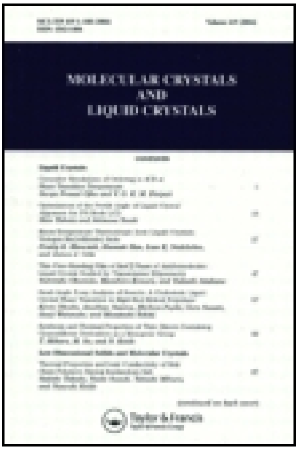

Molecular Crystals and Liquid Crystals

An X - Ray Study of the p-n-Alkoxycinnamic Acids. Part III.[1]

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An X-Ray Study of the *p*-n-Alkoxycinnamic Acids. Part III.[1]

Crystal Structures of Four Nematogenic Acids Having Two, Four, Six, and Eight Alkyl Chain Carbon Atoms

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The effect upon molecular packing of increasing chain length in a homologous series of mesogens has been examined in the case of the *p*-n-alkoxycinnamic acids by determination of the crystal structures of the four nematogenic acids having two, four, six, and eight carbon atoms in the alkyl chain. The chains have the all-*trans* extended conformation, and the molecules exist in the crystal as planar hydrogen-bonded dimers. The dimers are arranged in end-to end fashion in parallel rows. Similar side-to-side packing of pairs of dimers is found in each crystal structure giving a good fit between adjacent aromatic cores, but the amplitudes of thermal vibration of the chain carbon atoms increase markedly with increasing chain length, indicating a low packing efficiency for these moieties.

$C_{11}H_{12}O_3$ (2OCAC). Triclinic, $P\bar{1}$, $a = 9.111(8)$, $b = 7.683(5)$, $c = 7.282(5)$ Å, $\alpha = 97.74(7)$, $\beta = 92.45(6)$, $\gamma = 95.74(7)°$, $Z = 2$.
$C_{13}H_{16}O_3$ (4OCAC). Triclinic, $P\bar{1}$, $a = 14.686(3)$, $b = 11.726(3)$, $c = 7.763(2)$ Å, $\alpha = 90.02(2)$, $\beta = 99.36(2)$, $\gamma = 114.51(2)°$, $Z = 4$.
$C_{15}H_{20}O_3$ (6OCAC). Monoclinic, $C2/c$, $a = 25.865(15)$, $b = 7.498(3)$, $c = 15.153(9)$ Å, $\beta = 100.76(4)°$, $Z = 8$.
$C_{17}H_{24}O_3$ (8OCAC). Triclinic, $P\bar{1}$, $a = 20.199(20)$, $b = 7.677(9)$, $c = 5.667(6)$ Å, $\alpha = 98.64(9)$, $\beta = 105.67(12)$, $\gamma = 99.83(12)°$, $Z = 2$.

All four crystal structures were solved by Patterson methods using three-dimensional intensity data measured by counter diffractometry, and were refined by least-squares methods to yield R values of 0.081, 0.052, 0.060, and 0.149 for the ascending series.

INTRODUCTION

In a series of papers on the *p*-n-alkoxybenzoic acids,[2] we have drawn attention to the correlations between the types of crystal structure adopted by these compounds and the incidence and type of thermal mesomorphism which they show. In particular, we emphasized that for chains of intermediate length steric incompatibility between the component parts of the molecule lowered the packing efficiency in the solid, favoring formation of a nematic phase. We have extended that study by examining similar correlations in the series of *p*-n-alkoxycinnamic acids. Earlier studies described the crystal structures of the nematogenic *p*-methoxycinnamic acid[3] and the non-mesomorphic α-*trans*-cinnamic[3] and *p*-hydroxycinnamic acids.[1] Failure to form liquid crystals on heating was attributed in the case of cinnamic acid to inability of the herringbone arrangement of dimers of the acid present in the crystalline phase to transform to the parallel mode of packing needed in a mesophase, whereas in the case of the hydroxy acid an otherwise suitable parallel arrangement of dimers in the crystal was preserved by extensive hydrogen bonding between molecules to a temperature above the range of stability of a mesophase.

In this paper we describe the crystal structures of the four nematogenic acids (*n*OCAC) having two, four, six, and eight carbon atoms in the alkyl chain. Steric incompatibility is again shown to be important in these crystal structures in which a common mode of side-by-side packing of dimers which leads to efficient packing of the central cores is preserved in the face of decreasing efficiency of chain packing with increasing chain length. In all four structures the molecules are arranged in the staggered parallel rows characteristic of classical nematic precursor crystals.

