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An X-Ray Study of the *p*-n-Alkoxybenzoic Acids. Part VI. Isotypic Crystal Structures of Four Smectogenic Acids Having Seven, Eight, Nine, and Ten Alkyl Chain Carbon Atoms

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The isotypic crystal form for the smectogenic *p*-n-alkoxybenzoic acids has been determined by room-temperature single-crystal x-ray diffraction analyses for the acids having 7, 8, 9, and 10 carbon atoms in the alkyl chain. The molecules are present in the crystals as centrosymmetric hydrogen-bonded dimers. The alkyl chains adopt an all-*trans* extended conformation but a *gauche*-relation of the ether oxygen and C(γ) about the C(α)-C(β) bond of the chains imparts a markedly non-linear and non-planar conformation to the molecules. With these chain lengths, adoption of this conformation makes possible an imbricated stratified layer structure in which the alkyl chains and the central aromatic nuclei are segregated into separate close-packed strata. Antiparallel interdigitation of chains in adjacent layers gives a 2:1 ratio of chains to nuclei in the strata. Evidence is presented that the molecules in the smectic mesophase probably retain the conformation found in the crystal and it is shown that the change in chain tilt angle in passing from solid to smectic phases is not as great as previously supposed. $C_{14}H_{20}O_3$ (70BAC). Triclinic, $P\bar{1}$, $a = 4.739(5)$, $b = 8.034(7)$, $c = 17.948(18)$ Å, $\alpha = 82.32(8)$, $\beta = 93.78(7)$, $\gamma = 102.19(2)°$, $Z = 2$. $C_{15}H_{22}O_3$ (80BAC). Triclinic, $P\bar{1}$, $a = 4.825(1)$, $b = 8.123(2)$, $c = 19.036(4)$ Å, $\alpha = 81.15(2)$, $\beta = 94.57(2)$, $\gamma = 102.98(2)°$, $Z = 2$. $C_{16}H_{24}O_3$ (90BAC). Triclinic, $P\bar{1}$, $a = 4.743(1)$, $b = 8.049(2)$, $c = 20.484(4)$ Å, $\alpha = 82.38(2)$, $\beta = 93.36(2)$, $\gamma = 102.55(2)°$, $Z = 2$. $C_{17}H_{26}O_3$ (10OBAC). Triclinic, $P\bar{1}$, $a = 4.819(1)$, $b = 8.112(2)$, $c = 21.598(4)$ Å, $\alpha = 80.94(2)$, $\beta = 94.05(2)$, $\gamma = 102.87(2)°$, $Z = 2$. The small even-odd effect in the cell dimensions reflects a slight difference in the mode of chain packing in the solids.

INTRODUCTION

We have previously shown that the smectogenic members of the series of *p*-n-alkoxybenzoic acids having from seven to at least 18 carbon atoms in the alkyl chain crystallize from polar solvents in a stable isotypic form. Appearance of this crystal form coincides, indeed, with the appearance of smectic properties in the series.[1] We report here the structure of this isotypic crystal form for the first four members of the series showing smectic properties, those having seven, eight, nine, and ten carbon atoms in the alkyl chain. Although closely similar, as might be expected, the crystal structures of the acids of even and odd chain length differ somewhat in the mode of packing of the alkyl chains and, to a lesser extent, in the packing of the aromatic çores.

No direct extrapolation from the isotypic crystal form to the possible molecular organization in the mesophase is possible, however, as none of these four acids transforms directly to the smectic state from this crystal form on heating. All four crystals show solid-solid transitions before the solid-smectic transition, this polymorphism being readily apparent in the case of the two acids of even chain length, but less readily seen in the case of the two acids of odd chain length.[2,3]

We present evidence that despite the polymorphism the molecular conformation present in the isotypic crystal form is probably that also present in the smectic phase, and that the difference in molecular orientation in the crystal and smectic phases is not as great as hitherto supposed.[4]

Following the usage adopted in Part V, the acids are referred to by the acronym *n*OBAC, *n* indicating the number of carbon atoms in the alkyl chain.[5] Brief accounts of all four crystal structures have been given.[6,7]

EXPERIMENTAL

Samples of the acids having *n* = 8, 9, and 10 were prepared by standard methods.[3] A sample of 7OBAC (K & K Chemicals) was generously provided by Dr J. P. Heger, E. T. H. Lausanne. All samples were purified by repeated recrystallization from glacial acetic acid. Crystals suitable for X-ray study were grown by recrystallization of 7OBAC from glacial acetic acid, of 8OBAC and 9OBAC from propanol, and of 10OBAC from ethanol.

Transition temperatures and enthalpies measured by differential scanning calorimetry have been reported for the series by Herbert.[2] For crystals grown from glacial acetic acid or ethanol solutions, he noted the presence of solid-solid transitions on heating the acids of even chain length, but reported a direct transition from the solid to the smectic phase for the acids of odd chain length. Bennett and Jones,[3] and Gray and Jones[3] each note the existence of solid-solid transitions on cooling both even and odd members in crystals grown from acetic acid. The existence of solid-solid transitions for 8OBAC and 10OBAC, as reported by Herbert, was readily confirmed for our own samples by observation of the behavior of single crystals on heating them between crossed polarizers on a microscope. No evidence of such transitions could be found for 7OBAC and 9OBAC when observed in the same way as for the even members. However, solid-solid transitions were detectable when samples of the acids were subjected to differential scanning calorimetry using a Perkin Elmer DSC-II instrument. For 7OBAC, at a heating rate of 10° min^{-1}, three distinct thermal events were coalesced into the initial endotherm and these could be resolved when a heating rate of 2.5° min^{-1} was used. For 9OBAC, only a single endotherm marks the apparent solid-smectic transition, but careful examination of the traces shows that a separate thermal event precedes this endotherm and proceeds slowly merging with the main peak. By contrast with 7OBAC, thermal cycling and change of heating or cooling rate do not improve the resolution of these two events significantly. It is also difficult to obtain a reproducible smectic-nematic transition temperature. Herbert's failure to discern the solid-solid transitions for 9OBAC is understandable, given the lower sensitivity of the intrument used by him, but it is surprising that he did not observe the 7OBAC transitions. Transition temperatures for our samples were obtained by extrapolation of the thermogram traces to the onset of thermal activity for each event, and are given in Table I.

TABLE I

Transition temperatures for the four acids (deg. C)

n	$K_{II} \rightarrow K_I$	$K_I \rightarrow S_C$	$S_C \rightarrow N$	$N \rightarrow I$
7	88	90.5	95.5	147
8	74	99	104	146
9	87	90	?	143
10	85	97	125	143

Crystal data

Crystallographic data for the four acids are summarized in Table II. Crystal symmetry, including the non-occurrence of systematically absent reflections, was established from 25° precession photographs taken with Mo $K\alpha$ radiation. With two molecules in the unit cell, space group $P\bar{1}$ was chosen over $P1$ because of the known preference of these acids to crystallize as centrosymmetric hydrogen-bonded dimers. This choice is supported in each case by the statistical distribution of the diffracted intensities. Unit

TABLE II

Crystallographic data

	7OBAC	8OBAC	9OBAC	10OBAC
Crystal symmetry	triclinic	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	P	$P\bar{1}$
a (Å)	4.739(5)	4.825(1)	4.743(1)	4.819(1)
b	8.034(7)	8.123(2)	8.049(2)	8.112(2)
c	17.948(18)	19.036(4)	20.484(4)	21.598(4)
α (deg.)	82.32(8)	81.15(2)	82.38(2)	80.94(2)
β	93.78(7)	94.57(2)	93.36(2)	94.05(2)
γ	102.19(10)	102.98(2)	102.55(2)	102.87(2)
Cell volume (Å^3)	661.5	717.6	756.2	812.2
D_{obs}(g cm^{-3})	1.183(6)	1.15(1)	1.15(1)	1.14(1)
D_{cal}(g cm^{-3})	1.186	1.158	1.161	1.138
Z	2	2	2	2
Molecular volume (Å^3)	330.8	358.8	378.1	406.1
Points scanned	1973	2125	2164	2413
Significant I's	1276	1352	1731	1870
Scan range (2θ)	2°	4°	4°	4°
R (significant data)	0.074	0.041	0.037	0.033
R_w	0.062	0.042	0.041	0.036

cell dimensions were obtained by a least-squares fit ($\lambda = 1.5418$ Å) to the diffractometer values of $\pm 2\theta$ for 24 or more strong reflections measured from carefully centered crystals. Crystal densities were determined by flotation, using aqueous KI solution.

Intensity data

Intensity measurements were made by automatic single-crystal diffractometry in the same way as described in Part V. A single hemisphere of data was surveyed for each acid using Cu Kα radiation made monochromatic by Bragg reflection from a highly oriented graphite crystal of known dispersion. Both $0kl$ and $0\bar{k}\bar{l}$ zones were measured to check the equality of intensity, as a measure of crystal alignment, and the stability of the experimental conditions was checked by monitoring two reference reflections after every 50 measurement cycles. Results comparable to those reported in Part V were obtained in each case.

No corrections were made for absorption, which for the crystal sizes used should have been of little importance, and structure amplitudes and normalized structure amplitudes were derived in the usual ways.

Structure determination and refinement

Because of the isotypic nature of the unit cells of these acids, which differ only in the lengths of their c-axes (to a reasonable first approximation), solution of the structure of any one of them leads at once to solution of the others. The structure of 7OBAC was first determined from a three-dimensional sharpened Patterson function in which the characteristic vector pattern for a planar centrosymmetric dimer of "oxobenzoic acid" could be readily discerned. An electron-density synthesis based on such a residue centered at the space-group origin revealed the two additional in-plane carbon atoms of the chain, and the remaining chain atoms were found from successive syntheses.

For the other structures starting points for least-squares refinement were obtained by assuming an identity of corresponding x and y coordinates for all compounds for the 7OBAC residue, and by modifying the z coordinates by multiplication by c_7/c_n where c_n is the length of the c-axis in each case, Coordinates for the additional atoms were derived on the assumption of an extended all-*trans* planar conformation for the chains.

