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# An X-Ray Study of the *p*-n-Alkoxybenzoic Acids. Part V. Crystal Structures of the Nematogenic Acids Having Three and Five Alkyl-Chain Carbon Atoms

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The crystal structures of *p*-n-propoxy- and *p*-n-pentoxy-benzoic acids (3OBAC and 5OBAC) have been determined at room temperature by single-crystal x-ray analysis. Both crystals have sheet structures. Within each sheet the molecules are arranged as hydrogen-bonded dimers in head-to-tail fashion in parallel staggered rows. The long axes of the aromatic nuclei are almost normal to crystal *b*. The alkyl chains are in planar extended form, but the ether oxygen and C($\gamma$) are in a *gauche* relation about the C($\alpha$)-C($\beta$) bond of the chain. The stacking of sheets is slightly different in 3OBAC which undergoes a solid-solid transition before yielding a nematic phase, than in 5OBAC which transforms directly to the nematic state. The tight face-to-face overlap of phenyl rings characteristic of the crystal structures of the two lowest homologs in the series, which are non-mesogenic at atmospheric pressure, is absent in these crystal structures where the ring planes in adjacent sheets are inclined to one another by about 55°. Nematogenic behavior is attributed to parallel alignment of molecules in the solid coupled to a weakening of the solid-state intermolecular forces, arising from difficulty in accomodating the increasing steric bulk of the alkyl chains with respect to the aromatic nuclei.

$C_{10}H_{12}O_3$ (3OBAC). Monoclinic, $P2_1/c$, $a = 15.303(2)$, $b = 7.491(1)$, $c = 8.177(1)$ Å, $\beta = 95.70(2)°$, $Z = 4$.

$C_{12}H_{16}O_3$ (5OBAC). Monoclinic, $P2_1$, $a = 16.099(5)$, $b = 7.357(2)$, $c = 10.018(3)$, $\beta = 102.89(2)°$, $Z = 4$.

## INTRODUCTION

In many homologous series of thermal mesogens there is a characteristic change in thermal properties as the series is ascended. In the case of the *p*-n-alkoxybenzoic acids,[1] the first two members of the series are non-mesogenic at atmospheric pressure although yielding mesophases at higher pressure,[2] the next four members yield nematic phases at atmospheric pressure, and succeeding members yield a smectic phase followed by a nematic, the latter phase dropping out at a chain length of fourteen carbon atoms.

To see whether these changes in thermal behavior might be related to solid-state molecular organization, we have carried out single-crystal X-ray diffraction analyses for the first ten members of the series. A strong correlation is indeed found between crystal structure type and the occurrence and nature of thermal mesomorphism.

In earlier papers we have shown that:

1) the two lowest members of the series, *p*-methoxy- and *p*-ethoxy-benzoic acids, which are mesogenic only at high pressures, have crystals where the molecules are arranged as planar hydrogen-bonded dimers in head-to-tail fashion in parallel staggered rows, as in many normal nematogens.[3] The high melting points of these two crystals, which alone inhibit mesophase formation at atmospheric pressure,[1] arise from ability to pack the sterically bulky but still short alkyl chains in such a way that face-to-face stacking of molecules normal to the rows is still possible.[4,5]

2) In the nematogenic *p*-n-butoxybenzoic acid crystal the increased chain bulk prevents such efficient molecular packing. The intermolecular forces become much weaker as ring-to-chain interactions replace the predominant ring-to-ring overlaps of the two lowest members. As a result, with increasing temperature, the molecules may acquire translational degrees of freedom at temperatures where the thermal energy is insufficient to induce loss of long-range order about the director axis.[6]

3) The onset of smectic properties in the series is coincident with the adoption of a characteristic isotypic crystal structure by all acids in the series from the *p*-n-heptoxy-homolog up to at least the *p*-n-octadecocy-acid.[7]

We extend these observations in this series of papers by reporting in Part V the room-temperature crystal structures of the nematogenic *p*-n-propoxy- and *p*-n-pentoxy-benzoic acids (3OBAC and 5OBAC) which adopt weakly linked sheet structures. In Part VI we describe the isotypic crystal structures of the smectogenic acids having 7, 8, 9, and 10 carbon atoms in the alkyl chain, and in Part VII we report the crystal structures of one crystal form of *p*-n-hexoxybenzoic acid, a nematogen, and of a second crystal form of the smectogenic *p*-n-octoxybenzoic acid. These two crystal structures involve similar sheet elements differently stacked. Both forms undergo solid-solid transitions prior to mesophase formation. Part V also contains a general discussion of the possible interrelations between molecular structure, crystal structure, and thermal behavior.

## EXPERIMENTAL

Samples of 3OBAC and 5OBAC were prepared and purified following published methods.[1] Crystals suitable for X-ray study were grown by controlled cooling of saturated 95% ethanol solutions. Observed transition temperatures match published values[8] and are:

3OBAC

$$K_{II} \xrightarrow{122^\circ} K_I \xrightarrow{147^\circ} N \xrightarrow{153.5^\circ} I$$

5OBAC

$$K \xrightarrow{125^\circ} N \xrightarrow{149^\circ} I$$

### Crystal data

Crystallographic data for the two acids are summarized in Table I. Crystal symmetry was established from 25° precession photographs taken with Mo K$\alpha$ radiation. For 3OBAC ($K_{II}$) the systematic absences *h*0*l* with *l* odd and 0*k*0 with *k* odd uniquely determine the space group as $P2_1/c$. The absences 0*k*0 with *k* odd, found for 5OBAC, are compatible with space groups $P2_1$ or $P2_1/m$. The former was chosen on the basis of the distribution of maxima in the three-dimensional Patterson function. Unit cell dimensions were obtained in each case by a least-squares fit ($\lambda$ = 1.5418 Å) to the dif-

TABLE I

Crystallographic data

| | 3OBAC ($K_{II}$) | 5OBAC |
|---|---|---|
| Crystal symmetry | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1$ |
| *a* (Å) | 15.303(2) | 16.099(5) |
| *b* | 7.491(1) | 7.357(2) |
| *c* | 8.177(1) | 10.018(3) |
| $\beta$ (deg.) | 95.70(2) | 102.89(2) |
| Cell vol. (Å$^3$) | 932.7 | 1156.7 |
| Mol. wt. | 180.2 | 208.2 |
| $D_{obs}$ (g·cm$^{-3}$) | 1.278(8) | 1.18(2) |
| *Z* | 4 | 4 |
| $D_c$ (g·cm$^{-3}$) | 1.283 | 1.196 |
| Mol. vol. (Å$^3$) | 233.2 | 289.2 |
| Points scanned | 1386 | 1864 |
| Significant *I*'s | 1010 | 1124 |
| Scan range (2$\theta$) | 3° | 4° |
| *R* (significant data) | 0.037 | 0.099 |
| $R_w$ | 0.037 | 0.091 |

fractometer values of ±2° for 20 strong general reflections measured for a carefully centered crystal. Crystal densities were measured by flotation in aqueous KI solution.