EXPERIMENTAL

Preparation and Purification The four acids were prepared by refluxing equimolar amounts of the alkyl iodide and *p*-hydroxycinnamic acid in alcoholic potassium hydroxide solution, as described by Bennett and Jones,[4] and were purified by repeated recrystallization from glacial acetic acid and from ethanol. Crystals suitable for *x*-ray study were grown by controlled slow cooling of saturated ethanol solutions. Good crystals were obtained in this way for the three lowest homologs, but those obtained for 8OCAC were of generally poor quality, being thin and somewhat flaky.

Thermal Analysis As reported by Gray and Jones,[5] all four acids yield enantiotropic nematic phases on heating. C → N and N → I transition temperatures were determined by hot-stage microscopy on thin films of the acids contained between a microscope slide and cover slip, and are given in Table I. The C → N transition temperatures agree well with those reported by Gray and Jones, but the N → I transition temperatures found by us for the three highest homologs are about 2° lower than those previously reported.

The transitions were also studied by differential scanning calorimetry with a Perkin Elmer DSC-II instrument, calibrated with In metal as a standard. For a single cycle of heating and cooling ($10\ \mathrm{K\ min^{-1}}$) on each

TABLE I

Transition temperatures (K), enthalpies ($kJ\ mol^{-1}$), and entropies ($J\ mol^{-1}$)

	K → N			N → I		
n	*T*	ΔH	ΔS	*T*	ΔH	ΔS
2	467	38.9	83.4	471	8.1	17.4
4	428.5	32.1	74.9	460.5	4.8	10.5
6	426	26.0	61.2	452	2.7	5.9
8	417.5	23.4	56.4	445	2.5	5.5

sample no transitions other than those reported were observed in the temperature range 320–520 K, so that these crystalline forms appear to transform directly to the nematic state on heating. Transition enthalpies and entropies were derived for each acid from such single heatings and are given in Table I.[6] After only a few cycles of heating and cooling the same sample, additional peaks appeared reproducibly in the DSC traces. Those for the three higher acids could be interpreted in terms of monotropic solid-solid transitions taking place within a few degrees of the initial crystallization from the nematic melt, but for 2OCAC a smaller third peak appears at 477 K on heating, some 5.5 K above the initially observed N → I transition temperature. Samples of the four acids which had been subjected to repeated heating and cooling through the transition regions were examined by thin-layer chromatography using 10% ether in methanol as a solvent. No additional peaks indicative of reaction products were noted in these chromatograms and the R_f values of normally recrystallized and thermally cycled materials were the same in each instance.

Crystallographic Data These are summarized for the four acids in Table II. Crystal symmetry was established from 25° precession photographs of equatorial and general zones taken with Mo $K\alpha$ radiation. For 6OCAC, the systematic absences *hkl* with $h + k$ odd and *h*0*l* with *l* odd indicate the space group as *Cc* or *C*2/*c*. With eight molecules of the acid in the unit cell, and given the tendency of carboxylic acids to form centrosymmetric dimers, the latter space group is the more likely. This choice is supported by the statistical distribution of intensity for this crystal, which conforms to the pattern expected for a centrosymmetric crystal, and is confirmed by the successful refinement of the structure in this space group. The choice of the centrosymmetric space group $P\bar{1}$ over the non-centrosymmetric $P1$ for two of the other three acids was also made on the basis of the intensity statistics derived for these crystals. The crystallographic asymmetric unit of 2OCAC, 6OCAC, and 8OCAC thus contains a single monomeric unit of the acid in each case,

TABLE II

Crystallographic data

	2OCAC	4OCAC	6OCAC	8OCAC
Crystal symmetry	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	9.111(8)	14.686(3)	25.865(15)	20.199(20)
b	7.683(5)	11.726(3)	7.498(3)	7.677(9)
c	7.282(5)	7.763(2)	15.153(9)	5.667(6)
α (deg.)	97.74(7)	90.02(2)	90.00(−)	98.64(9)
β	92.45(6)	99.36(2)	100.76(4)	105.67(12)
γ	95.74(5)	114.51(2)	90.00(−)	99.83(12)
Cell vol. (Å^3)	501.7	1196.7	2887.3	815.6
Mol. wt.	192.21	220.26	248.31	276.37
D_o (g cm^{-3})	1.265(8)	1.22(1)	1.15(1)	1.11(2)
Z	2	4	8	2
D_c (g cm^{-3})	1.272	1.223	1.143	1.125
Molecular vol. (Å^3)	250.9	299.2	360.9	407.8
Points scanned	1433	3406	2120	2355
Significant Fs	1051	2482	1172	885
Scan range (2θ deg.)	2	4	4	4
R (sig. data)	0.081	0.052	0.060	0.149
R_w	0.056	0.057	0.056	0.194
R (all data)	0.122	0.081	0.116	0.274

but that for 4OCAC contains two monomeric units of the acid with no necessary symmetry relation between the two.