Refinement was by the block-diagonal least-squares method in each case, using 3 × 3 and 6 × 6 blocks for positional and thermal parameters respectively. Anisotropic thermal parameters were adopted for C and O only. All hydrogen atoms were readily identified from difference electron-density maps and their positional and isotropic thermal parameters were included in the refinement. Convergence was complete in each case with shift to error ratios <0.10 for all parameters in the final cycles.

Final difference electron-density maps were calculated at the end of the refinement. For 7OBAC no structurally significant density remained. For the other compounds the residual density was concentrated about the midpoints of C—C and C—H bonds in the ring system, and to a lesser extent at the mid-points of C—C bonds in the chains. No attempt was made to take account of this density, but its distribution attests to the good quality of three of the four analyses. The somewhat poorer quality of the determination for 70BAC is most probably related to rather poorer crystal quality.

Scattering functions and weighting schemes adopted were the same as those used in Part V. With the exception of program *ORTEP*,[8] for which a CDC Cyber 172 computer was used, all calculations were carried out using programs written in this laboratory for the XDS Sigma 2 computer also used to control the diffractometer.

RESULTS

Molecular geometry and conformation

Atomic parameters defining the crystal structures of the four acids are given with their standard deviations in Tables III–VI. The numbering scheme adopted is that described in Part V, with hydrogen atoms numbered to correspond

TABLE III

Atomic parameters defining the crystal structure of 7OBAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	−2194(6)	−356(3)	746(2)	5.70	231	258	311
O(2)	−589(6)	2039(3)	−15(1)	5.49	226	268	293
O(3)	−7807(6)	4750(3)	2245(1)	5.14	230	252	281
C(1)	−3552(8)	2199(4)	986(2)	4.13	211	227	247
C(2)	−5113(9)	1369(9)	1598(2)	5.16	220	262	281
C(3)	−6526(9)	2255(5)	2004(2)	5.17	216	264	284
C(4)	−6364(8)	3982(5)	1796(2)	4.37	224	230	251
C(5)	−4849(8)	4844(5)	1183(2)	4.46	222	238	252
C(6)	−3434(8)	3922(5)	783(2)	4.60	214	231	275
C(7)	−2007(8)	1229(5)	550(2)	4.51	211	227	275
C(8)	−7842(8)	6536(5)	2049(2)	4.86	235	252	257
C(9)	−9322(8)	7069(5)	2668(2)	5.00	235	254	264
C(10)	−7551(9)	7096(5)	3407(2)	5.28	237	251	285
C(11)	−9121(9)	7476(5)	4060(2)	5.37	250	251	281
C(12)	−7311(9)	7459(5)	4797(2)	5.66	249	261	292
C(13)	−8911(10)	7680(6)	5467(2)	6.50	250	299	309
C(14)	−7084(11)	7672(7)	6193(3)	7.95	257	331	356
H(2)	−533(7)	13(4)	175(2)	5.4(8)			
H(3)	−752(7)	163(4)	245(2)	5.6(8)			
H(5)	−479(7)	612(4)	101(2)	5.9(8)			
H(6)	−232(8)	457(5)	37(2)	6.8(9)			
H(8a)	−874(7)	668(4)	153(2)	5.6(8)			
H(8b)	−596(8)	717(4)	199(2)	6.5(9)			
H(9a)	−1104(7)	627(4)	276(2)	5.1(8)			
H(9b)	−948(7)	832(4)	246(2)	5.8(8)			
H(10a)	−717(8)	591(5)	355(2)	7.6(10)			
H(10b)	−581(8)	807(5)	333(2)	8.0(11)			
H(11a)	−1073(9)	650(5)	418(2)	8.8(12)			
H(11b)	−949(8)	876(5)	391(2)	7.4(10)			
H(12a)	−686(8)	632(4)	490(2)	6.7(9)			
H(12b)	−568(9)	852(5)	473(2)	8.3(11)			
H(13a)	−1047(9)	661(5)	550(2)	8.7(11)			
H(13b)	−946(10)	893(6)	556(2)	10.8(13)			
H(14a)	−791(11)	791(6)	664(3)	13.1(16)			
H(14b)	−649(11)	662(6)	632(3)	11.8(15)			
H(14c)	−544(11)	874(6)	616(3)	13.2(16)			

Positional parameters are given as fractions of the unit cell edges, $\times 10^4$ for C and O and $\times 10^3$ 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 vibration (Å $\times$ 10^3) along the principal axes of the thermal ellipsoids. Observed B values are given for H. Estimated standard deviations are given in parentheses and are applicable to the least significant digits quoted.

TABLE IV

Atomic parameters defining the crystal structure of 8OBAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	−2265(4)	−397(2)	686(1)	5.4	208	246	316
O(2)	−551(4)	2030(3)	−11(1)	5.1	218	244	296
O(3)	−7673(4)	4609(2)	2087(1)	5.0	211	244	292
C(1)	−3539(6)	2120(3)	901(2)	3.9	194	214	257
C(2)	−5188(7)	1274(4)	1461(2)	4.9	208	242	293
C(3)	−6559(7)	2127(4)	1846(2)	4.9	216	232	294
C(4)	−6298(6)	3876(4)	1662(2)	4.2	200	216	270
C(5)	−4703(6)	4744(4)	1097(2)	4.5	217	219	272
C(6)	−3334(6)	3863(4)	718(2)	4.3	211	224	263
C(7)	−2033(6)	1199(4)	503(2)	4.3	193	223	274
C(8)	−7634(7)	6403(4)	1909(2)	5.0	204	245	298
C(9)	−9034(6)	6897(4)	2502(2)	5.1	199	252	301
C(10)	−7228(7)	6891(4)	3195(2)	5.6	200	255	330
C(11)	−8598(7)	7371(4)	3797(2)	5.7	208	265	322
C(12)	−6879(7)	7258(4)	4502(2)	5.9	215	257	334
C(13)	−8228(7)	7709(4)	5112(2)	5.9	227	275	309
C(14)	−6571(8)	7582(5)	5825(2)	7.0	248	301	338
C(15)	−7979(9)	8046(6)	6424(2)	8.5	289	327	364
H(2)	−534(5)	14(3)	160(1)	6.3(7)			
H(3)	−780(5)	148(3)	226(1)	5.3(6)			
H(5)	−450(5)	597(3)	95(1)	6.3(7)			
H(6)	−209(5)	450(3)	30(1)	6.0(7)			
H(8a)	−863(6)	655(4)	143(2)	8.4(9)			
H(8b)	−550(5)	709(3)	188(1)	5.4(7)			
H(9a)	−1100(5)	606(3)	261(1)	6.1(7)			
H(9b)	−939(6)	806(3)	234(1)	7.0(7)			
H(10a)	−678(6)	577(3)	332(2)	8.4(9)			
H(10b)	−520(7)	777(4)	309(2)	9.3(9)			
H(11a)	−1060(6)	657(4)	386(2)	8.4(9)			
H(11b)	−903(7)	855(4)	365(2)	9.1(9)			
H(12a)	−650(6)	612(4)	461(1)	7.5(8)			
H(12b)	−494(6)	809(3)	441(1)	7.8(8)			
H(13a)	−1008(6)	694(4)	520(2)	8.9(9)			
H(13b)	−865(6)	888(4)	500(3)	8.7(9)			
H(14a)	−619(7)	642(4)	593(2)	11.1(10)			
H(14b)	−465(7)	844(4)	575(2)	11.0(10)			
H(15a)	−683(10)	794(6)	691(2)	17.1(15)			
H(15b)	−963(9)	725(5)	654(2)	14.3(13)			
H(15c)	−820(9)	930(5)	636(2)	15.1(14)			
H(O)	−77(8)	−177(5)	32(2)	14.4(13)			

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

TABLE V
Atomic parameters defining the crystal structure of 9OBAC

Atom	x	y	z	B	r_1	r_1	r_3
O(1)	−2255(3)	−364(1)	649(1)	4.70	193	225	302
O(2)	−592(3)	2044(2)	−9(1)	4.38	194	220	284
O(3)	−7884(3)	4726(1)	1964(1)	3.95	183	203	275
C(1)	−3591(3)	2183(2)	853(1)	3.14	191	200	207
C(2)	−5203(4)	1353(2)	1390(1)	4.04	188	220	264
C(3)	−6653(4)	2227(2)	1745(1)	4.08	191	202	279
C(4)	−6452(4)	3970(2)	1570(1)	3.28	180	212	217
C(5)	−4865(4)	4827(2)	1033(1)	3.48	188	203	236
C(6)	−3439(4)	3918(2)	683(1)	3.41	190	208	224
C(7)	−2065(4)	1228(2)	478(1)	3.47	204	209	216
C(8)	−7885(4)	6512(2)	1801(1)	3.74	198	214	239
C(9)	−9345(4)	7025(2)	2351(1)	3.78	192	224	238
C(10)	−7598(4)	7031(2)	2993(1)	4.19	195	227	264
C(11)	−9107(4)	7395(2)	3573(1)	4.07	194	236	248
C(12)	−7326(4)	7342(2)	4214(1)	4.38	209	234	261
C(13)	−8876(4)	7566(2)	4811(1)	4.28	207	234	255
C(14)	−7088(4)	7530(2)	5447(1)	4.50	215	246	254
C(15)	−8666(5)	7717(3)	6045(1)	5.22	215	260	291
C(16)	−6871(5)	7721(3)	6679(1)	6.59	225	303	328
H(2)	−529(3)	18(2)	150(1)	5.0(4)			
H(3)	−766(4)	167(2)	216(1)	5.5(4)			
H(5)	−484(3)	603(2)	90(1)	4.5(4)			
H(6)	−230(3)	453(2)	30(1)	5.0(4)			
H(8a)	−882(3)	669(2)	135(1)	5.0(4)			
H(8b)	−588(3)	720(2)	176(1)	4.6(4)			
H(9a)	−1120(4)	616(2)	245(1)	5.4(4)			
H(9b)	−966(3)	814(2)	221(1)	4.9(4)			
H(10a)	−693(3)	589(3)	310(1)	5.5(4)			
H(10b)	−578(4)	786(2)	293(1)	6.2(5)			
H(11a)	−1090(4)	653(2)	362(1)	5.3(4)			
H(11b)	−974(3)	854(2)	345(1)	4.8(4)			
H(12a)	−681(4)	621(2)	429(1)	6.1(5)			
H(12b)	−566(4)	828(2)	415(1)	6.5(5)			
H(13a)	−1052(4)	663(2)	488(1)	6.7(5)			
H(13b)	−957(4)	863(2)	473(1)	6.6(5)			
H(14a)	−637(4)	642(2)	553(1)	7.0(5)			
H(14b)	−531(4)	848(2)	542(1)	6.6(5)			
H(15a)	−1052(4)	674(2)	609(1)	8.1(6)			
H(15b)	−943(4)	879(2)	596(1)	7.6(5)			
H(16a)	−625(4)	669(3)	678(1)	9.5(6)			
H(16b)	−527(5)	864(3)	666(1)	11.1(7)			
H(16c)	−792(4)	788(3)	710(1)	8.7(6)			
H(O)	56(6)	119(3)	−31(1)	13.3(8)			

Positional parameters are given as fractions of the unit cell edges, × 10^4 for C and O, and × 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 vibration (Å × 10^3) along the principal axes of the thermal ellipsoids. Observed B values are given for H.