### Intensity data

Intensities of X-ray spectra were measured by standard automatic diffractometry using a Picker full-circle instrument operated under the control of an XDS Sigma 2 computer. Cu K$\alpha$ radiation was used with scintillation counting and pulse-height analysis. A single quadrant of reciprocal space was surveyed in each case, Accuracy of crystal setting was confirmed by separate measurement of symmetry related zones ($R_I < 0.035$) and stability of the experimental conditions was established by monitoring two reference reflections ($R_I < 0.020$) after every 50 measurement cycles.

### Structure determination and refinement

*3OBAC* The structure was solved directly from the sharpened three-dimensional Patterson function. Vectors corresponding to a planar centrosymmetric dimer of "oxobenzoic acid" lying more or less normal to the crystal *b*-axis could be clearly discerned. An electron-density synthesis based on ths model yielded the locations of the three alkyl carbon atoms of the chain.

Refinement proceeded smoothly by the block-diagonal least-squares method (3 × 3 and 6 × 6 blocks). Anisotropic thermal parameters were used for C and O atoms.[9] All hydrogen atoms were located from a three-dimensional difference electron-density synthesis and their positional and isotropic thermal parameters were refined. In a final difference synthesis the remaining significant electron density was concentrated at the mid points of bonds and in positions corresponding to lone pairs of electrons on oxygen atoms.

*5OBAC* The statistical distribution of intensity for this crystal is compatible with a centrosymmetric arrangement of atoms in the crystal, and suggests that the space group should be the centrosymmetric $P2_1/m$. The nature of the Patterson function, however, argues against that choice in favor of the non-centrosymmetric group $P2_1$. In the former group the asymmetric unit of the crystal consists of a single monomer of the acid. In the latter group the asymmetric unit must contain two such monomers, but there is no necessary symmetry relation between them. The anomalous intensity distribution may be explained by the presence of a non-crystallographic approximate center of symmetry between two independent monomers linked as a hydrogen-bonded dimer.

A vector plane corresponding to such a dimeric "oxybenzoic acid" moiety was clearly visible slightly tilted with respect to the $v = 0$ plane of the Patterson function. The tilt is sufficiently large to lead to unacceptable packing between mirror-related molecules in space group $P2_1/m$ and the remaining vector patterns in the function also rule out that space group. A model was therefore chosen in which a centrosymmetric dimer of "oxybenzoic acid" was placed with its long axis along an axis parallel to $[10\bar{2}]$ and correctly placed relative to the $2_1$-axis. The approximate location of the dimer along the former axis was found from the minimal residual for a series of structure factor calculations made with the molecule translated by 0.25 Å increments. An electron-density synthesis carried out for the parameters corresponding to that minimum yielded peaks attributable to the ten alkyl carbon atoms.

Refinement was by the block-diagonal least-squares method with anisotropic thermal parameters adopted for C and O.[9] A difference electron-density synthesis revealed peaks for the ring hydrogen atoms and for the methylene hydrogen atoms of the first four carbon atoms of each chain. No density could be found associated with the carboxy hydrogen atoms or those of the methyl groups. Contributions for observable hydrogen atoms were included in the structure factor calculations, but their parameters were not varied.

For both compounds scattering functions for C and O were taken from Cromer and Waber,[10] and for H from Stewart *et al.*[11] The weighting scheme used in the least-squares refinement was taken from Corfield *et al.*[12] with analytically derived values of $p$. With the exception of program *ORTEP*,[13] for which a CDC Cyber 172 computer was used, all programs used were written in this laboratory for the XDS Sigma 2 computer.

## RESULTS

### Molecular geometry and conformation

Atomic parameters defining the crystal structures of the two acids are given with their standard deviations in Tables II and III. A consistent numbering scheme has been adopted in this and the succeeding papers. Carbon atoms of the phenyl ring are numbered C(1)–C(6). The carboxy carbon, C(7), is attached to the ring at C(1) and the carboxy oxygens are O(1) and O(2) with O(1) *cis* to C(6). The ether oxygen is O(3) and is attached to the ring at C(4). The atoms of the alkyl chain are numbered from C(8) upwards with C(5) of the ring chosen *cis* to that atom. In 5OBAC the second independent molecule in the asymmetric unit is distinguished from the first by the use of primes in the numbering.

TABLE II

Atomic parameters defining the crystal structure of 3OBAC

| Atom | $x$ | $y$ | $z$ | $B$ | $r_1$ | $r_2$ | $r_3$ |
|---|---|---|---|---|---|---|---|
| O(1) | 66(1) | 728(3) | −1969(2) | 4.89 | 202 | 223 | 309 |
| O(2) | 1029(1) | −804(2) | −284(2) | 4.78 | 195 | 223 | 309 |
| O(3) | 3224(1) | −53(2) | −6373(2) | 3.63 | 195 | 205 | 241 |
| C(1) | 1416(1) | −78(3) | −2929(2) | 3.12 | 181 | 191 | 215 |
| C(2) | 2242(1) | −870(3) | −2618(3) | 3.35 | 181 | 201 | 233 |
| C(3) | 2825(1) | −830(3) | −3788(3) | 3.42 | 179 | 216 | 227 |
| C(4) | 2596(1) | −29(3) | −5298(3) | 3.14 | 189 | 200 | 209 |
| C(5) | 1770(1) | 738(3) | −5644(3) | 3.58 | 180 | 214 | 240 |
| C(6) | 1192(1) | 699(3) | −4447(3) | 3.59 | 183 | 220 | 234 |
| C(7) | 802(1) | −72(3) | −1650(3) | 3.64 | 191 | 213 | 228 |
| C(8) | 3021(2) | 785(3) | −7950(3) | 3.80 | 201 | 224 | 233 |
| C(9) | 3842(2) | 716(4) | −8841(3) | 4.27 | 204 | 246 | 252 |
| C(10) | 4581(2) | 1844(4) | −8030(3) | 5.48 | 214 | 271 | 298 |
| H(2) | 65(1) | −132(3) | −466(2) | 5.1(6) | | | |
| H(3) | 160(1) | −123(3) | −671(2) | 4.2(5) | | | |
| H(5) | 340(1) | 140(3) | −365(2) | 4.6(5) | | | |
| H(6) | 241(1) | 139(3) | −152(2) | 4.4(5) | | | |
| H(8a) | 284(1) | −206(3) | −774(2) | 4.9(5) | | | |
| H(8b) | 253(1) | −8(3) | −864(2) | 5.4(5) | | | |
| H(9a) | 404(1) | 62(3) | −104(3) | 6.7(6) | | | |
| H(9b) | 365(1) | −116(3) | −999(2) | 6.2(6) | | | |
| H(10a) | 446(2) | −315(4) | −786(3) | 11.2(9) | | | |
| H(10b) | 475(2) | −150(3) | −682(3) | 7.6(7) | | | |
| H(10c) | 511(2) | −173(3) | −875(3) | 8.4(7) | | | |
| H(O) | −50(2) | 74(5) | −78(4) | 15.2(12) | | | |

Atomic positions 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 with the root-mean square amplitudes of vibration (Å $\times$ $10^3$) along the principal axes of the thermal ellipsoids, and for H as observed $B$ values. Estimated standard deviations are given in parentheses and are applicable to the least significant digits given.