Unit cell dimensions were obtained in all cases by a least-squares fit to the observed diffractometer values of $\pm 2\theta$ for a least 24 strong general reflections measured from carefully centered crystals. Crystal densities were measured by flotation, that for 8OCAC being determined using an aqueous KI solution, and those of the others using toluene-carbon tetrachloride mixtures.

Intensity Data Intensities of the x-ray spectra were measured by standard automatic diffractometry from single crystals by use of a Picker full-circle instrument controlled by an XDS Sigma 2 computer. Cu $K\alpha$ radiation was used, made monochromatic ($\lambda = 1.5418$ Å) by Bragg reflection of the direct beam from a highly oriented graphite crystal, with scintillation counting and pulse-height analysis. The θ–2θ scan method was used with a scan speed of 2° min^{-1}. Background intensities were measured for 10 s intervals at beginning and end of the scans with both crystal and counter at rest. For the triclinic crystals a single hemisphere of reciprocal space was examined to $2\theta = 120°$, and for the monoclinic 6OCAC a single quadrant was examined. Accuracy of crystal setting was checked by separate measurement of symmetry related reflections in the equatorial zones ($R_I < 0.032$) and stability of the experimental conditions was monitored by measurement of the intensities of two reference reflections for each crystal after every 50 measurement cycles ($R_I < 0.024$). Significant scattered intensity was assumed when the number of counts above background $> 2\sigma(I)$. No absorption corrections were made and structure amplitudes were derived in the usual way.

Structure Determination and Refinement All four structures were solved by interpretation of the sharpened three-dimensional Patterson functions in terms of the vector image expected for a planar centrosymmetric dimer of 'oxo-cinnamic acid'. For 2OCAC, 6OCAC, and 8OCAC the centers of the dimers were taken to be coincident with the space-group origin. For 4OCAC a formally but non-crystallographically centrosymmetric dimer was assumed and the vector relating pairs of such dimers about the space-group center of symmetry was derived from the highest non-origin peak in the Patterson map. The positions of the alkyl carbon atoms were found readily, in all cases from three-dimensional difference electron-density maps.

Refinement was by the block-diagonal least-squares method, initially with isotropic thermal parameters assumed for all atoms and finally with anisotropic thermal parameters adopted for O and C. Hydrogen atoms were located from difference electron-density maps calculated in the plane of the central aromatic residue and in planes normal to and above and below the plane of the carbon chain. All H atoms were found in this way for 2OCAC where two separate locations, equally populated, were identified for the carboxy hydrogen. All H atoms except for the carboxy hydrogen were located in 4OCAC, and in 6OCAC all except those attached to the two terminal methyl carbons were found. Positional and isotropic thermal parameters of these H atoms were refined in the least-squares process for these three acids. Hydrogen atoms attached to the central aromatic nucleus could be identified for 8OCAC, but the extremely high thermal amplitudes of vibration of the chains made location of methylene hydrogens impossible. No contributions from hydrogen were included in refinement of 8OCAC.

Refinement was terminated at convergence with shift-to-error ratios <0.1. Final difference electron-density maps for 4OCAC and 6OCAC were devoid of structurally significant density, that for 8OCAC contains significant unresolved peaks in the chain region (besides those from the ring hydrogens) indicating that the thermal refinement of this region is only a poor approximation, and that for 2OCAC contains a significant peak of height $0.5e$ in the vicinity of the ether oxygen, attributed to a product of radiation damage to the acid. Both these anomalies are discussed in detail in the next section.

The scattering curves for C and O were taken from Cromer and Waber,[7] and for H from Stewart *et al.*[8] The weighting scheme used in the least-squares refinement was taken from Corfield *et al.*,[9] with analytically derived values of *p*. All computations were carried out on the XDS Sigma 2 computer also used to control the diffractometer, with programs written in this laboratory. Thermal ellipsoid plots were produced on a Tektronix plotter at the Crystallography Laboratory, Department of Inorganic Chemistry, University of Bristol, with the Nicolet XTL system of Sheldrick.[10] We are indebted to Dr. J. A. K. Howard for use of this instrument.