TABLE VI

Atomic parameters defining the crystal structure of 10OBAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	−2284(3)	−405(1)	604(1)	5.3	208	251	308
O(2)	−556(2)	2030(1)	−9(1)	5.0	224	223	291
O(3)	−7767(2)	4587(1)	1840(1)	4.9	208	233	295
C(1)	−3582(3)	2111(2)	794(1)	3.8	208	218	230
C(2)	−5251(4)	1251(2)	1289(1)	4.8	204	240	286
C(3)	−6641(4)	2104(2)	1624(1)	4.9	211	231	294
C(4)	−6369(3)	3859(2)	1467(1)	3.9	203	231	233
C(5)	−4760(3)	4733(2)	967(1)	4.3	209	232	253
C(6)	−3367(3)	3858(2)	638(1)	4.1	215	229	241
C(7)	−2058(3)	1197(2)	446(1)	4.1	217	224	240
C(8)	−7712(4)	6385(2)	1688(1)	4.7	207	254	269
C(9)	−9096(4)	6875(2)	2214(1)	4.9	213	258	272
C(10)	−7318(4)	6837(2)	2824(1)	5.3	220	251	302
C(11)	−8680(4)	7288(2)	3365(1)	5.3	219	263	293
C(12)	−6968(4)	7155(2)	3977(1)	5.4	225	256	297
C(13)	−8335(4)	7560(2)	4527(1)	5.4	232	263	285
C(14)	−6646(4)	7415(2)	5141(1)	5.5	239	264	265
C(15)	−8031(4)	7810(2)	5690(1)	5.5	251	258	284
C(16)	−6399(5)	7665(3)	6306(1)	6.7	262	298	314
C(17)	−7812(5)	8081(3)	6842(1)	8.5	254	343	374
H(2)	−539(3)	5(2)	138(1)	6.6(4)			
H(3)	−783(3)	149(2)	199(2)	6.6(4)			
H(5)	−459(3)	593(2)	86(1)	5.7(4)			
H(6)	−218(3)	447(2)	29(1)	6.0(4)			
H(8a)	−872(3)	659(2)	127(1)	7.1(4)			
H(8b)	−558(3)	709(2)	164(1)	5.6(4)			
H(9a)	−1101(3)	605(2)	230(1)	5.3(4)			
H(9b)	−955(3)	802(2)	209(1)	6.3(4)			
H(10a)	−688(4)	568(2)	295(1)	7.7(5)			
H(10b)	−542(4)	766(2)	275(1)	7.6(5)			
H(11a)	−1061(4)	650(2)	344(1)	8.0(5)			
H(11b)	−905(4)	847(2)	326(1)	7.9(5)			
H(12a)	−657(3)	597(2)	407(1)	6.8(4)			
H(12b)	−504(3)	794(2)	393(1)	7.5(5)			
H(13a)	−1027(4)	677(2)	459(1)	8.4(5)			
H(13b)	−875(4)	874(2)	443(1)	8.0(5)			
H(14a)	−625(4)	624(2)	523(1)	7.9(5)			
H(14b)	−465(4)	819(2)	509(1)	8.4(5)			
H(15a)	−995(4)	704(2)	575(1)	9.3(5)			
H(15b)	−855(4)	896(2)	560(1)	9.1(5)			
H(16a)	−596(4)	650(2)	639(1)	10.1(6)			
H(16b)	−439(4)	844(2)	625(1)	9.7(5)			
H(17a)	−964(5)	726(3)	692(1)	12.8(7)			
H(17b)	−821(5)	927(3)	675(1)	14.5(8)			
H(17c)	−683(5)	794(3)	723(1)	12.2(7)			
H(O)	−77(4)	−120(3)	28(1)	12.0(7)			

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

TABLE VII

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

Bond	7OBAC	8OBAC	9OBAC	10OBAC	Mean
O(1)—C(7)	1.261(4)	1.272(3)	1.268(1)	1.272(1)	1.268
O(2)—C(7)	1.277(4)	1.271(3)	1.275(2)	1.273(2)	1.274
O(3)—C(4)	1.372(4)	1.363(3)	1.362(1)	1.361(2)	1.365
O(3)—C(8)	1.434(4)	1.440(3)	1.432(2)	1.438(1)	1.436
C(1)—C(2)	1.379(5)	1.381(4)	1.385(4)	1.384(2)	1.382
C(2)—C(3)	1.375(5)	1.376(4)	1.374(2)	1.373(2)	1.375
C(3)—C(4)	1.374(5)	1.389(3)	1.386(3)	1.389(2)	1.385
C(4)—C(5)	1.377(5)	1.379(4)	1.386(2)	1.379(2)	1.380
C(5)—C(6)	1.393(5)	1.385(4)	1.386(2)	1.379(2)	1.386
C(6)—C(1)	1.373(5)	1.388(3)	1.381(2)	1.386(2)	1.382
C(7)—C(1)	1.495(5)	1.472(4)	1.472(2)	1.466(2)	1.476
C(8)—C(9)	1.506(5)	1.510(4)	1.504(4)	1.505(2)	1.506
C(9)—C(10)	1.522(5)	1.521(4)	1.513(2)	1.519(2)	1.518
C(10)—C(11)	1.524(5)	1.509(4)	1.513(2)	1.511(2)	1.514
C(11)—C(12)	1.529(5)	1.523(5)	1.520(2)	1.511(2)	1.521
C(12)—C(13)	1.512(6)	1.504(4)	1.513(2)	1.510(2)	1.510
C(13)—C(14)	1.516(6)	1.521(5)	1.513(2)	1.509(2)	1.515
C(14)—C(15)	—	1.508(5)	1.514(2)	1.510(2)	1.511
C(15)—C(16)	—	—	1.509(2)	1.499(2)	1.504
C(16)—C(17)	—	—	—	1.502(3)	—

Angle	7OBAC	8OBAC	9OBAC	10OBAC	Mean
O(1)—C(7)—O(2)	122.7(3)	122.5(3)	122.3(2)	121.8(2)	122.4
O(1)—C(7)—C(1)	118.8(3)	118.8(3)	119.3(2)	119.3(2)	119.1
O(2)—C(7)—C(1)	118.4(3)	118.7(2)	118.3(1)	118.9(1)	118.6
C(2)—C(1)—C(7)	120.2(3)	121.0(3)	120.4(2)	120.7(2)	120.6
C(6)—C(1)—C(7)	120.4(3)	120.5(3)	121.0(1)	120.9(2)	120.7
C(2)—C(1)—C(6)	119.4(3)	118.6(3)	118.6(2)	118.5(2)	118.8
C(1)—C(2)—C(3)	120.5(3)	121.4(3)	121.1(2)	121.0(2)	121.0
C(2)—C(3)—C(4)	119.4(4)	119.3(3)	119.7(2)	119.8(2)	119.6
C(3)—C(4)—C(5)	121.6(4)	120.3(3)	120.3(2)	119.8(2)	120.5
O(3)—C(4)—C(3)	114.8(3)	114.8(3)	115.3(1)	115.1(2)	115.0
O(3)—C(4)—C(5)	123.7(3)	124.9(3)	124.5(1)	124.9(1)	124.5
C(4)—C(5)—C(6)	118.0(3)	119.5(3)	119.0(1)	119.4(2)	119.0
C(5)—C(6)—C(1)	121.1(3)	120.9(3)	121.4(1)	121.3(2)	121.2
C(4)—O(3)—C(8)	118.3(3)	118.2(2)	118.5(1)	118.4(1)	118.4
O(3)—C(8)—C(9)	106.9(3)	106.3(3)	106.6(1)	106.8(2)	106.7
C(8)—C(9)—C(10)	113.1(3)	112.9(3)	113.6(2)	113.3(2)	113.2
C(9)—C(10)—C(11)	114.0(3)	113.7(3)	115.0(2)	114.5(2)	114.3
C(10)—C(11)—C(12)	112.8(3)	113.8(3)	113.6(2)	114.1(2)	113.6
C(11)—C(12)—C(13)	113.8(4)	114.7(3)	114.6(2)	114.7(2)	114.5
C(12)—C(13)—C(14)	113.2(4)	115.7(3)	114.5(2)	115.0(2)	114.6
C(13)—C(14)—C(15)	—	114.3(3)	114.3(2)	114.8(2)	114.5
C(14)—C(15)—C(16)	—	—	114.5(2)	115.8(2)	115.2
C(15)—C(16)—C(17)	—	—	—	114.6(2)	—

to the atom of attachment. Bond lengths and angles in the four compounds are given in Table VII with mean values provided for comparison. The pattern of bond distances and angles found is comparable to that discussed in Part V, and little additional comment is needed. We draw attention, however, to the excellent agreement between corresponding distances and angles in the acids with $n = 8$, 9, and 10. None of the individual differences for corresponding quantities is significant in terms of the calculated standard deviations, and the largest individual deviations from means among the three are 0.007 Å in a bond distance and 0.7° in a bond angle.