TABLE III

Atomic parameters defining the crystal structure of 5OBAC

| Atom | $x$ | $y$ | $z$ | $B$ | $r_1$ | $r_2$ | $r_3$ |
|---|---|---|---|---|---|---|---|
| O(1) | −689(6) | −758(−) | −2823(10) | 6.38 | 205 | 257 | 367 |
| O(2) | 294(6) | 782(16) | −1427(8) | 5.36 | 195 | 279 | 296 |
| O(3) | 1960(6) | 83(14) | −6559(9) | 4.97 | 190 | 226 | 319 |
| C(1) | 576(9) | −52(22) | −3622(11) | 3.93 | 150 | 222 | 279 |
| C(2) | 1384(7) | 693(20) | −3320(11) | 3.31 | 132 | 224 | 241 |
| C(3) | 1834(8) | 699(22) | −4350(13) | 4.39 | 158 | 246 | 285 |
| C(4) | 1463(11) | 7(22) | −5636(17) | 6.66 | 170 | 214 | 422 |
| C(5) | 644(7) | −745(21) | −5899(13) | 4.26 | 122 | 264 | 303 |
| C(6) | 166(7) | −746(20) | −4900(12) | 3.46 | 155 | 193 | 265 |
| C(7) | 82(8) | 1(23) | −2471(14) | 4.63 | 156 | 232 | 313 |
| C(8) | 1591(9) | −584(26) | −7921(12) | 6.10 | 149 | 246 | 386 |
| C(9) | 2192(10) | −156(28) | −8841(15) | 6.35 | 229 | 280 | 332 |

TABLE III (*continued*)

| Atom | $x$ | $y$ | $z$ | $B$ | $r_1$ | $r_2$ | $r_3$ |
|---|---|---|---|---|---|---|---|
| C(10) | 3057(13) | −1138(25) | −8450(18) | 7.81 | 225 | 252 | 427 |
| C(11) | 3599(12) | −690(27) | −9480(17) | 7.62 | 265 | 290 | 368 |
| C(12) | 4485(13) | −1587(40) | −9145(22) | 10.59 | 242 | 361 | 462 |
| O(1′) | −601(6) | 890(18) | 448(10) | 6.50 | 183 | 278 | 369 |
| O(2′) | −1616(6) | −53(17) | −1024(9) | 6.15 | 207 | 278 | 337 |
| O(3′) | −3322(5) | −496(16) | 4040(8) | 5.17 | 209 | 229 | 317 |
| C(1′) | −1836(7) | 115(20) | 1208(11) | non-positive definite | | | |
| C(2′) | −2625(9) | −695(25) | 882(13) | 5.67 | 190 | 257 | 336 |
| C(3′) | −3128(9) | −827(23) | 1864(12) | 4.85 | 188 | 246 | 297 |
| C(4′) | −2814(9) | −188(22) | 3195(12) | 4.43 | 158 | 213 | 313 |
| C(5′) | −2007(10) | 589(22) | 3502(14) | 5.66 | 167 | 269 | 339 |
| C(6′) | −1518(10) | 758(22) | 2524(15) | 5.53 | 193 | 288 | 299 |
| C(7′) | −1282(10) | 64(23) | 159(12) | 5.20 | 181 | 237 | 329 |
| C(8′) | −2918(10) | −116(28) | 5510(14) | 7.04 | 195 | 277 | 391 |
| C(9′) | −3516(9) | −1057(26) | 6289(13) | 5.77 | 174 | 242 | 361 |
| C(10′) | −4435(11) | −306(29) | 6017(15) | 6.84 | 236 | 317 | 322 |
| C(11′) | −4988(13) | −1272(29) | 6838(18) | 8.44 | 253 | 292 | 414 |
| C(12′) | −5902(10) | −539(32) | 6543(21) | 8.85 | 212 | 347 | 417 |

Idealized hydrogen positions

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| H(2) | 165 | 125 | −232 | H(2′) | −286 | −124 | −13 |
| H(3) | 247 | 124 | −415 | H(3′) | −376 | −142 | 159 |
| H(5) | 38 | −133 | −689 | H(5′) | −175 | 108 | 453 |
| H(6) | −48 | −125 | −510 | H(6′) | −90 | 138 | 279 |
| H(8a) | 98 | 7 | −831 | H(8′a) | −289 | 133 | 571 |
| H(8b) | 150 | −204 | −789 | H(8′b) | −228 | −69 | 579 |
| H(9a) | 189 | −54 | −987 | H(9′a) | −355 | −248 | 601 |
| H(9b) | 231 | 129 | −880 | H(9′b) | −324 | −93 | 737 |
| H(10a) | 295 | −259 | −845 | H(10′a) | −472 | −46 | 494 |
| H(10b) | 339 | −70 | −744 | H(10′b) | −441 | 112 | 628 |
| H(11a) | 326 | −115 | −1048 | H(11′a) | −510 | −270 | 659 |
| H(11b) | 368 | 77 | −950 | H(11′b) | −471 | −110 | 791 |
| H(12a) | 483 | −113 | −815 | H(12′a) | −626 | −127 | 716 |
| H(12b) | 441 | −305 | −913 | H(12′b) | −619 | −74 | 547 |
| H(12c) | 483 | −121 | −991 | H(12′c) | −589 | 89 | 679 |

Positional parameters are given in the same form as in Table II,[15] as are the thermal parameters for C and O. For H the isotropic values were taken as 1.0 + $B$ for the carbon attachment. Hydrogens attached to C(12) and C(12′) were not located in the difference maps and are given in postulated positions assuming a staggered conformation about the C(11)-C(12) and C(11′)-C(12′) bonds.

Bond lengths and angles are given in Table IV. The accuracy of the analysis of 3OBAC is good and is significantly better than for 5OBAC where poor crystal quality limits the accuracy of intensity measurement.

The two acids are present in the crystal as hydrogen-bonded dimers. In 3OBAC the dimer has an exact center of symmetry coincident with the space-group origin. In 5OBAC there is only an approximate center of sym-

TABLE IV

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

| Bond | 3OBAC | 5OBAC I | 5OBAC II |
|---|---|---|---|
| O(1)—C(7) | 1.279(2) | 1.335(16) | 1.230(18) |
| O(2)—C(7) | 1.262(2) | 1.176(16) | 1.265(16) |
| O(3)—C(4) | 1.365(2) | 1.352(19) | 1.321(15) |
| O(3)—C(8) | 1.440(2) | 1.447(16) | 1.498(16) |
| C(1)—C(2) | 1.398(3) | 1.382(18) | 1.375(19) |
| C(2)—C(3) | 1.371(3) | 1.386(16) | 1.410(18) |
| C(3)—C(4) | 1.386(3) | 1.390(21) | 1.398(17) |
| C(4)—C(5) | 1.392(3) | 1.400(21) | 1.390(21) |
| C(5)—C(6) | 1.383(3) | 1.392(16) | 1.392(20) |
| C(6)—C(1) | 1.383(3) | 1.400(16) | 1.386(18) |
| C(7)—C(1) | 1.473(3) | 1.539(17) | 1.523(17) |
| C(8)—C(9) | 1.514(3) | 1.512(20) | 1.533(22) |
| C(9)—C(10) | 1.512(3) | 1.539(26) | 1.546(23) |
| C(10)—C(11) |  | 1.529(25) | 1.517(26) |
| C(11)—C(12) |  | 1.540(28) | 1.532(27) |

