.21486	0.006	0.009
	8	−0.68903	0.71873	0.09306	0.28101	0.006	0.012
Alkyl chain	6	−0.86548	0.07548	0.49523	2.38259	0.042	0.068
	8	0.74282	−0.10809	0.66071	0.97241	0.067	0.158

Equations are given for the 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 cell origin For 6OBAC $X = x + z.\cos\beta$, $Y = y$, and $Z = z.\sin\beta$. For 8OBAC the conversion matrix is:

$$\begin{matrix} 13.44160 & 0.00000 & 0.00000 \\ 0.09267 & 4.86852 & 0.00000 \\ -5.48929 & 0.40748 & 10.87906 \end{matrix}$$

Equations for the least-squares mean planes through the atoms of the carboxy groups, phenyl rings, and alkyl chains are given in Table VI. In 6OBAC the phenyl ring is inclined at 2.6° to the plane of the carboxy group and at 65.2° to that of the alkyl chain; for 8OBAC these angles are 5.3 and 58.1°. Angles made by the chain and core axes with the unit-cell axes are given in Table VII. The core axis is defined as C(4)...C(4′) in each case and the chain axis is defined as C(8)... C(12) for 6OBAC and as C(8)... C(14) for 8OBAC. The chains are in the all *trans* extended conformation.

TABLE VII

Angles (deg.) made by chain and core axes with the unit cell axes

	6OBAC			8OBAC		
Axis	*a*	*b*	*c*	*a*	*b*	*c*
Chain	59.0	87.8	69.7	50.1	92.7	166.8
Core	75.5	46.4	68.1	56.2	48.0	132.9

Molecular packing

The dimer conformations found in these two crystal structures are very much alike and closely resemble those found in the isotypic series described in Part VI. As in that series the dimers form stacks with a translational repeat along the stacking axis of rather less than 5 Å. The principal difference between the various crystal structures is in the way in which these stacks are packed together.

Views of the dimer packing, in projection down the stacking axis (the crystal *b*-axis), are shown for 6OBAC in Figure 1 and for 8OBAC in Figure 2. The relative heights of the dimer components are indicated by differing line thicknesses, those in heavier outline being closer to the viewer. In projection the two structures look very similar. In each case the chain axes are almost normal to the axis of projection, but whereas the core axes in 8OBAC are

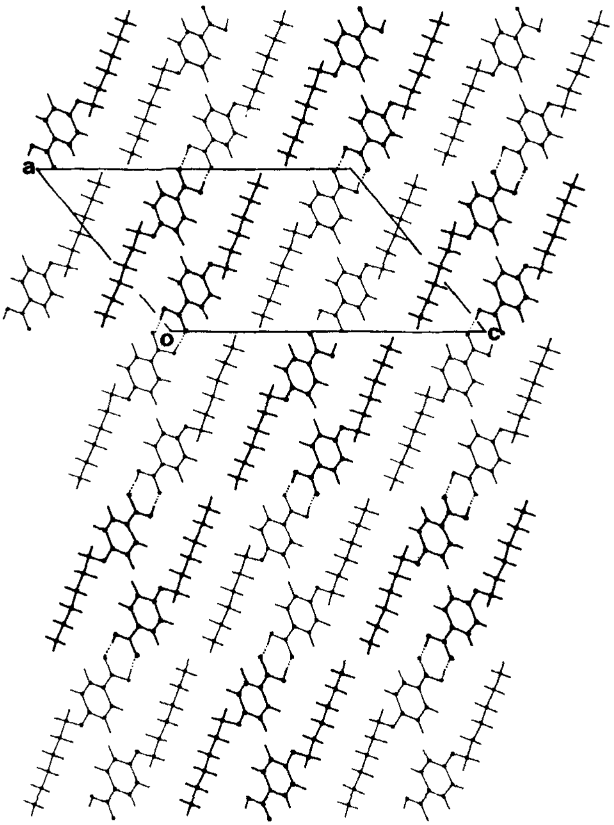

FIGURE 1 Molecular packing in the crystal of 6OBAC seen in *b*-axis projection.