The molecules are present in the crystals as centrosymmetric hydrogen-bonded dimers. The O---O separations in the hydrogen bonds, for the series in ascending order, are: 2.601, 2.621, 2.615, and 2.617 Å. The close equivalence of the carboxy C—O distances, exact in 8OBAC and 10OBAC, and the roughly central location of the protons in the O—H---O hydrogen bonds reflect the disordering of the carboxy group discussed in Part V.

The *gauche*-relation of the ether oxygen and C(γ) about the C(α)—C(β) bond of the chain, noted in the lower acids, is also present here. The O(3)—C(8)—C(9)—C(10) torsion angles for the ascending series are: 69.0°, 70.4°, 69.3°, and 69.9°.

The alkyl chains have an all-*trans* planar extended conformation with the angles between these planes and the planes of the phenyl rings being 107.6°, 107.1°, 107.4°, and 107.6° in the ascending series. The resulting overall molecular conformation is thus both non-linear and non-planar and is shown for a dimer of 7OBAC in Figure 1.

Equations of least-squares mean planes through the atoms of the carboxy groups, phenyl rings, and alkyl chains are given in Table VIII. The angles made by the axis of the alkyl chain, defined for 7OBAC and 8OBAC as C(8) --- C(14) and for 9OBAC and 10OBAC as C(8) --- C(16), with the unit cell axes are given in Table IX.

These angles are, of course, quite similar for each compound as would be expected from the isotypic nature of the unit cells, and the small angle made by the chain axis with the crystal c-axis accounts for the progressive increase in the length of c as the series is ascended. The increment for $n = 7 \rightarrow 9$ is 2.536 Å and that for $n = 8 \rightarrow 10$ is 2.562 Å.

Molecular packing

The molecular packing in these isotypic crystals of the smectogenic acids is discernbile in the crystal structures of 3OBAC and 5OBAC, in each case non-mesomorphic lowest members of the series. Although a progressive trend toward segregation of lateral chain-chain and ring-ring interactions is discernible in the crystal structures of 3OBAC and 5OBAC, in each case

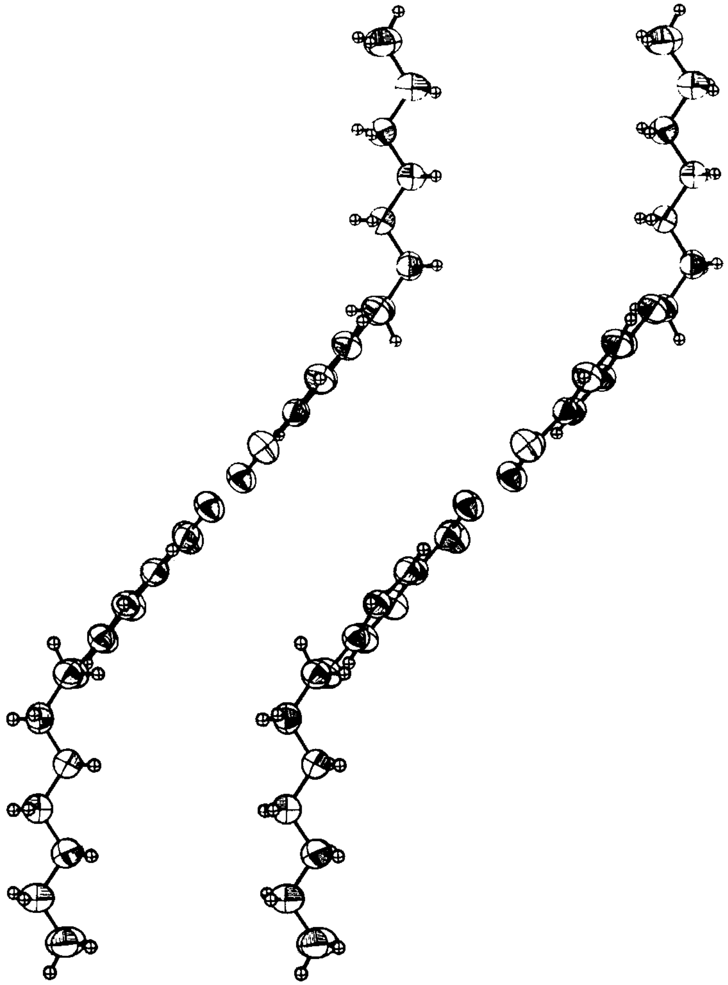

FIGURE 1 Stereoscopic view of the non-linear and non-planar conformation of the dimers of 7OBAC as found in the crystal.

the chain packing remains irregular and this tendency toward segregation does not disrupt the arrangement of molecules in stacked two-dimensional sheets. With the extension of the chain length to seven or more carbon atoms a distinctive three-dimensionally imbricated layer structure emerges characterized by the complete segregation of the aliphatic chains and the central residues into close-packed alternating strata. The chains of molecules in successive layers are antiparallel and interdigitated so that there are twice as many chains as aromatic cores in adjacent strata.

TABLE VIII

Equations of selected least-squares mean planes

Plane	n	a	b	c	d	Δ_{ave}	Δ_{max}
Carboxy group	7	0.75030	0.27864	0.59951	−0.03648	0.003	0.006
	8	0.72869	0.26926	0.62969	−0.04305	0.000	0.000
	9	0.74433	0.27758	0.60739	−0.04079	0.000	0.000
	10	0.72863	0.27036	0.62929	−0.03991	0.001	0.002
Phenyl ring	7	0.75173	0.28340	0.59547	−0.04100	0.003	0.006
	8	0.73822	0.25782	0.62325	−0.10562	0.005	0.009
	9	0.74807	0.27805	0.60256	−0.05675	0.002	0.004
	10	0.73816	0.25566	0.62430	−0.10408	0.005	0.010
Alkyl chain	7	−0.21434	−0.95252	0.21627	−3.53411	0.056	0.091
	8	−0.27306	−0.93249	0.23645	−2.99011	0.032	0.047
	9	−0.19869	−0.96056	0.19453	−3.75855	0.056	0.132
	10	−0.27146	−0.93666	0.22109	−3.11660	0.039	0.078

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. The conversion matrices are:

$$\mathit{8}\quad \begin{matrix} 4.82460 & 0.00000 & 0.00000 \\ -1.82393 & 7.91579 & 0.00000 \\ -1.51778 & 2.65439 & 18.78912 \end{matrix} \qquad \mathit{10}\quad \begin{matrix} 4.81860 & 0.00000 & 0.00000 \\ -1.80715 & 7.90835 & 0.00000 \\ -1.52384 & 3.14163 & 21.31378 \end{matrix}$$

$$\mathit{7}\quad \begin{matrix} 4.73920 & 0.00000 & 0.00000 \\ -1.69676 & 7.85268 & 0.00000 \\ -1.18280 & 2.19766 & 17.77394 \end{matrix} \qquad \mathit{9}\quad \begin{matrix} 4.74300 & 0.00000 & 0.00000 \\ -1.74893 & 7.85618 & 0.00000 \\ -1.20090 & 2.51507 & 20.29391 \end{matrix}$$

TABLE IX

Angles between the alkyl chain axis and the unit cell axes

Axis	$n =$ 7	8	9	10
a	92.5°	92.2	91.8	91.7
b	76.0	74.9	77.5	75.9
c	6.8	7.3	5.6	6.1

Packing in 7OBAC is illustrated in a-axis projection in Figure 2. The The relative heights in a of components of the dimers are indicated by the varying line thicknesses used. The chains shown in heaviest outline are above and their axes are almost parallel to the plane of the diagram; the central cores slope through the plane, and the chains shown in lightest outline are below and parallel to the plane. Note that the lower chain of a given dimer emerges below and to the right of the centrosymmetically related chain of a dimer displaced by a single translation in c and in b. The arrangement of the dimers in 7OBAC, seen in b-axis projection, is shown in Figure 3. Once again relative height along the projection axis is indicated

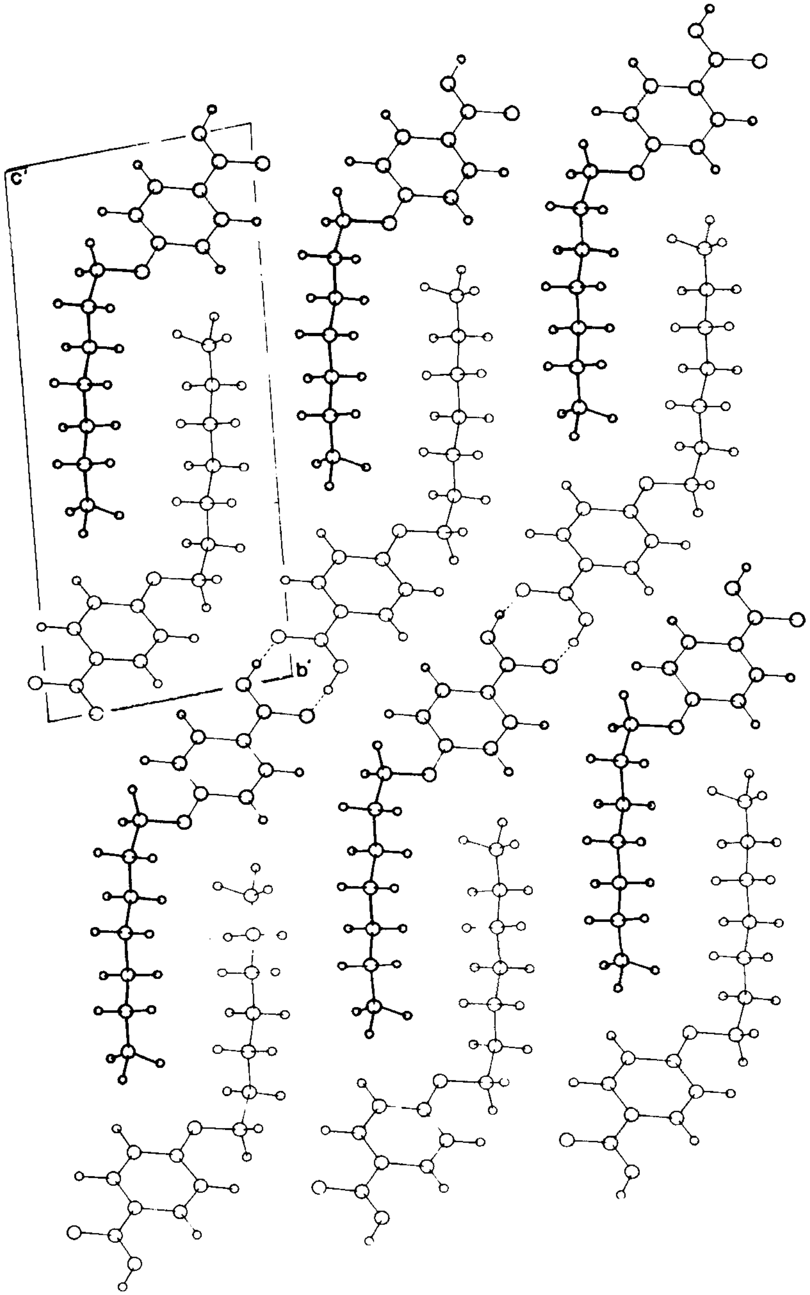

FIGURE 2 Molecular packing in the crystal of 7OBAC seen in *a*-axis projection.