RESULTS AND DISCUSSION

Molecular geometry and conformation

Atomic parameters for the crystal structures of the four acids are given in Tables III–VI. Views of the independent molecules projected onto their least-squares mean planes and with the thermal ellipsoids of the C and O atoms drawn to enclose the 50% boundary envelope are shown in Figures 1(a)–(d). All four acids are present in the crystal as planar hydrogen-bonded dimers with the alkyl chains in all-*trans* extended conformations. The dimers of 2OCAC, 6OCAC, and 8OCAC are centrosymmetric by crystallographic requirement, but that for 4OCAC is not and shows significant deviations from centrosymmetry. The marked anisotropy of these dimers is clear from the representation of 4OCAC shown in Figure 1(b).

The same numbering scheme has been used for all four acids and is shown for 2OCAC in Figure 1(a). The additional alkyl chain carbon atoms of the higher homologs are numbered by extension from C(12) to C(17). Hydrogen atoms are numbered to correspond to the atom of attachment, e.g. H(12a) is one of a pair of methylene hydrogen atoms attached to C(12). The two independent monomers in 4 OCAC are distinguished as A and B.

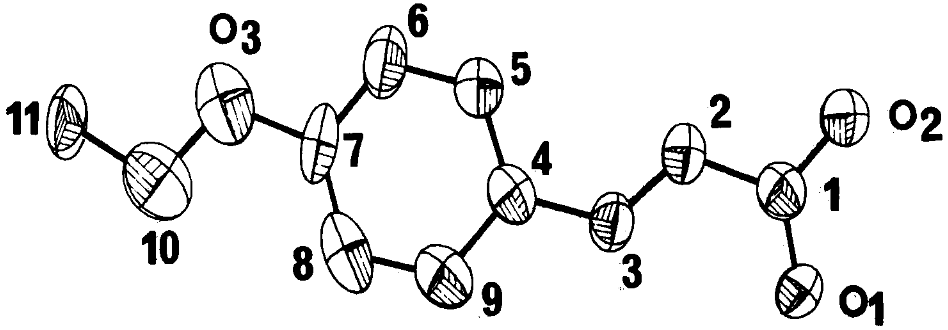

FIGURE 1 (a) Projection of a monomer of 2OCAC onto its least-squares mean plane, and showing the numbering scheme adopted. Atoms are carbon unless otherwise labelled and hydrogen atoms have been omitted. Thermal ellipsoids are drawn to the 50% boundary level.

TABLE III

Atomic parameters defining the crystal structure of 2OCAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	1673(3)	949(4)	1067(5)	5.19	182	232	332
O(2)	−57(3)	2151(4)	−423(5)	5.91	207	229	359
O(3)	6926(4)	10813(5)	3398(5)	7.27	262	300	343
C(1)	1176(5)	2242(6)	493(6)	4.39	219	233	254
C(2)	2028(4)	3975(5)	848(6)	4.55	198	245	272
C(3)	3359(4)	4240(5)	1708(6)	4.07	196	228	254
C(4)	4308(4)	5906(5)	2149(6)	4.16	207	230	250
C(5)	3915(5)	7479(6)	1663(7)	5.17	227	249	288
C(6)	4795(5)	9035(6)	2089(7)	6.13	207	267	344
C(7)	6125(5)	9084(5)	3051(6)	5.18	162	253	327
C(8)	6591(5)	7549(7)	3575(7)	5.63	192	295	300
C(9)	5663(6)	5965(6)	3112(7)	4.87	220	237	284
C(10)	8257(6)	10928(8)	4335(8)	7.94	274	328	345
C(11)	8876(5)	12830(6)	4565(8)	6.31	167	278	367
H(Oa)	105(10)	−23(10)	82(10)	11.5(17)			
H(Ob)	−68(10)	96(10)	−67(10)	12.7(18)			
H(2)	154(4)	495(5)	57(5)	5.0(9)			
H(3)	383(5)	315(5)	205(6)	6.8(11)			
H(5)	306(4)	743(5)	95(5)	4.9(9)			
H(6)	454(5)	1048(7)	182(7)	8.3(13)			
H(8)	748(5)	730(6)	413(6)	9.8(14)			
H(9)	596(4)	491(5)	338(5)	4.8(9)			
H(10a)	793(7)	1012(8)	524(9)	15.0(20)			
H(10b)	839(6)	983(7)	347(8)	12.2(18)			
H(11a)	885(6)	1350(7)	321(8)	12.6(18)			
H(11b)	825(5)	1367(6)	517(6)	8.2(13)			
H(11c)	985(5)	1322(6)	510(6)	9.2(14)			

Positional parameters are given as fractions of the unit cell edges (× 10^4 for C and O, × 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, and as refined B values for H. Estimated standard deviations are given where appropriate, in parentheses, in this and succeeding tables.