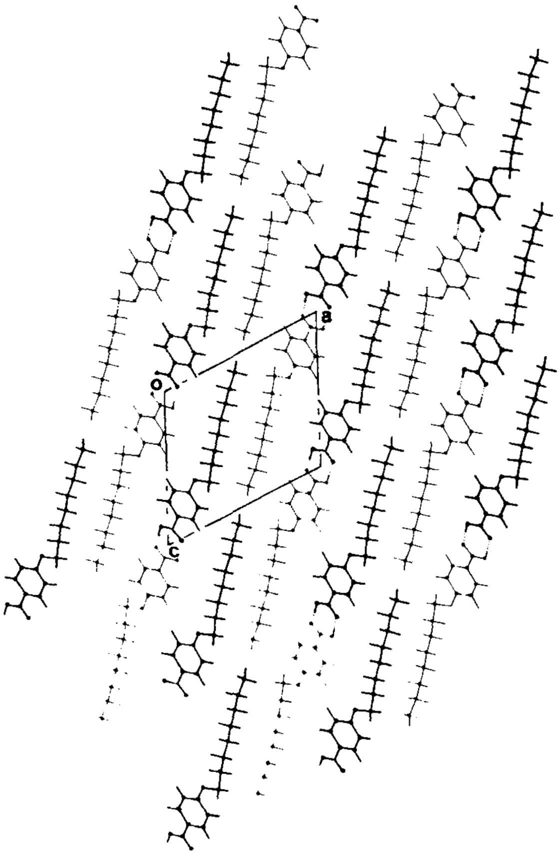

FIGURE 2 Molecular packing in the crystal of 8OBAC seen in *b*-axis projection.

uniformly inclined at 48.0° to the axis of projection, in 6OBAC the core axes are alternately inclined to *b* at ±46.4°. Both structures feature lateral juxtaposition of antiparallel chains of dimers in adjacent stacks of common orientation, the overlap being somewhat greater in 8OBAC than in 6OBAC. These chain-chain interactions are sufficiently pronounced that it is possible to trace complete surfaces of aliphatic character through the two crystal structures, roughly parallel to the *bc*-face in 8OBAC and roughly normal to $[10\bar{1}]$ in 6OBAC.

Although in these projections the dimers appear to be arranged in staggered parallel rows, the packing in three dimensions is quite different from that found in the nematogenic 3OBAC and 5OBAC structures. It is possible to define a sheet element in the structure of 8OBAC, which is illustrated in Figure 3. By contrast with the sheets in 3OBAC and 5OBAC, where the mole-

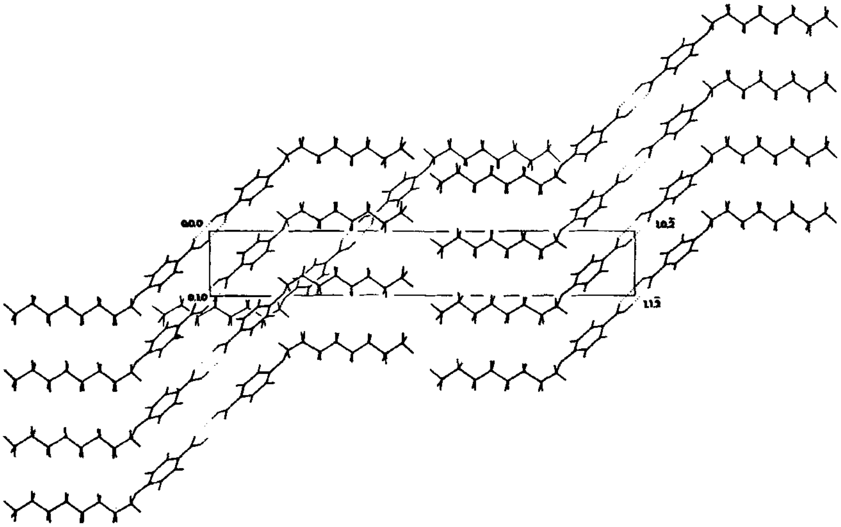

FIGURE 3 Sheet element in the structure of 8OBAC showing head-to-tail arrangement of dimers. Numerals indicate translations in *a*, *b*, and *c*, respectively.

cules lie in staggered parallel rows with the core axis defining the director within the sheet, the dimers in this sheet element are arranged in ribbons with a head-to-tail relation from ribbon to ribbon. A single dimer in an adjacent sheet element has been drawn to show the inherent interactions.

The somewhat more complex interrelations of chains and cores in 6OBAC are shown in partial projection down *a* in Figure 4.

Lateral and vertical relationships between molecules in parallel stacks are shown for 6OBAC in Figure 5 and for 8OBAC in Figure 6. With respect to the core axes and the plane of the phenyl rings, the longitudinal displacement of dimers within a stack in 6OBAC is 3.25 Å, the lateral displacement is 1.35 Å, and the vertical displacement is 3.43 Å. For 8OBAC these displacements are, respectively, 3.1, 1.45, and 3.43 Å. The lateral displacements are somewhat greater, and the vertical displacements somewhat smaller than for the isotypic series.