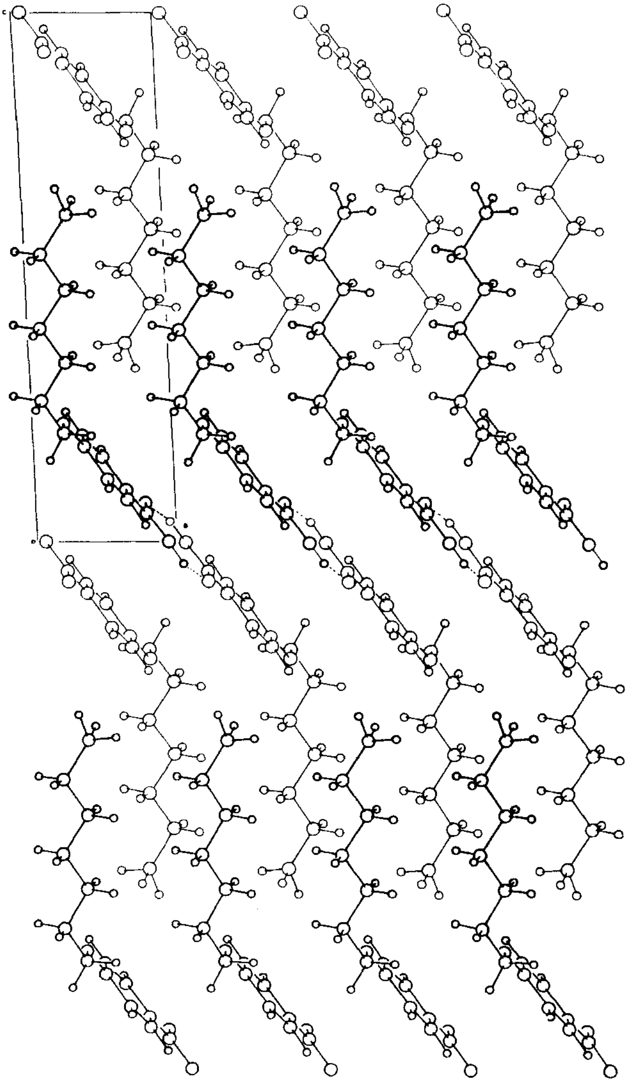

FIGURE 3 Molecular packing in the crystal of 7OBAC seen in *b*-axis projection.

by varying line thickness. The parallel stacking of the cores along *a* is clearly evident.

Views of the packing in 8OBAC, 9OBAC, and 10OBAC, seen in *a*-axis projection in Figures 4, 5, and 6, show that the only change in the structure with increasing chain length is an increase in the length of the chain strata, orientation and thickness of the core strata remaining the same. Similar

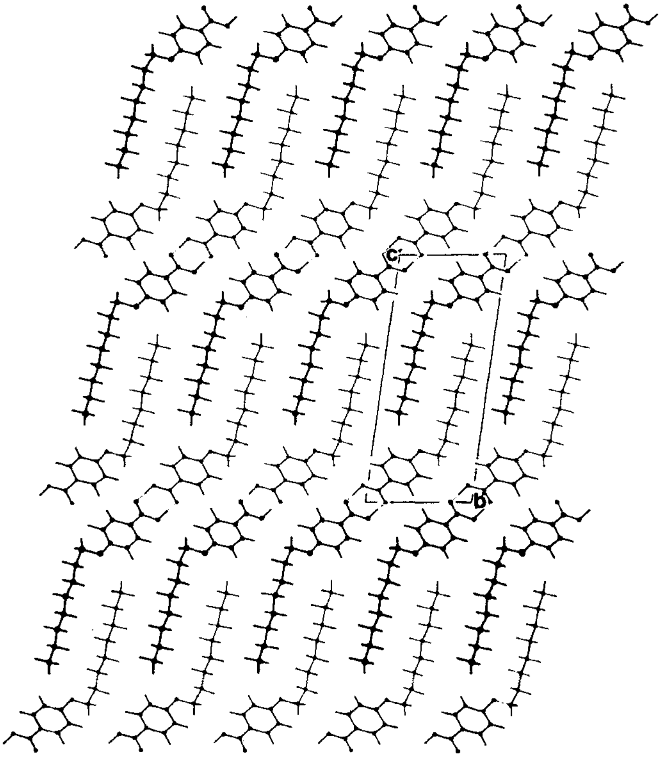

FIGURE 4 Molecular packing in the crystal of 8OBAC seen in *a*-axis projection.

indications are given in the comparison of the packing in *b*-axis projection in 8OBAC and 10OBAC, seen in Figure 7.

Although the overall isotypic character of the unit cell dimensions for the four acids is not in question, inspection of the values given in Table I shows that there is an even-odd effect present. The dimensions for 7OBAC and 9OBAC, excluding the length of the *c*-axis, are much closer to one another than to those for 8OBAC and 10OBAC which, in turn, are almost identical. These differences reflect a significant difference in the close packing of chains between the acids of even and odd chain length, and a small difference in the close packing of cores between the two sets.

Chain packing in 9OBAC and 10OBAC is compared, in *b*-axis projection, in Figure 8. In the even acids the terminal C—C bond of a given chain is parallel to the C(α)—C(β) bond of a centrosymmetrically related antiparallel chain, whereas in the odd series the terminal bond of one chain is parallel to the C(β)—C(γ) bond of an antiparallel chain. This reflects a difference in the interaction between the terminal methyl groups of molecules in one

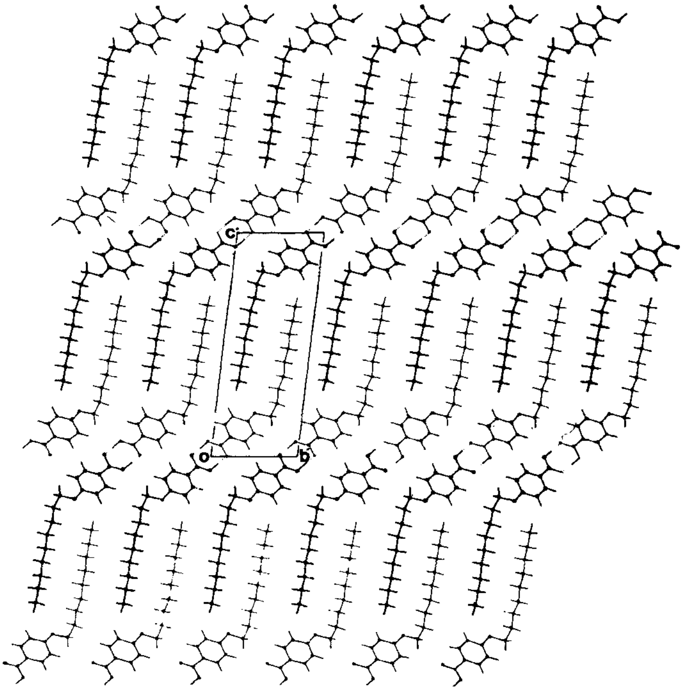

FIGURE 5 Molecular packing in the crystal of 9OBAC seen in *a*-axis projection.

layer with the central core of molecules in the next. As a result the optimal lateral and longitudinal interactions between antiparalllel sets of chains are slightly different in the two cases, although those between parallel chains remain comparatively unaffected.

A cross-sectional view normal to the chain axes (as defined above) is shown for the odd and even series in Figure 9 where the van der Waals envelopes for hydrogen have been drawn with a radius of 1.2 Å. Along the a' direction (the projection of a) the chains in a given row are parallel and there is little difference between the two series apart from a slightly larger angle between a' and the projection of the C—C bonds in the even series than in the odd. Normal to a' the direction of the chain axes alternates from row to row. Disregarding this difference in chain direction, the chain packing is sufficiently regular in each case to be described in terms of triclinic distortions of the monoclinic M_2 subcell described for close-packed hydrocarbon structures by Segerman.[9] For the odd series the subcell dimensions are:

$$a = 8.41, \quad b = 4.74, \quad c = 2.545\text{Å}$$

$$\alpha = 91.5, \quad \beta = 99.1, \quad \gamma = 110.9°;$$

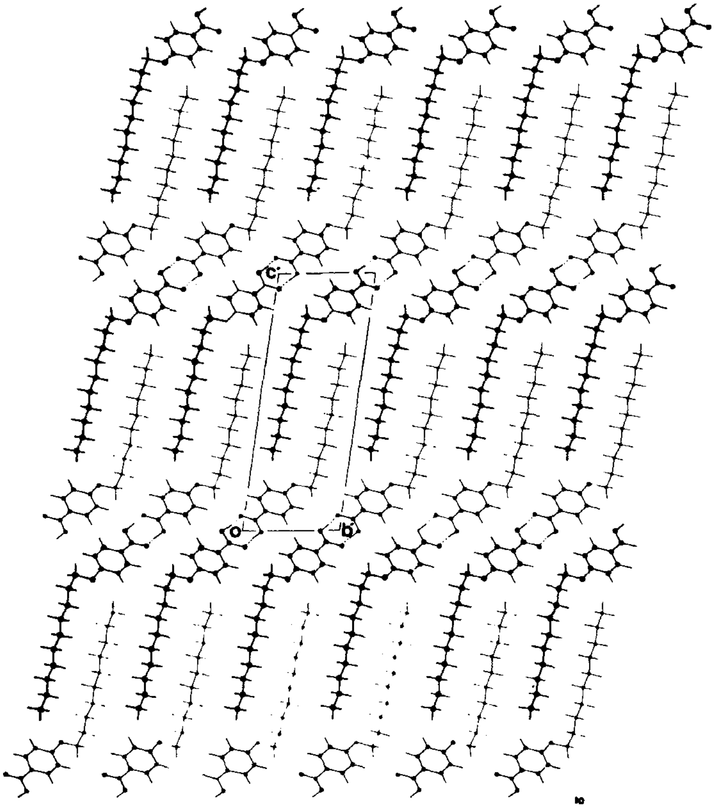

FIGURE 6 Molecular packing in the crystal of 10OBAC seen in *a*-axis projection.