Bond lengths and angles in the acids are given in Table VII. The accuracy of the analyses for 4OCAC and 6OCAC is reasonably good, and the values of corresponding bond lengths and angles in the cinnamic acid residues of these two compounds do not differ significantly from their mean values

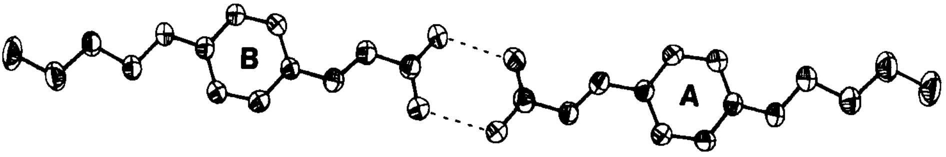

FIGURE 1(b) Projection of a dimer of 4OCAC onto its least-squares mean plane. Thermal ellipsoids are drawn to the 50% boundary level.

TABLE IV

Atomic parameters defining the crystal structure of 4OCAC

Atom	x	y	z	B	r_1	r_2	r_3
Molecule A							
O(1)	1423(2)	−1802(2)	3886(3)	5.38	204	225	335
O(2)	2240(2)	−318(2)	6073(3)	4.97	205	230	307
O(3)	4633(2)	−6063(2)	7561(2)	4.74	182	233	304
C(1)	2066(2)	−1361(3)	5283(4)	3.89	206	214	244
C(2)	2631(2)	−2064(2)	6061(4)	3.71	195	214	239
C(3)	2551(2)	−3117(2)	5282(3)	3.65	193	213	236
C(4)	3084(2)	−3888(2)	5868(3)	3.37	191	204	223
C(5)	3732(2)	−3650(2)	7493(3)	3.85	197	206	255
C(6)	4231(2)	−4385(3)	7998(3)	4.09	189	219	268
C(7)	4108(2)	−5397(2)	6908(3)	3.60	184	221	233
C(8)	3472(2)	−5658(3)	5293(4)	4.23	206	211	272
C(9)	2971(2)	−4904(3)	4798(4)	4.05	190	218	265
C(10)	4542(2)	−7133(3)	6530(4)	4.45	182	233	304
C(11)	5179(2)	−7699(3)	7625(4)	5.14	204	241	263
C(12)	5119(3)	−8861(3)	6733(5)	5.99	198	262	296
C(13)	5738(3)	−9459(3)	7846(5)	7.73	210	282	323
H(2)	308(2)	−172(2)	717(3)	5.9(7)			
H(3)	207(2)	−340(2)	421(3)	4.9(6)			
H(9)	254(2)	−509(2)	362(3)	4.8(6)			
H(8)	336(2)	−635(2)	446(3)	7.4(8)			
H(5)	469(2)	−420(2)	913(3)	5.5(6)			
H(6)	383(2)	−299(2)	831(3)	4.3(6)			
H(10a)	382(2)	−773(2)	629(3)	5.4(6)			
H(10b)	477(2)	−686(2)	544(3)	5.4(6)			
H(11a)	483(2)	−806(2)	872(4)	8.2(8)			
H(11b)	593(2)	−699(3)	800(4)	8.0(8)			
H(12a)	428(3)	−950(4)	670(5)	16.5(14)			
H(12b)	537(3)	−848(4)	556(5)	14.7(13)			
H(13a)	647(3)	−895(3)	826(5)	14.5(13)			
H(13b)	558(3)	−948(4)	926(6)	17.1(15)			
H(13c)	567(3)	−1019(4)	746(5)	15.7(14)			
Molecule B							
O(1)	1262(2)	964(2)	4617(2)	5.20	219	225	314
O(2)	512(2)	−510(2)	2394(3)	5.34	200	233	329
O(3)	−1843(1)	5162(2)	−50(2)	4.13	184	224	269
C(1)	661(2)	521(3)	3172(4)	4.05	212	225	242
C(2)	104(2)	1220(3)	2305(4)	4.15	201	231	253
C(3)	198(2)	2320(3)	2932(3)	3.71	204	212	233
C(4)	−325(2)	3056(2)	2147(3)	3.32	192	209	214
C(5)	−1089(2)	2626(3)	659(4)	4.06	193	223	260
C(6)	−1571(2)	3348(3)	−27(3)	4.06	199	208	267
C(7)	−1312(2)	4533(2)	738(3)	3.40	189	215	218
C(8)	−556(2)	4995(3)	2214(4)	3.80	196	219	241
C(9)	−80(2)	4250(3)	2887(3)	3.94	199	227	242
C(10)	−1693(2)	6337(3)	783(4)	4.17	195	234	256
C(11)	−2378(2)	6817(3)	−319(4)	4.13	198	231	254
C(12)	−2312(2)	8028(3)	475(4)	5.52	203	275	305
C(13)	−2940(3)	8586(3)	−663(5)	6.82	206	295	360
H(2)	−36(2)	79(3)	113(4)	7.7(8)			