Within the dimer stacks of 6OBAC there is a limiting C ... *C* contact between C(5) and C(7) of adjacent dimers (3.39 Å) and there are two other C...C contacts <3.5 Å [C(6)...C(7), 3.57 Å, and C(4)...C(9), 3.59 Å]. Limiting C ... H contacts are found between H(8b) and C(4), C(5), and C(6) (2.95, 2.84, and 2.85 Å, respectively) and between H(9b) and C(3) (2.95 Å). Also within the stacks, O(1) and C(7′) are only 3.19 Å apart. By contrast with these close contacts, there are no really close contacts between the chains of dimers within the stacks, all but one of the interchain H...H

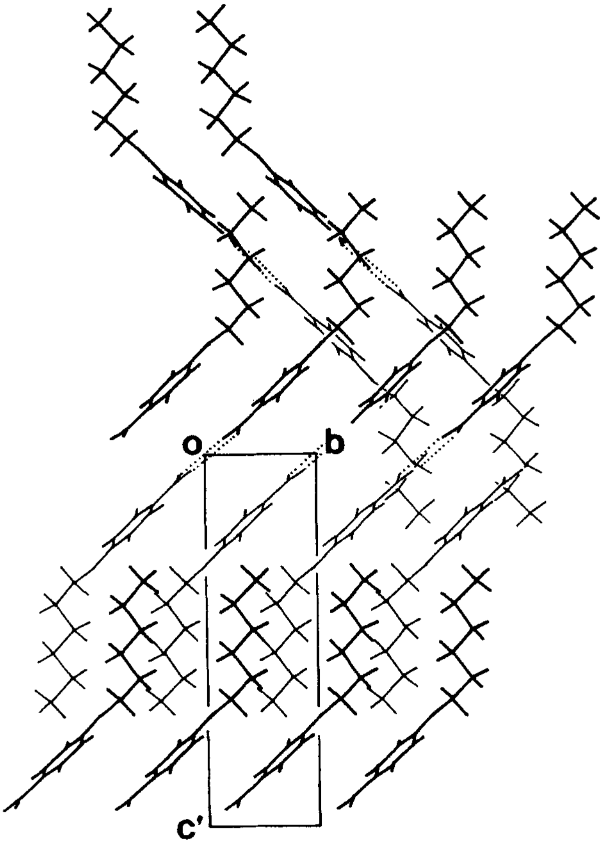

FIGURE 4 Molecular packing in the crystal of 6OBAC seen in partial projection down *a*.

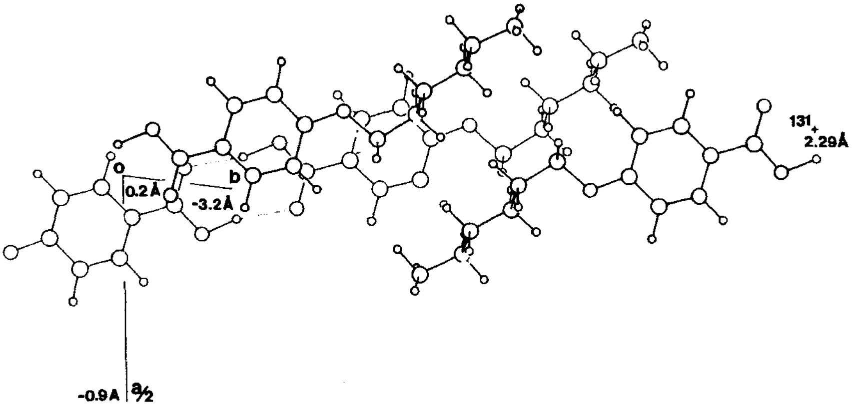

FIGURE 5 Lateral and vertical relations between parallel molecules of 6OBAC seen in projection onto the phenyl-ring planes.

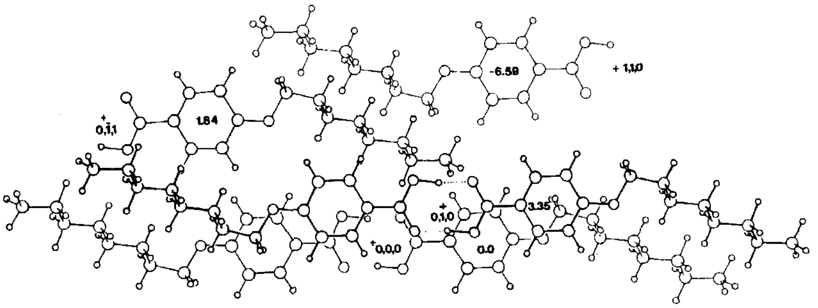

FIGURE 6 Lateral and vertical relations of dimers on 8OBAC seen in projection onto the phenyl-ring planes.

approaches being >3.0 Å. Short interchain H...H contacts occur laterally between centrosymmetrically related dimers with H(8a)...H(12′a) and H(10a)...H(10′a) at $1-x$, $2-y$, and $1-z$, both being 2.36 Å, and H(9a)...H(11′a) at $1-x$, $3-y$, and $1-z$ being 2.48 Å. Limiting chain terminus contacts are found between H(13a) and H(13′b) of 2.46 Å, and ring-chain contacts H(6)...H(13c), 2.41 Å, and H(2)...H(10′b), 2.35 Å, are noted. The structure is quite tightly packed overall.