and for the even series are:

$$a = 8.46, \quad b = 4.82, \quad c = 2.545 \text{ Å}$$

$$\alpha = 91.6, \quad \beta = 101.5, \quad \gamma = 110.9°.$$

The relationship between the unit cell and subcell *a* and *b* axes is shown in Figure 9. For the even series the longitudinal displacement of corresponding atoms from chain to chain within a row is 0.2 Å and between neighboring antiparallel chains is 0.4 or 0.5 Å. For the odd series the longitudinal displacement of parallel chains is 0.2 Å, but for antiparallel chains is 0.0 or 1.0 Å.

A cross-sectional view of the packing of cores in the even series is shown in Figure 10. van der Waals Envelopes are drawn with radius 1.7 Å for carbon, 1.4 Å for oxygen, and 1.2 Å for hydrogen. The cores are close packed and the typical cross-sectional interactions shown reflect lateral fitting

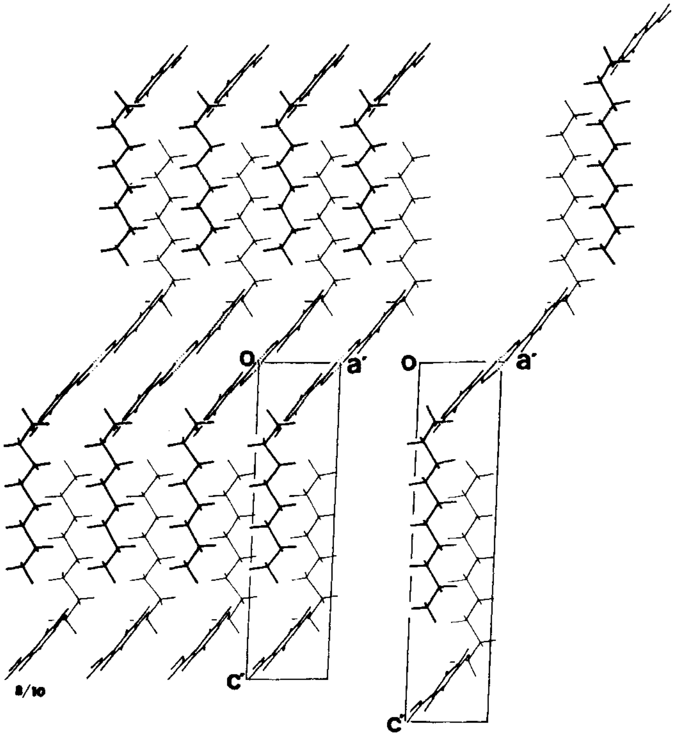

FIGURE 7 Molecular packing in crystals of 8OBAC (left) and 10OBAC (right) seen in *b*-axis projection.

of the protuberances of one molecule into the interstices of neighbors. The arrangement of core centers for the two series are almost identical, but the angle made by the lateral axis of the rings with *a'* is 76° compared to 73° in the even series.

For 7OBAC shorter intermolecular contacts between chain hydrogen atoms are shown in Figure 11, and between atoms in the core in Figure 12. The contacts in 9OBAC are comparable to those shown in these two figures. For the even series the closest intermolecular approaches between chain hydrogen atoms involve H(11b) and H(15b) in neighboring antiparallel chains in 8OBAC, and H(11b) and H(17b) similarly in 10OBAC. These contacts are 2.37 and 2.40 Å, respectively. The shortest contacts involving ring hydrogen atoms are between H(2) and H(8b) of molecules separated by $-b$ (2.24 Å in 8OBAC, 2.23 Å in 10OBAC) and between H(6) atoms in molecules separated by $+b$ (2.27 Å in each case). Whereas there are no C --- C approaches <3.60 Å in 7OBAC and 9OBAC, there are three such separations in both 8OBAC and 10OBAC.

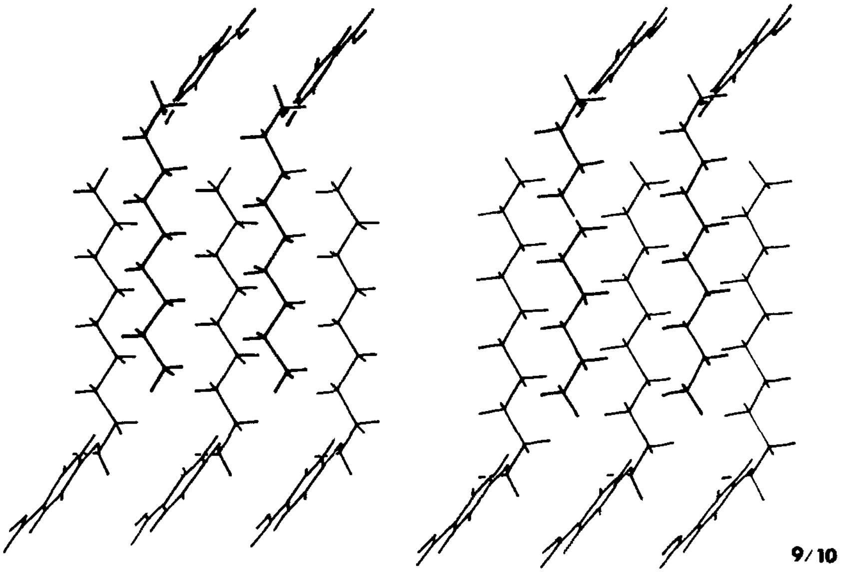

FIGURE 8 Chain packing in crystals of 9OBAC (left) and 10OBAC (right) seen in *b*-axis projection.

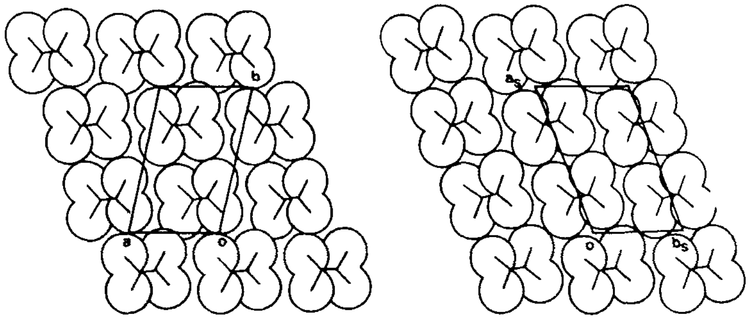

FIGURE 9 Cross-sectional views of chain close packing in the odd (left) and even (right) members. Projections of the unit cell axes are given for the odd members and of the subcell axes for the even members.

Additional details of the molecular packing in 7OBAC and 8OBAC are shown in Figures 13 and 14, which are projections of dimers related by translations in and onto the least-squares mean planes of their phenyl rings. The dimers form stacks along *a* and in all four crystals the vertical interplanar separation of corresponding rings within a stack is 3.56 Å. There is no direct face-to-face overlap of the phenyl rings such as is found in the two lowest homologs. The lateral displacement (parallel to C(2)···

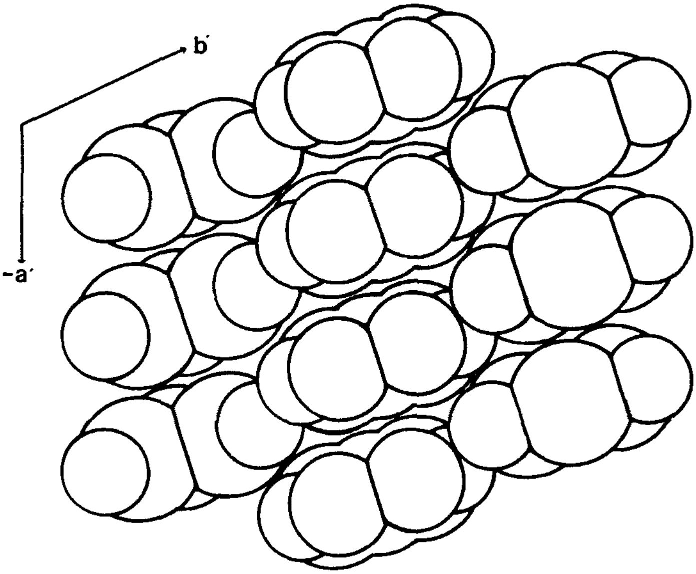

FIGURE 10 Cross-sectional view of close-packing of cores showing typical lateral and vertical interactions.

C(6)) of corresponding atoms in dimers within a stack is about 1.0 Å for the odd members and about 1.2 Å for the even members. The intrastack longitudinal displacement (in the direction C(4) --- C(4′)) of corresponding atoms is about 3.0 Å in all cases. For 7OBAC and 9OBAC the longitudinal displacement from stack to stack is about 6.0 Å, the lateral displacement is about 5.8 Å, and the vertical displacement is about 1.0 Å. For 8OBAC and 10OBAC these interstack displacements are, respectively, 5.8, 5.8, and 0.7 Å.