| Angle | 3OBAC | 5OBAC I | 5OBAC II |
|---|---|---|---|
| O(1)—C(7)—O(2) | 123.0(2) | 120.5(12) | 124.2(13) |
| O(1)—C(7)—C(1) | 117.8(2) | 113.4(11) | 117.0(12) |
| O(2)—C(7)—C(1) | 119.2(2) | 125.7(13) | 117.6(12) |
| C(2)—C(1)—C(7) | 120.1(2) | 116.4(14) | 118.6(11) |
| C(6)—C(1)—C(7) | 121.2(2) | 118.5(12) | 121.1(11) |
| C(2)—C(1)—C(6) | 118.7(2) | 125.0(11) | 119.9(11) |
| C(1)—C(2)—C(3) | 120.2(2) | 117.5(11) | 120.6(12) |
| C(2)—C(3)—C(4) | 120.4(2) | 120.1(13) | 120.1(13) |
| C(3)—C(4)—C(5) | 120.3(2) | 120.7(14) | 118.0(12) |
| C(4)—C(5)—C(6) | 118.6(2) | 120.9(13) | 121.9(13) |
| C(5)—C(6)—C(1) | 121.7(2) | 115.7(11) | 119.5(13) |
| C(3)—C(4)—O(3) | 115.8(2) | 115.0(14) | 114.2(12) |
| C(5)—C(4)—O(3) | 123.9(2) | 124.3(14) | 127.7(11) |
| C(4)—O(3)—C(8) | 117.9(2) | 116.7(11) | 113.7(10) |
| O(3)—C(8)—C(9) | 107.5(2) | 108.7(12) | 103.4(12) |
| C(8)—C(9)—C(10) | 113.0(2) | 114.4(14) | 115.7(14) |
| C(9)—C(10)—C(11) |  | 110.3(14) | 113.1(15) |

metry in the dimer, with significant deviations from true inversion symmetry in the overall conformation. The carboxy group in 3OBAC is not in a form with pure hydroxy and carbonyl C—O bond lengths. Instead, the two C—O distances, 1.262(2) and 1.279(2) Å, are fairly similar and the carboxy hydrogen atom is located close to the mid-point of the O—H---O hydrogen bond for which the O---O separation is 2.611 Å. These features match those found for the carboxy groups in 2OBAC, 4OBAC, and the higher homologs, as well as in crystals of other aromatic carboxylic acids.[14] They may be interpreted in terms of static or dynamic disordering of the two C—O bond types. The presence of only a single peak corresponding to the carboxy hydrogen atom in the difference maps favors a dynamic alternation of bond types but is not conclusive. A double peak has been found for the hydrogen atom in one of the two independent molecules in the asymmetric unit 4OBAC.[6] There is an effective equivalence of C—O bond lengths in one of the molecules of 5OBAC, though not in the other. Given the low accuracy of the determination this difference is more apparent than real. The independent O ··· O separations in the dimer are 2.589 and 2.610 Å.

Other bond lengths and angles have expected values. Agreement between corresponding dimensions for the accurately determined 3OBAC and the higher homologs reported in Parts VI and VII is good. For example, the mean difference in equivalent bond lengths in the benzoic acid moieties of 3OBAC and 9OBAC is only 0.005 Å. The exocyclic C—C—O angles at C(4) have the usual asymmetry attributable to steric interactions between the ring hydrogen at C(5) and the methylene hydrogens of C(8). For the eight compounds reported in this present group of papers the mean values of these two angles are 115.1° and 124.7°. The mean value of the valence angle at the ether oxygen is 118.4° for the same compounds (except 5OBAC) and at C(8) the O—C—C valence angle has a mean value of 106.9°. The mean aliphatic C—C bond length is 1.516 Å and the mean C—C—C valence angle in the chains is 113.9°.

Both 3OBAC and 5OBAC are non-planar. Although the alkyl chains of each adopt a planar all-*trans* extended conformation, the linkage of the chain to the "oxobenzoic acid" residue involves a *gauche*-relation of the O(3)-C(8) and C(9)-(10) bonds about the C(8)-C(9) bond of the chain. The torsion angles O(3)-C(8)-C(9)-C(10) are 66.4° for 3OBAC and 64.5 and −63.1° for 50BAC. These values are comparable to the 64° torsion angle about the C(8)-C(9) bond in one of the two crystallographically independent molecules of 4OBAC, and *gauche*-conformations also are present in the crystal structures described in Parts VI and VII.

Although the aromatic residues of the molecules are quite planar their conformations are most accurately defined in terms of the rigorously planar four-atom carboxy group centered on C(7) and the phenyl group. The overall molecular conformations may then be described in terms of the angles between these two planes and the plane of the aliphatic chain. Information on these planes is given in Table V. The angles between the carboxy and phenyl planes are small: 2.5° in 3OBAC, 6.3° and 3.5° in 5OBAC. These are comparable to the angles found in 1OBAC, 2OBZC, and 4OBAC. They reflect tilts of the two planes relative to one another rather than twists of the two about the C(1)-C(7) bond axis. The angles between the alkyl chain planes and the ring planes are large: 113.0° in 3OBAC, 116.9° and 110.4° in

TABLE V

Selected least-squares mean planes

| Plane | $n$ | $a$ | $b$ | $c$ | $d$ | $\Delta_{ave}$ | $\Delta_{max}$ |
|---|---|---|---|---|---|---|---|
| Carboxy group | 3 | 0.37119 | 0.85752 | 0.35619 | −0.00924 | 0.005 | 0.010 |
| | 5 | 0.33885 | −0.85533 | 0.39192 | −0.75366 | 0.020 | 0.040 |
| | 5′ | 0.34302 | −0.87975 | 0.32922 | −0.77485 | 0.032 | 0.064 |
| Phenyl ring | 3 | 0.33067 | 0.87198 | 0.36098 | −0.12446 | 0.005 | 0.009 |
| | 5 | 0.31908 | −0.90109 | 0.29363 | −0.46051 | 0.009 | 0.015 |
| | 5′ | 0.35686 | −0.89395 | 0.27111 | −0.90009 | 0.007 | 0.013 |
| Alkyl chain | 3 | 0.27443 | −0.78258 | 0.55880 | −2.62899 | — | — |
| | 5 | 0.25856 | 0.77999 | 0.56988 | −3.60741 | 0.014 | 0.020 |
| | 5′ | 0.11022 | 0.65906 | 0.74397 | −3.28833 | 0.006 | 0.010 |

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 in which $X = x + z.\cos\beta$, $Y = y$, and $Z = z.\sin\beta$.

5OBAC. The angle between the chain axis and the axis C(1)–C(4) is 135° in 3OBAC, 146° and 148° in 5OBAC.