Within the stacks in 8OBAC much the same limiting contacts are present. C(5)...C(7) is 3.38 Å, C(6)...C(7) is 3.49 Å, but C(2)...C(4), 3.61 Å, and C(3)...C(8), 3.69 Å, are the only other C...C contacts <3.7 Å. O(1) and C(7′) are 3.19 Å apart, the same distance as in 6OBAC. H(8a) makes limiting contacts with C(4), C(5), and C(6) of the ring of an adjacent dimer in the stack (2.92, 2.89, and 2.99 Å, respectively). There are again no close interchain contacts within the stacks, the limiting chain-chain interactions being from laterally juxtaposed antiparallel chains, with H...H contacts in the range 2.4–2.6 Å. There is also a short interterminal contact H(15c)...H(15′c) of 2.22 Å.

DISCUSSION

The existence of these two crystal forms and of the isotypic form described in Part VI demonstrates that there are several quite different and energetically almost equivalent ways of packing together these dimers when the chain length has reached a point that close-packed chain-chain interactions become determinants of solid-state organization. The isotypic form seems, at first glance, to be the more promising basis from which to derive the smectic organization as it already has a well defined layer structure in which the effect of chain-chain interactions becomes progressively more important as the chain length increases, and it is known that the range of stability of the smectic phase increases also with chain length. However, as we have seen, the mesophase X-ray periodicities[12] seem to point to a structure in which there is no significant interdigitation of the chains in adjacent layers, and although the structure of 8OBAC reported here has sheets of dimers arranged in just such a head-to-tail fashion, it also has antiparallel alignment of chains in adjacent sheets. The antiparallel alignment of chains which is a feature of all the crystal structure forms for the smectogens thus far analyzed is a consequence of a structural feature which is common to all—the arrangement of the dimers in stacks. Although this arrangement allows a very efficient close-packing of the dimer cores, it does not bring the chains of adjacent dimers within the stacks into particularly close contact, space being filled by the lateral juxtaposition of the chains of adjacent stacks. It may well be that at higher thermal energies the close-packing of the cores is abandoned in favor of other arrangements which allow a closer approach of parallel chains. However, the correlation does exist that all the smectogenic crystal forms known at this stage do feature dimer stacks with some degree of antiparallel chain alignment, a type of packing quite different from that found in the lower nematogenic forms.

Little can be said about the packing arrangement found in 6OBAC as to why this material ultimately yields a nematic rather than a smectic phase. The crystal structure has a form of chain alignment very close to that found in this form of 8OBAC, but the structure also has a type of axial crossing (see Figure 4) thus far found only in two other nematogens, both of which also undergo solid-solid transitions before forming a mesophase.[2-4] One may speculate that with increasing temperature the interchain forces will not remain strong enough to preserve this axial crossing and that at some point the molecules will dispose themselves about a common director axis with three translational degrees of freedom, but it is obviously futile to attempt such an extrapolation of packing mode through five phase transitions. On the other hand, the existence of this wide spectrum of solid-state structures of progessively increasing energy offers a chance to study the path to the mesophase at successive stages of the gradually altering balance between thermal energy and intermolecular attractive forces.

In the same way, before a convincing model for the smectic phase of these materials can be offered, we need to know the structures of the intermediate higher temperature solid-state structures so that we can say something about the direction of structural alteration with increasing temperature. We can perhaps get some idea of this direction from the two known forms of 8OBAC. Both crystal forms seem to be stable at room temperature and each transforms to a mestastable phase at 74°C. In terms of the molecular volume, which is 355.9 Å^3 in the form described in this paper and 358.8 Å^3

in the isotypic form, the non-isotypic form should be marginally more stable. It is possible, from a comparison of Figure 2 in this paper with Figure 4 in Part VI, to visualize a fairly conservative mechanism by which this form might pass over to the isotypic variety, although there is no evidence that such a transition does, in fact, take place. The mechanism would involve a rotation of stacks of dimers about the *b*-axis accompanied by closing up of the separation of core centers along *a* and establishment of complete interdigitation of the chains along *c*. If this is indeed the direction of change and if the smectic phase does not involve interdigitation at all, then it is almost inevitable that the transition to the smectic phase is accompanied by a change in the stacking of dimers present in the crystal structures now known. A proper understanding of these matters, however, requires additional knowledge of the organization in the intermediate phases.

Acknowledgment

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