Complete listings of shorter intermolecular contacts are available from the authors.

DISCUSSION

Although this isotypic crystal form with its well defined layer structure forms a useful structural basis for resolving the problem of the disparate steric bulk of cores and chains, and although it stands in sharp contrast to the sheet-like structures of the nematogenic acids, it is not possible to extrapolate directly from it to the probable molecular arrangement in the smectic phase because nothing is known, as yet, of the structure of the intervening solid phase which, thermodynamic data suggest, should be much closer in structure to the mesophase. However, certain aspects of

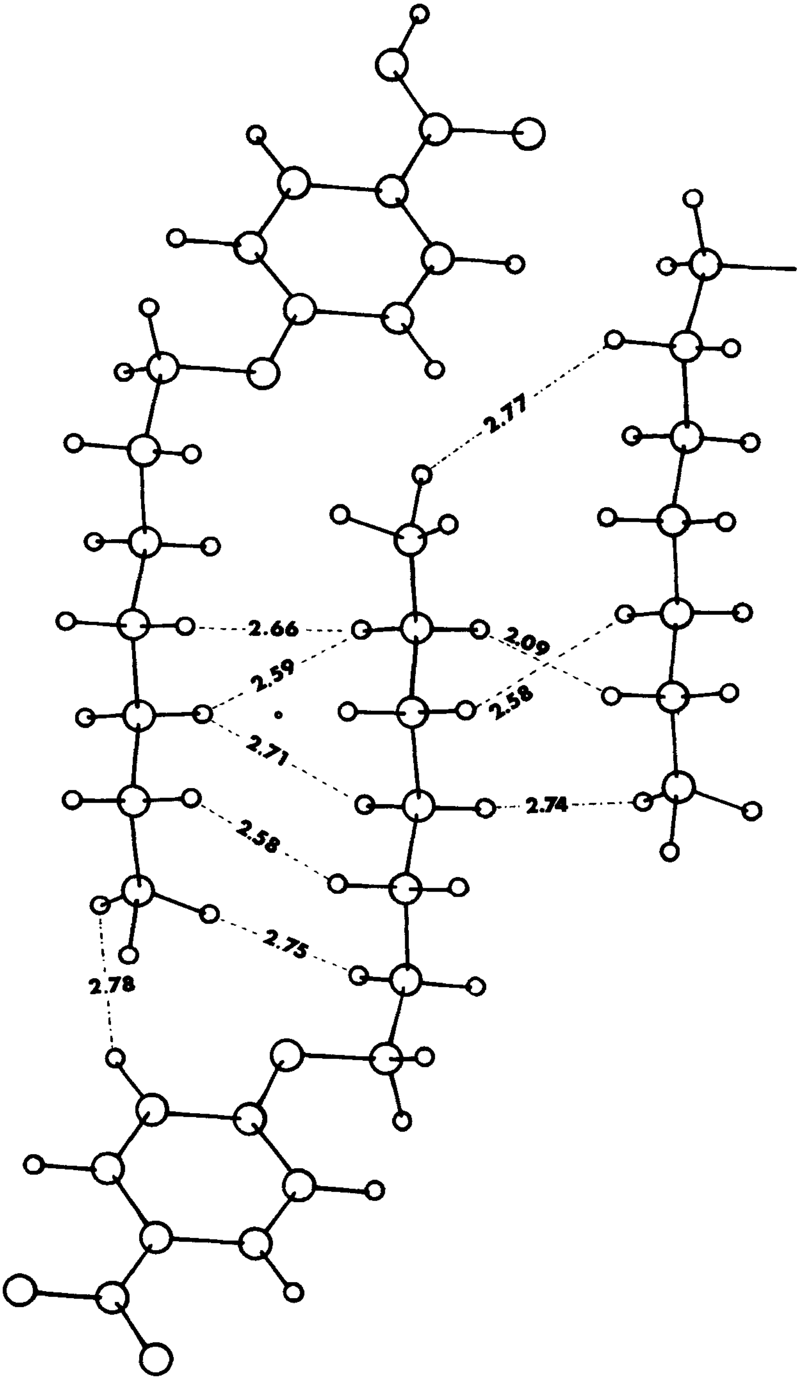

FIGURE 11 H—H contact distances (Å) between methylene groups in chains of 7OBAC.

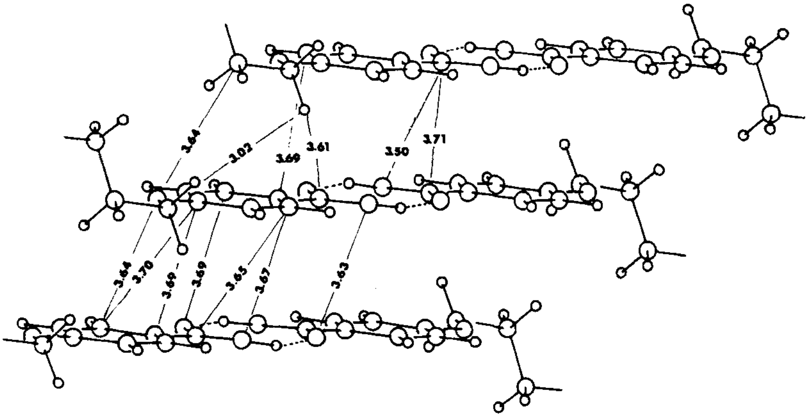

FIGURE 12 Shorter intermolecular contacts (Å) between cores in the crystal of 7OBAC.

the isotypic crystal structures are clearly relevant to the problem of molecular organization in the smectic phase and, by taking into account available diffraction data for the smectic phase of the even-membered series,[4] we may draw some useful conclusions.

The smectic phase of these acids has been identified by microscopic observation as a smectic C.[10] A tilt angle has been measured by optical means by Taylor, Arora, and Fergason,[11] and by X-ray diffraction by Chistyakov *et al.*[12] These values lie between 45 and 55°, depending on the method of measurement used, and are largely independent of temperature so that the smectic phase may be assigned to the C_1 category of de Vries which also includes the higher homologs of the *p,p′*-di-n-alkoxybenzenes.[14] These workers assumed a molecular conformation which was planar and grossly linear, such as has recently been found in the crystal structure of *p,p′*-di-n-heptoxyazoxybenzene.[15,16] However, Blumstein and Patel,[4] by an elegant separation of the contributions to the smectic periods of the chains and cores, have shown that the axes of these two components make a significant angle with one another in the mesophase. Although they assume a planar *anti*-conformation in the smectic phase, and derive a large conformational difference in the molecule between the smectic and crystal phases, an analysis of their data shows that it is quite likely that the molecular conformation present in the smectic phase is the same as that present in this isotypic crystal form and that there is only a difference of about 20° in chain orientation in the two phases.

Although on purely steric grounds, in an individual dimer, the planar *anti*-conformation would be slightly more favored than the non-planar *gauche*-conformer,[17] the latter is preferred in the solid, presumably because

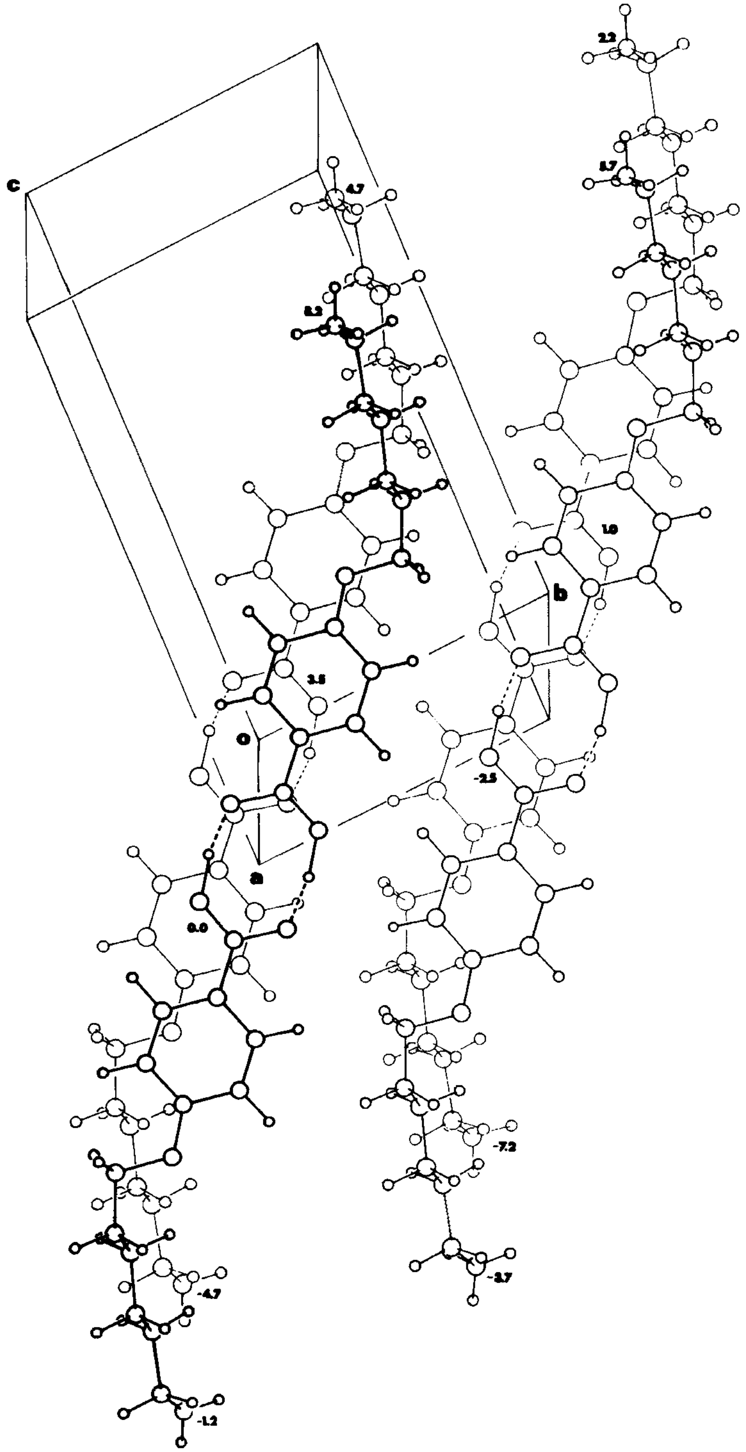

FIGURE 13 Projection onto the least-squares mean plane of the phenyl groups in 7OBAC showing relations between and within parallel stacks of dimers.