## Molecular packing

The most important result of these crystal structure analyses is the determination of molecular organization in the solid phase. Molecular packing in 3OBAC is illustrated by Figures 1–3, and in 5OBAC by Figures 4–6. For purposes of comparison packing in 1OBAC, seen in projection down the short crystal axis, is shown in Figure 7.

The crystal structures of both 3OBAC and 4OBAC are based upon sheet elements shown in *b*-axis projection in Figures 1 and 4. The dimers are arranged in head-to-tail fashion in parallel staggered rows normal to *b* and parallel to $[10\bar{2}]$. The dimers repeat by unit translations in *a* and *c* so that within a given sheet all have the same orientation and are at the same height with respect to *b*. Organization of the molecules within the sheets is very similar in each case. The normals to the phenyl ring planes are inclined to *b* at 29° in 3OBAC and at 26° and 27° in 5OBAC. The orientation of these normals with respect to *a* is 71° in 3OBAC and 60° and 71° in 5OBAC. With respect to *c* the angle are 69° in 3OBAC, 73° and 74° in 5OBAC.

The chain termini are related by crystallographic centers of symmetry at $\frac{1}{2}, 0, 0$ in 3OBAC and by approximate non-crystallographic centers of symmetry in 5OBAC. In each case the terminal C—C bonds of the chains are juxtaposed across these centers forming a pseudo ring. An exact center of symmetry at $0, 0, \frac{1}{2}$ relates the rings of laterally antiparallel pairs of molecules in 3OBAC and similar approximate centers may be seen in the 5OBAC sheet. Comparison with Figure 7 shows that whereas the methoxy carbons

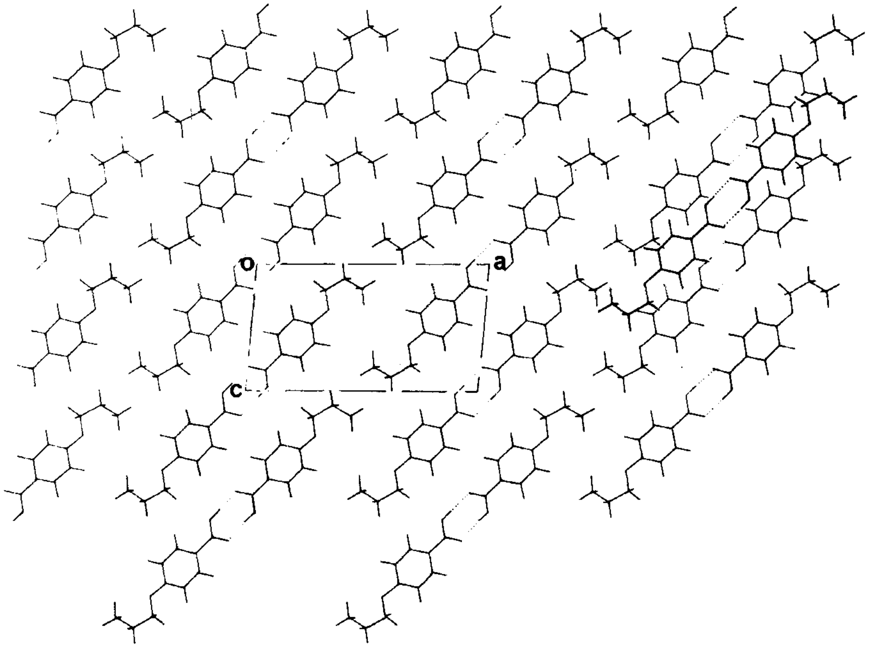

FIGURE 1 Sheet element in the crystal of 3OBAC seen in *b*-axis projection. A dimer in an adjacent sheet is shown in heavier outline at the top right-hand corner.

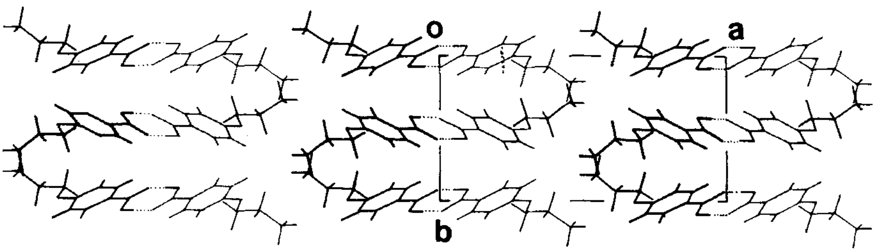

FIGURE 2 Stacked sheet elements in 3OBAC seen in *c*-axis projection. Relative height is indicated by varying line thickness.

in 1OBAC are alongside the carboxy groups of neighbours, in 3OBAC and 5OBAC the chain ends are alongside the phenyl rings of neighbours.

There is a discernible progressive trend towards segregation of the chains and aromatic residues into strata parallel to *c*, a trend which is emphasized when the stacking of sheets along *b* is also taken into account. A single molecule of an adjacent sheet is drawn in bold outline in the upper right-hand corner of both Figure 1 and Figure 4 to show the relation of adjacent sheets, and edge-on views of the sheet stacking are shown in Figures 2 and 5.

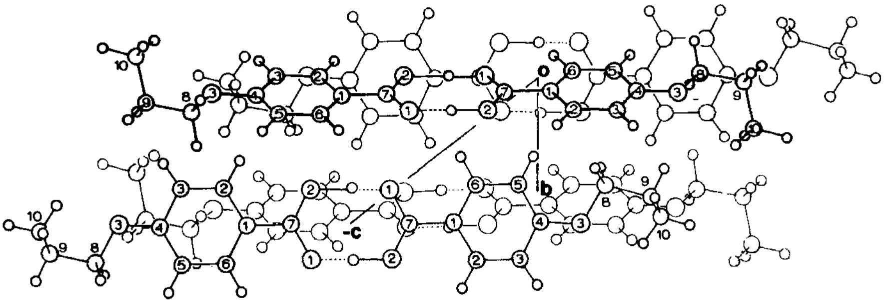

FIGURE 3 Projection of molecules onto the phenyl ring plane of 3OBAC showing nearest neighbor packing.

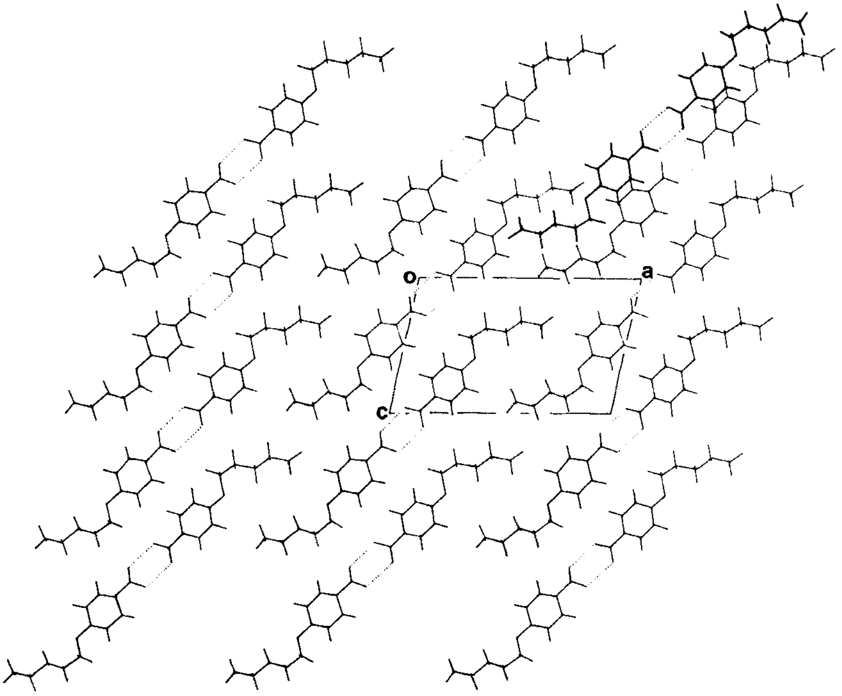

FIGURE 4 Sheet element in the crystal of 5OBAC seen in *b*-axis projection. A dimer in an adjacent sheet is shown in heavier outline in the top right-hand corner.