TABLE IV (*continued*)

Atom	x	y	z	B	r_1	r_2	r_3
H(3)	67(2)	265(2)	410(3)	5.6(7)			
H(9)	44(2)	456(2)	396(3)	4.4(6)			
H(8)	−36(2)	586(2)	282(3)	5.6(6)			
H(6)	−212(2)	301(2)	−109(3)	5.6(7)			
H(5)	−131(2)	179(2)	11(3)	6.2(7)			
H(10a)	−186(2)	619(2)	204(3)	4.7(6)			
H(10b)	−96(2)	693(2)	96(3)	5.4(6)			
H(11a)	−311(2)	611(2)	−51(3)	5.5(7)			
H(11b)	−220(2)	693(2)	−148(3)	5.5(6)			
H(12a)	−251(2)	790(3)	165(4)	9.3(9)			
H(12b)	−158(2)	864(3)	72(4)	8.7(9)			
H(13a)	−272(2)	874(3)	−179(4)	8.5(8)			
H(13b)	−368(2)	796(3)	−93(4)	8.6(8)			
H(13c)	−292(2)	932(3)	−5(4)	10.6(10)			

Positional parameters are given as fractions of the unit cell edges (C and O × 10^4, H × 10^3). 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, and as refined B values for H.

which, in turn, are in good agreement with the values found in other cinnamic acid derivatives studied in this way.[1,11] There is an anomaly in the geometry of the ether linkages in 2OCAC which flaws the overall reliability of the results from that compound, and which is discussed in more detail below. Within the cinnamic acid residue, however, good agreement is found with the results for 4OCAC and 6OCAC. The accuracy of the determination for 8OCAC is quite poor by comparison, being limited both by the poor quality of the crystals available and the very high thermal motions of the atoms of the chains which lead to a marked fall off in scattered x-ray intensity with increasing scattering angle. Whereas the determination of the structure is certainly correct, the individual dimensions given are probably subject to larger errors than those quoted, and the possibility of some disorder in the alkyl chain cannot be ruled out.

Although the molecules are more or less planar, their conformations are more accurately defined in terms of four independently planar units (*a*)–(*d*), and it is convenient to discuss the geometry of these residues separately. Equations for the various least-squares mean planes are given in Table VIII.

(*a*) *Carboxy groups: C(1), C(2), O(1), O(2)* These are disordered in 2OCAC, 4OCAC, and 6OCAC in a way which is common in crystals of aromatic carboxylic acids.[12] Thus, there is no significant difference between the individual C—O bond lengths in 4OCAC or 6OCAC, and two equally populated hydrogen positions are found (O—H 1.01 and 1.02 Å) along the