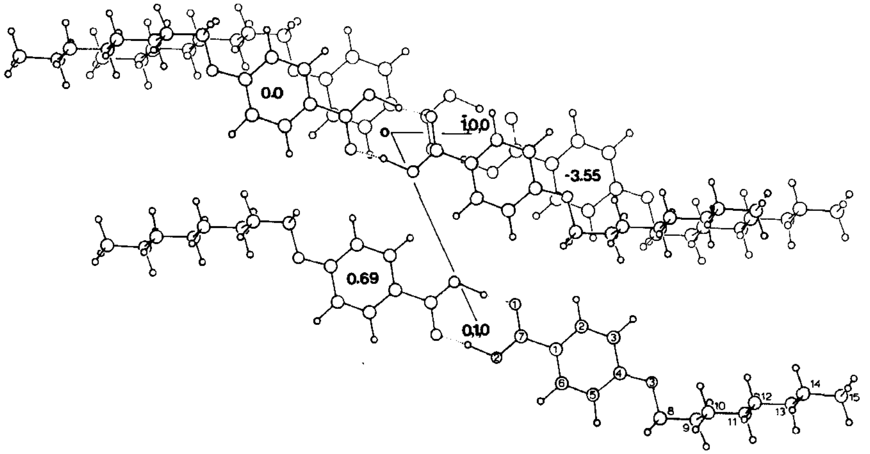

FIGURE 14 Projection onto the least-squares mean plane of the phenyl groups in 80OBAC showing relations between stacked dimers.

it favors aggregation of the dimers in stacks having the central cores parallel and still reasonably overlapped, an arrangement which minimizes core-core dispersion energy. The geometry of stacking may be seen in more detail in Figures 13 and 14. That this particular type of stacking is energetically favorable is further demonstrated by its occurrence not only in this form but in the second crystal form of 8OBAC reported in Part VII.

Blumstein and Patel give mesophase periodicities for the smectic phases of the acids of even-chain length in the range $n = 8 \rightarrow 18$. There is a regular increment in mesophase period as the series is ascended which may be attributed to the increase in chain length, the mean value being 2.253 ± 0.020 Å per CH_2 group per dimer. By equating this increment to the increase in projected chain length they arrive at a tilt angle for the chain axis of 25° [$\cos^{-1}$ (2.253/2.540)]. If the actual values for C—C chain bond lengths and C—C—C chain valence angles (1.516 Å and 113.9°) found in the crystal structure analyses are used in this calculation a tilt angle of 27.5° results. With this tilt angle for the chain axis, the observed mesophase periodicites of Blumstein and Patel are matched within the limits of error by the projected lengths of the molecules in the conformation found in the crystal. The geometry for 8OBAC is shown in Figure 15, and the observed and calculated quantities are compared in Table X. It is not necessary, as might be thought implicit in Figure 15, that the plane of the alkyl chain be parallel to a plane containing the normal.

The agreement between the two sets of numbers, while perhaps fortuitous, is suggestive and it is not necessary to assume, as did Blumstein and Patel, that a gross conformational change takes place in passing from the crystal

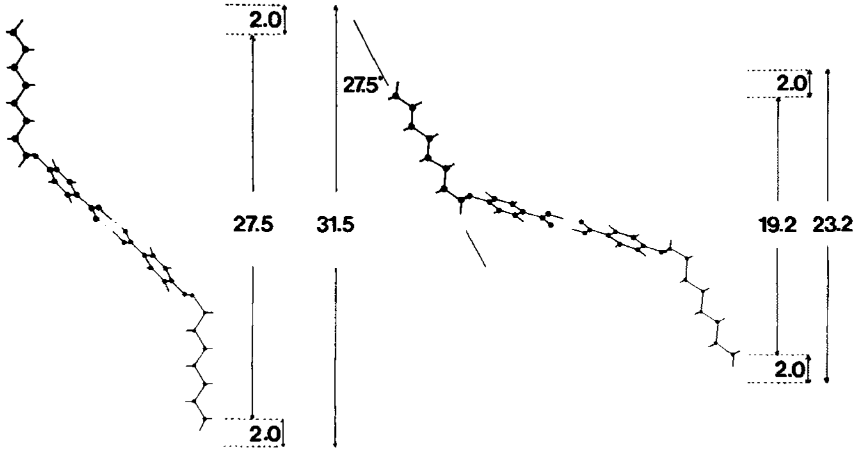

FIGURE 15 Projected molecular length for 8OBAC with the chain axis vertical (left) and inclined to the vertical by 27.5° (right). A van der Waals radius of 2.0 Å has been assumed for the terminal methyl groups.

TABLE X

Observed crystal,[a] powder,[b] and mesophase[b] periods (Å) and calculated projected dimer lengths (Å) for the even-chain acids

n	Crystal d_{001}	Powder $d(\pm 0.1)$	Mesophase $d(\pm 0.5)$	Projected length
8	18.79	18.5	22.9	23.2
10	21.31	21.1	27.8	27.7
12	23.84[c]	23.4	32.2	32.2
14	26.36	25.8	36.6	36.7
16	28.89	28.5	41.1	41.2
18	31.41	31.0	45.6	45.7

[a] This work.
[b] Data from Blumstein and Patel, Ref. 4.
[c] Values for this and higher homologs by extrapolation.

to the mesophase. They were led to that mistaken conclusion by a misinterpretation of the physical significance of the low-angle crystal periodicities which they observed. In deriving the agreement between projected molecular length and mesophase periodicity we have made use of the general assumption that the mesophase period, p, corresponds to layer thickness, t, which can be related to molecular length, l, through the relation: $p = t = l.\cos\alpha$, α being the tilt angle for the molecule with respect to the layer normal. In its simple form this relation holds only for linear molecules in the special case where the mesophase is made up of discrete non-interpenetrating layers and where the reference coordinate frame is orthogonal. Quite misleading conclusions may be drawn if the relation is applied in situations where these conditions do not hold, and a clear example of this danger is provided by the interpretation of the crystal periodicites made by Blumstein and Patel.

As with the mesophase periods, there is a regular increment in crystal period as the series is ascended, but the size of this increment is only 1.244 ± 0.014 A per CH_2 group per dimer, about half of that observed in the smectic phase. By the same arguments as advanced above, and assuming this value to be an increment in projected *dimer* length, they arrive at a tilt angle for the chain of 60.7°. This tilt is substantially different from that in the mesophase and, more importantly, substantially different from that actually present in the crystal. By extrapolation to layer thickness for $n = 0$ in each case, Blumstein and Patel were forced to the conclusion that whereas the tilt angles of chain and core were roughly the same in the crystal they were quite different in the smectic phase, i.e. the molecule undergoes a conformational change in passing from one phase to the other.

The conditions of recrystallization reported by these authors make it likely that they are dealing with the same crystal modification as we describe here, and their reported crystal periodicities correspond closely to the expected d_{001} spacings for this form. Inspection of Figures 2 and 3 shows that the angle made by the chain axis with c is quite small, about 7°, but that the crystal c-period does not reflect a dimer repeat but, as far as the chains are concerned, a monomer repeat. The actual increment per CH_2 group per dimer is therefore twice that assumed by Blumstein and Patel. This leads to a value of $\cos \alpha$ for the chain axis of $2.488/2.540 = 0.9795$, giving $\alpha = 11.6°$, a calculated value much closer to the true state of affairs in the crystal and requiring no conformational change in the molecule between the two phases and a much smaller orientational change in passing from one phase to the other than suggested by them.

It is only fair to acknowledge that the the argument concerning the identity of molecular conformation in crystal and smectic phases rests upon the same fragile assumptions as were made by Blumstein and Patel. With the crystal structures in hand it is easy to see the proper interpretation of the crystal periodicities, but with no additional information on the structure of the smectic phase it is not easy to see whether a comparable error of interpretation may not have been made. All that can be rigorously said on the basis of the diffraction data is that a periodicity based on monomer chain increments in the crystal is replaced by a periodicity based on dimer increments in the smectic phase. The magnitude of the increment in the mesophase leads to the conclusion that the chains remain in the extended all-*trans* conformation. Significant chain-chain interactions also seem to be necessary to explain the increasing stability of the smectic phase with increasing chain length. On the other hand, a segregated layer structure based on the crystal structure pattern would be expected to show periodicities in the smectic phase much closer to the crystal periods, even though loss of regularity in the layer structure would destroy the exact crystallographic centers of symmetry present in the solid. In a speculative vein, we might expect retention of the stacks of dimers which are a feature of the crystal structure of 8OBAC in both modifications, but some rearrangement of the stacks in such a way as to produce a true dimer periodicity. A possible model for this may be provided by the crystal structure of 8OBAC described in Part VII, in which antiparallel alignment of the chains is combined with a genuine head-to-tail dimer periodicity. Transformation between the two crystal forms (if any occurs) might take place by concerted rotations of the dimers around the *a*-axis of the isotypic form accompanied by translation along *b*, such a combination of motions being possible with comparatively little increase in free volume locally.

However, these ideas must remain speculative in the absence of information on the structure of the crystal form intermediate between these forms and the smectic phase. The comparatively low enthalpies of transition between that phase and the smectic phase, typically less than 3 kcal mol^{-1} for the acids described here, encourage a belief that with that structure available the path to the smectic phase might be discernible and the organization in it predictable. Studies designed to elucidiate the structure of the intermediate solid phase are in progress.

Acknowledgments

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17. If only steric factors are important, the number and type of *gauche*-interactions determines stability. The conformation adopted involves the ether oxygen in one O --- C and one O --- H interaction, whereas an *anti*-conformation would involve two O --- H *gauche*-interactions. The former conformation is thus slightly less favorable in the isolated molecule than is the latter.