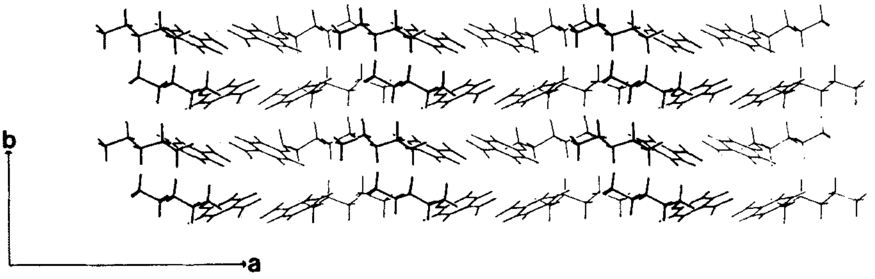

FIGURE 5 Stacked sheet elements in 5OBAC seen in *c*-axis projection.

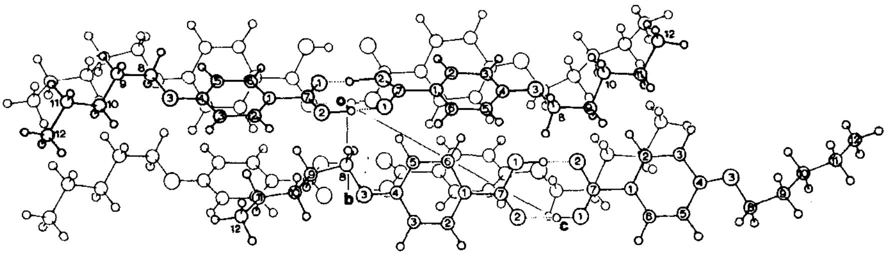

FIGURE 6 Projection of molecules onto the phenyl ring plane of a reference dimer of 5OBAC showing nearest neighbor packing

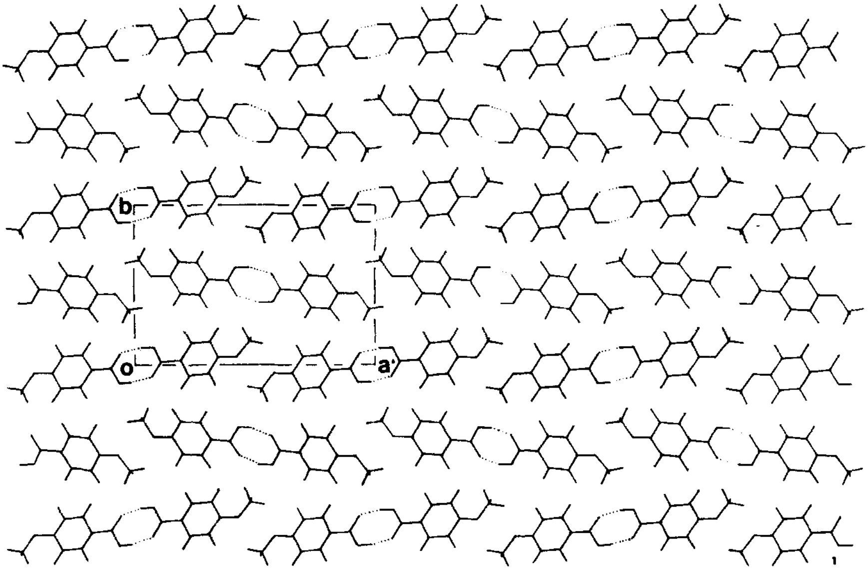

FIGURE 7 Molecular packing in 1OBAC seen in *c*-axis projection.

For 3OBAC the action of the space group $2_1$ axes upon a given sheet is equivalent to rotation of the sheet by 180° about the crystal *b*-axis followed by half translations in *b* and *c*. The carboxy groups of dimers in adjacent sheets thus straddle the *bc*-plane, and in three dimensions the structure has a layer character, but with the molecular long axes inclined to the *bc*-plane by only about 40°.

In 5OBAC the $2_1$ axes once again produce rotation of the sheet about *b* but with translation only by *b*/2. The exact half translation in *c* of dimers in adjacent sheets in 3OBAC is replaced here by comparatively small translations in both *a* and *c*. The effect is to enhance both parallel and antiparallel overlap of the alkyl chains from sheet to sheet. The general packing of the chains remains loose, however, as may be seen from the high thermal parameters for the chain atoms, particularly those of the terminal methyl groups ($B_{eq}$ = 8.9 and 10.6 Å$^2$). The failure to observe the methyl protons may indicate that there is comparatively unrestricted rotation about the terminal C—C bonds in each case, but the nature of the experiment does not allow us to distinguish between that possibility and a general increase in thermal vibration leading to simple smearing out of these hydrogens. In considering intermolecular contacts hydrogen positions have been assumed for the methyl groups by assuming an all-*trans* conformation for the chain.

Lateral and vertical intermolecular contacts may be visualized from Figures 3 and 6, which are projections of adjacent molecules onto the least-squares mean plane of the central "oxobenzoic acid" residues of reference dimers. The ring planes of overlapping molecules in the Figures are inclined to one another by 59° in 3OBAC and by 52° in 5OBAC. The longitudinal displacement of parallel dimers of 3OBAC is 6.4 Å, the lateral displacement is 4.5 Å, and the vertical separation is 2.5 Å. For 5OBAC these displacements are, respectively, 8.4, 4.9, and 2.6 Å. There are no C --- C contacts in 3OBAC $<$ 3.6 Å and only six C --- H contacts $<$3.0 Å[15] There are two limiting C --- C contacts in the crystal structure of 5OBAC [C(6) --- C(6′), 3.48 Å; C(3) --- C(4′), 3.49 Å] but almost all C --- C approaches are $>$3.5 Å. There are 10 C --- H contacts $<$3.0 Å. The packing is therefore quite loose by comparison with that found in 1OBAC and 2OBAC. In neither structure is there any evidence that strong dipole-dipole interactions are of any importance in the solid state.