TABLE V

Atomic parameters defining the crystal structure of 6OCAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	−596(1)	−799(4)	212(2)	6.47	218	244	372
O(2)	32(1)	792(4)	1067(2)	6.69	221	251	377
O(3)	−2487(1)	−102(3)	4160(2)	6.96	219	296	358
C(1)	−413(1)	16(5)	936(2)	5.17	213	236	308
C(2)	−715(1)	155(5)	1659(2)	5.25	218	236	310
C(3)	−1201(1)	−454(5)	1577(2)	4.92	217	256	272
C(4)	−1544(1)	−366(5)	2231(2)	4.32	212	241	247
C(5)	−1388(1)	409(5)	3068(2)	5.07	229	233	293
C(6)	−1703(1)	471(5)	3682(2)	5.46	241	250	294
C(7)	−2204(1)	−256(5)	3486(2)	5.23	216	256	294
C(8)	−2377(1)	−1028(5)	2671(3)	5.72	200	270	323
C(9)	−2051(1)	−1081(5)	2046(2)	5.37	232	255	292
C(10)	−3010(2)	−746(6)	4017(3)	8.42	239	289	423
C(11)	−3199(2)	−356(7)	4926(3)	10.23	245	348	455
C(12)	−3723(2)	−912(8)	4931(4)	12.46	283	377	502
C(13)	−3878(2)	−476(7)	5851(3)	11.56	268	343	500
C(14)	−4403(2)	−1058(9)	5923(5)	15.99	372	428	535
C(15)	−4557(2)	−577(9)	6780(4)	14.76	231	427	570
H(O)	−27(1)	−85(6)	−41(3)	14.2(15)			
H(2)	−54(1)	71(4)	232(2)	9.9(10)			
H(3)	−134(1)	−100(3)	107(1)	3.7(6)			
H(5)	−106(1)	92(4)	320(2)	6.3(8)			
H(6)	−158(1)	98(4)	428(2)	7.5(9)			
H(8)	−270(9)	−151(4)	254(2)	5.9(8)			
H(9)	−216(1)	−168(4)	147(2)	6.5(8)			
H(10a)	−326(1)	−22(4)	339(2)	7.9(9)			
H(10b)	−301(1)	−203(4)	387(2)	7.2(9)			
H(11a)	−321(2)	94(6)	505(3)	16.7(16)			
H(11b)	−312(2)	−110(6)	533(3)	18.2(18)			
H(12a)	−399(2)	5(6)	440(3)	16.8(16)			
H(12b)	−364(2)	−234(8)	479(4)	15.6(16)			
H(13a)	−389(2)	80(7)	604(3)	19.2(18)			
H(13b)	−368(2)	−76(6)	637(3)	15.7(16)			
H(14a)	−460(2)	−25(7)	540(4)	21.9(20)			
H(14b)	−433(2)	−246(10)	602(4)	33.2(29)			
H(15a)	−495(−)	−106(−)	679(−)				
H(15b)	−455(−)	86(−)	686(−)				
H(15c)	−428(−)	−117(−)	733(−)				

Positional parameters are given as fractions of the unit cell edges (× 10^4 for C and O, × 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, and as refined B values for H.

[a] The H(15) atoms are placed in idealized calculated positions to give a staggered conformation about the C(14)—C(15) bond.

O(1)...O(2′) axis in 2OCAC. No electron density corresponding to the carboxy protons could be found for 4OCAC, and the proton in 6OCAC is 1.38 Å from O(1) and 1.26 Å from O(2′). No attempt was made to refine

TABLE VI

Atomic parameters defining the crystal structure of 8OCAC

Atom	x	y	z	B	r_1	r_2	r_3
O(1)	462(4)	1119(10)	2987(14)	7.46	264	306	346
O(2)	53(4)	2150(10)	−455(14)	7.63	261	289	372
O(3)	2085(5)	11758(15)	11637(21)	12.6	353	397	445
C(1)	375(6)	2456(14)	1831(21)	6.28	246	282	314
C(2)	610(7)	4279(15)	3318(21)	7.01	243	267	369
C(3)	960(6)	4650(15)	5798(21)	6.33	270	281	297
C(4)	1248(6)	6482(16)	7345(21)	6.48	254	279	322
C(5)	1134(7)	8030(15)	6394(24)	8.22	221	305	413
C(6)	1389(8)	9691(17)	7760(24)	9.60	227	372	417
C(7)	1789(6)	9825(18)	10134(26)	9.56	206	308	475
C(8)	1916(7)	8431(22)	11343(26)	10.3	296	339	433
C(9)	1610(7)	6562(21)	9786(25)	9.54	278	313	433
C(10)	2468(9)	12334(34)	14034(30)	17.9	297	401	655
C(11)	2667(10)	14369(27)	14610(34)	15.3	350	429	523
C(12)	3155(14)	15181(39)	17251(43)	23.5	405	505	689
C(13)	3370(10)	17249(30)	17910(28)	17.0	266	421	630
C(14)	3874(12)	18067(40)	20639(45)	22.2	407	525	633
C(15)	4043(10)	20103(30)	21041(35)	16.7	325	455	568
C(16)	4535(15)	20922(43)	23701(68)	30.3	443	534	819
C(17)	4730(14)	22957(27)	24245(56)	23.2	366	497	706

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

partial occupancies of ordered carboxy residues in alternate locations as it is not clear whether the disorder is static or dynamic in nature. The low accuracy of the analysis 8OCAC makes it impossible to tell whether disorder is present in that case also. Comparable patterns of bond angles are found in the three more accurate structures with O(1)-C(1)-C(2) uniformly $>$ 120° and O(2)-C(1)-C(2) uniformly $<$ that value. The mean C—O bond length of 1.267(9) Å may be compared with the mean value of 1.271 Å found for the correspondingly disordered crystals of the *p*-n-alkoxybenzoic acid series.[2]

The O···O separations in the hydrogen bonds are: 2.645 Å in 2OCAC; 2.570 and 2.620 Å in 4OCAC; 2.634 Å in 6OCAC; and 2.58 Å in 8OCAC. All are typical values for such a system.[2]