## DISCUSSION

### General

With the addition of the crystal structures reported in this present series of papers to those reported previously we now have information on at least one crystal form of each of the acids in the series, up to and including that with 10 carbon atoms in the alkyl chain. We are therefore in a position to study the effect of increasing chain length upon molecular packing in the crystal and to see whether the changes in crystal structure are related to changes in mesomorphism. This examination is less complete than it might be, in that the crystal forms reported for 3OBAC and 6OBAC undergo solid-solid transitions before yielding nematic phases (and so cannot be directly related to mesophase organization) as do the isotypic crystal forms of the smectogenic acids. However, where information on two crystal forms is available, as for 8OBAC, some idea may be gained of the nature of possible transitions, and useful conclusions may be drawn nonetheless on the basis of our present knowledge.

Mesophases exist in the temperature range where the molecules have enough thermal energy to acquire certain degrees of freedom but not others. The restrictions on available degrees of freedom which characterize the various mesophases ultimately derive from the marked formanisotropy of the molecules. The high overall length-to-breadth ratio in linear mesogens favors extended parallel or near parallel alignment of molecules in the solid phase,[3] and such alignment persists in the mesophases over distances which are large compared to molecular dimensions. Higher thermal energies are needed to destroy that alignment, but the densities of condensed phases suggest that a fair degree of parallel alignment must still persist at the local molecular level even in the so-called isotropic liquid.

The differences in energy needed for molecules in a parallel matrix to acquire various degrees of freedom may be linked, qualitatively at least, to the amount of local free volume needed by a given molecule to allow a particular motion to be executed. Thus, in the nematic state, translational motions of molecules require least free volume, because molecules may move relative to one another while still remaining in very close contact with a full complement of nearest neighbours. The movements are seen as predominantly cooperative at the local level with insertion of a molecule between neighbors by opening of a wedge between them requiring extra energy and being much less common. Rotation about the long molecular axis may also proceed without the need for excessive local free volume if it is also seen as predominantly a cooperative motion locally and not that of a free rotor surrounded by non rotors. Rotations of individual molecules about other axes, *or even large excursions about such axes*, cannot take place without creation of much larger local free volumes, and cooperative motions of similar type are also restricted by this criterion, except in the special case of crossed-sheet structures.[3]

When one adopts this view of molecular motions in the mesophases, the reasons for supposing that crystal structure may be related to mesomorphism become clear. At a given temperature and pressure within the solid phase, the crystal structure is the packing arrangement of lowest energy for the molecules. It is a well-known feature of the structure of molecular crystals that in the absence of strong directional forces, such as hydrogen bonding, minimization of intermolecular energy is achieved by minimization of free volume. The molecules in this context may properly be viewed in terms of a hard-shell model, their dimensions being defined by sharply demarcated minimum contact distances between atoms in neighboring molecules. Because we move from the crystal where free volume is a minimum to a mesophase where certain molecular degrees of freedom are constrained by lack of available free volume it is reasonable to suppose that the motions which manifest themselves do so in response to incremental rather than large-scale changes in local free volume between the two phases.

Such a view certainly seems justified in the case of materials undergoing a solid-nematic transition. The now quite extensive data on crystal structures of nematogens show them to be of types embodying either completely three-dimensional parallel arrangements of the molecular long axes, or else bilayer sheets where overall parallelism in the mesophase may result by cooperative rotations requiring little increase in free volume.[3]

Much less evidence is available on the crystal structures of materials yielding smectic phases and what is known suggests that the relationships between these mesophases and the solid-state structures are more subtle than for the solid-nematic relation. However, to the extent that a smectic phase involves some constraint on longitudinal translational motion of the molecules, we may hope to find some indication of the nature of the constraint from the crystal structure. If the constraint derives from one or two particularly strong interactions between molecules then these should also feature in the thermally less excited solid phase. Equally, if the constraint has its origin in the sum of a large number of weak interactions, such as those between alkyl chains of a certain length, these too might be expected to be a feature of the solid. If the constraint is steric in origin, as seems probable in several smectic A phases and which also seems likely, in part, in this series, then such a feature might be present or not in the crystal depending on whether or not a conformational change occurs at the transition.[16] In all cases we expect the transitions between solid and mesophase to proceed with some recognizable retention of molecular alignment and, in some cases, with actual retention of some aspects of relative molecular position.

Although extended parallel alignment of the molecules in the solid phase seems to be a necessary condition for mesophase formation it is not a sufficient condition at all pressures. This is clearly seen in this series of acids where the two lowest homologs do not individually yield mesophases at ambient pressure. It has been clearly demonstrated that this failure arises from the high melting points (184 and 197°C) of the two solids.[1] These, in turn, arise from particularly effective molecular packing modes in the two crystals which feature pleated-sheet structures with face-to-face parallel overlap of molecules in stacks coupled to very efficient space filling arising from the lateral juxtaposition of the short but bulky alkyl residues alongside the sterically least bulky groups of the dimers—the hydrogen bonded carboxy groups. In the absence of any other constraints, at temperatures where the high packing energy can be overcome the molecules separate with sufficient energy to pass directly to the liquid or even the gaseous state.

Interestingly, however, at 5 at pressure both acids yield a nematic phase and at pressures around 90 at even smectic phases are found.[2] This observation lends strength to the arguments concerning free volume for the effect of increased pressure may readily be interpreted as a constraint upon the volume change possible at the transition from the solid, the available free volume determining the type of mesophase found.

If, at atmospheric pressure, tight molecular packing inhibits mesophase formation we might expect that looser packing would favor such behavior as part of the necessary free volume is already present in the solid phase. An examination of the crystal structures of the nematogenic acids shows that this is indeed the case, looser packing being a consequence of the increasing difficulty of packing together the sterically disparate components of the molecules as the chain grows in legnth.

## Steric disparity in the dimer components

The molecules are present in the solid phase as hydrogen-bonded dimers. The dimers are composed of two sterically distinct molecular parts which are illustrated in cross section in Figure 8. They are:

1) The "oxybenzoic acid" residue—a planar lathe-like unit which in dimer form has a length of about 17.8 Å. Its van der Waals breadth reaches a maximum of 6.7 Å across the phenyl ring from H to H, tapering to 5.0 Å across the carboxy group. The unit has a maximum thickness of 3.4 Å normal to the phenyl ring plane, falling to 2.8 Å normal to the carboxy oxygen atoms and to 2.4 Å normal to the C—H bond axes at the hydrogen atoms.

2) The alphatic chain whose length is a function of the number of carbon atoms it contains and which in an extended conformation has a roughly square cross section of 4.3 Å on a side.

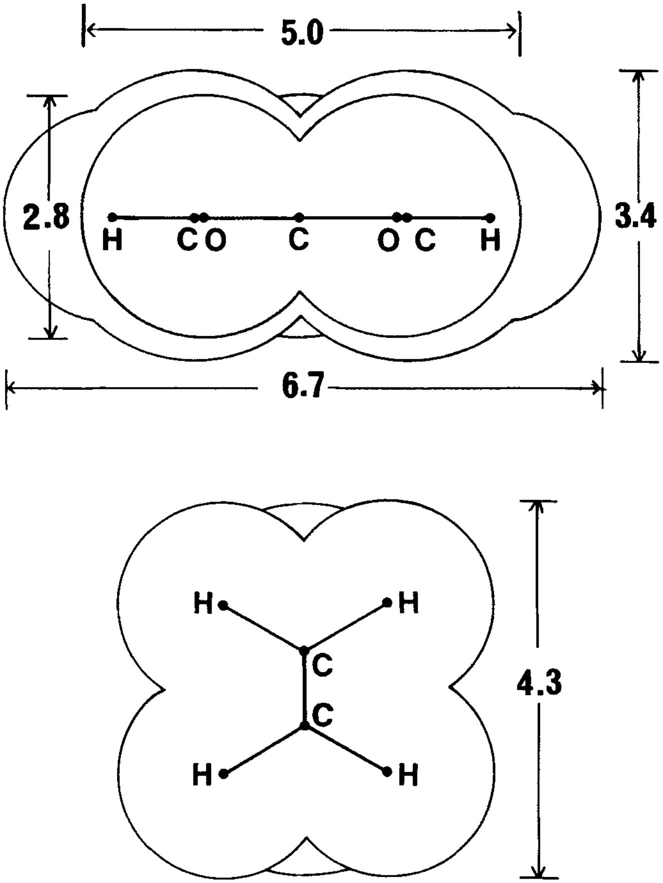

FIGURE 8 Cross-sectional views of the two sterically distinct components of the acids. Top: normal to the plane of the central nucleus. Bottom: normal to the chain axis. Atoms are drawn with van der Waals radii of 1.7 Å for C, 1.4 for Å for O, and 1.2 Å for H. Dimensions shown are in Å.

The difficulties which arise in crystal packing because of these steric disparities in the two molecular components play an important role in mesophase formation.

Where the first of these units is the dominant component and the chains are short, as with the two lowest members of the series, the dimers are more or less planar (though significantly not so in detail) and the packing problem is resolved without difficulty. Indeed the packing energies are so high that these compounds have melting points above the range of mesophase stability and no mesophases form at atmospheric pressure.

Where the chains are of intermediate length, containing from three to six carbon atoms, the packing problem is not so readily solved. Crystal structures result which have fairly weak intermolecular interactions and which therefore form natural precursors for both solid-solid and solid-nematic conditions.

With a sufficiently long chain length, from seven carbon atoms upward, a smectic phase forms and the acids adopt a characteristic isotypic stratified layer structure with segregation of the chains and aromatic cores into separate close packed strata. The difference in steric bulk between the chains and cores is resolved by interdigitation of the chains of successive layers to give a 2:1 ratio of chains to cores in the strata. Imbrication of dimers from layer to layer resulting from a non-planar and non-linear dimer conformation also seems to provide a natural steric constraint on relative longitudinal translational motions, favoring a smectic phase.

Immediate evidence for the increasingly difficult problems faced in packing the dimers in the crystal when the chains are of intermediate length, and the more efficient packing which results when the chain length exceeds a critical value, is provided by the molecular volumes in the various crystals. We consider the increments in molecular volume in the crystals per $CH_2$ group as a function of chain length. Because of the odd-even effect which is present in this as in other homologous series of mesogens it is proper to compare these increments by taking odd with odd and even with even chain lengths. The quantities being compared are then the increments in crystal volume per pair of methylene groups. The data are given in Table VI. For purposes of comparison with the volumes occupied by a methylene group in close-packed crystals we note that in the orthorhombic subcell of the A-form of n-tritriacontane that volume is about 23.5 Å$^3$,[17] on the monoclinic subcell of n-hexatriacontane it is about 23.4 Å$^3$,[18] and in the triclinic subcell of 3-thiadodecanoic acid it is about 23.2 Å$^3$.[19]

For the isotypic series the volume increment per $CH_2$ group is about 23.7 Å$^3$, only slightly greater than those found for the close packed systems quoted. However, as may be seen from Table VI, the volume increments in passing from $n = 1 \rightarrow 3 \rightarrow 5$ and from $n = 2 \rightarrow 4$ are significantly greater than would result from close packing of chains. Indeed, that for the last of these transitions is $>25\%$ greater than would be expected on that basis. The smaller than standard increments for $n = 4 \rightarrow 6$ and $n = 5 \rightarrow 7$ likewise testify to the inefficiency of packing in the intermediate homologs.

We attribute the ready formation of nematic phases by the homologs from $n = 3 \rightarrow 5$ to the fact that a favorable spatial alignment of the molecules in the crystal is accompanied by a weakening of the intermolecular forces because of less efficient chain packing. The packing arrangements *within* the sheet elements of 3OBAC and 5OBAC are very similar to one another,

TABLE VI

Molecular volumes in crystals of the *p*-n-alkoxybenzoic acids

| $n$ | Molecular volume (Å$^3$) | $2\Delta V/CH_2$ (Å$^3$) | Crystal density (g cm$^{-3}$) |
|---|---|---|---|
| 1 | 183.0 | — | 1.380 |
| 3 | 233.2 | 50.2 | 1.283 |
| 5 | 289.2 | 56.0 | 1.196 |
| 7 | 330.8 | 41.6 | 1.186 |
| 9 | 378.1 | 47.3 | 1.161 |
| 2 | 206.3 | — | 1.338 |
| 4 | 268.8 | 62.5 | 1.200 |
| 6 | 311.0 | 43.2 | 1.187 |
| 8[a] | 358.8 | 47.8 | 1.158 |
| 10 | 406.1 | 47.3 | 1.138 |

[a] Values for $n = 8$ are for the isotypic crystal form.

to that in 4OBAC, and to those in 1OBAC and 2OBAC. The difference in crystal structure between the three ambient pressure nematogens and the two non-mesogens is principally in the way in which the sheet elements are stacked atop one another. In the three nematogens the exact face-to-face stacking of molecules in successive sheets which characterizes the non-mesogenic lowest homologs is absent. Instead the sheets are stacked in such a way that the aromatic rings do not overlap at all (3OBAC and 4OBAC) or else they do so at a substantial angle to one another (5OBAC). A significant contribution to packing energy is thereby lost, and in the more open crystal structures which result the energy needed to induce translational displacements of the molecules is more readily separated from the larger energy needed to bring about rotations or oscillations forbidden in the mesophase. In adopting this approach to the problem of mesophase formation, we see that the concept of the mesophase as a *destabilized solid* is quite as valid as the view which presents it as a *stabilized liquid.*

There is one other feature of the crystal structures of the homologs from $n = 3$ upwards which distinguishes them from those of the two lowest members. This is the presence in the higher homologs of a *gauche*-relation of the ether oxygen atom and C($\gamma$) about the C($\alpha$)—C($\beta$) bond of the chain. As a result the molecules are no longer completely planar. This feature is not of critical importance for the nematogens as the shorter chain lengths in these molecules do not disturb the overall linearity of the dimers to an extent which causes sheet packing to be abandoned in favor of imbricated structures such as are found for the room temperature forms of the smectogenic acids. Adoption of the *gauche*-conformation in the solid phase of the smectogenic acids is of great importance and its role both in reconciling steric disparities between the molecular components and in leading to layer imbrication is discussed in detail in Part VI.

## Acknowledgment

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