(*b*) *Ethylenic linkages: C*(*1*), *C*(*2*), *C*(*3*), *C*(*4*) None of the individual bond lengths in the three accurately determined structures differ significantly from the corresponding mean values: C(1)-C(2) 1.464 Å, C(2)-C(3) 1.324 Å, and C(3)-C(4) 1.453 Å; which are unexceptional for such a system. The

TABLE VII

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

	2OCAC	4OCAC		6OCAC	8OCAC
Bond		A	B		
C(1)-O(1)	1.246(5)	1.264(3)	1.266(3)	1.267(4)	1.31(1)
C(1)-O(2)	1.273(5)	1.275(3)	1.269(3)	1.272(4)	1.25(1)
C(1)-C(2)	1.458(5)	1.462(3)	1.474(3)	1.463(4)	1.45(2)
C(2)-C(3)	1.325(5)	1.327(3)	1.324(3)	1.321(4)	1.35(3)
C(3)-C(4)	1.461(5)	1.452(3)	1.450(3)	1.450(4)	1.47(2)
C(4)-C(5)	1.380(6)	1.402(3)	1.399(4)	1.385(4)	1.41(2)
C(4)-C(9)	1.387(6)	1.388(3)	1.390(3)	1.395(4)	1.37(2)
C(5)-C(6)	1.363(6)	1.365(3)	1.371(3)	1.346(4)	1.32(2)
C(6)-C(7)	1.368(6)	1.388(3)	1.384(3)	1.386(4)	1.35(2)
C(7)-C(8)	1.387(6)	1.385(3)	1.388(4)	1.361(5)	1.38(2)
C(8)-C(9)	1.403(7)	1.385(4)	1.383(3)	1.382(4)	1.50(2)
C(7)-O(3)	1.436(5)	1.356(3)	1.358(3)	1.367(4)	1.53(3)
O(3)-C(10)	1.355(6)	1.434(3)	1.438(3)	1.419(4)	1.33(3)
C(10)-C(11)	1.497(6)	1.514(4)	1.500(4)	1.575(6)	1.51(3)
C(11)-C(12)	—	1.492(4)	1.507(4)	1.418(6)	1.52(3)
C(12)-C(13)	—	1.524(5)	1.514(4)	1.556(7)	1.53(4)
C(13)-C(14)	—	—	—	1.450(7)	1.57(3)
C(14)-C(15)	—	—	—	1.472(8)	1.51(3)
C(15)-C(16)	—	—	—	—	1.53(4)
C(16)-C(17)	—	—	—	—	1.51(4)

	2OCAC	4OCAC		6OCAC	8OCAC
Angle		A	B		
O(1)-C(1)-C(2)	123.7(4)	122.4(3)	123.4(3)	122.4(3)	120.5(10)
O(1)-C(1)-C(2)	119.9(4)	119.8(2)	119.8(2)	121.1(3)	118.1(10)
O(2)-C(1)-C(2)	116.4(4)	117.8(3)	116.8(3)	116.4(3)	121.3(10)
C(1)-C(2)-C(3)	122.7(4)	122.2(3)	123.9(3)	122.4(3)	122.5(10)
C(2)-C(3)-C(4)	127.6(4)	128.3(3)	126.7(3)	127.8(3)	124.4(10)
C(3)-C(4)-C(5)	122.8(4)	122.8(2)	123.4(2)	122.4(3)	122.1(10)
C(4)-C(5)-C(6)	122.7(4)	121.4(2)	121.4(3)	122.6(3)	123.0(12)
C(3)-C(4)-C(9)	120.3(4)	120.2(2)	119.9(2)	121.2(3)	115.9(11)
C(5)-C(6)-C(7)	120.0(4)	120.7(3)	120.7(3)	120.0(3)	115.9(12)
C(6)-C(7)-C(8)	120.3(4)	119.4(3)	119.6(3)	119.8(3)	127.3(13)
C(5)-C(4)-C(9)	116.9(4)	117.1(2)	116.7(2)	116.5(3)	122.7(12)
C(6)-C(7)-O(3)	113.6(4)	115.2(2)	115.5(2)	114.6(3)	114.4(11)
C(8)-C(7)-O(3)	126.1(4)	125.4(2)	124.9(2)	125.6(3)	118.2(12)
C(7)-C(8)-C(9)	118.5(4)	119.3(3)	118.8(3)	119.7(3)	116.0(12)
C(8)-C(9)-C(4)	121.6(4)	122.2(3)	122.8(3)	121.5(3)	115.0(13)
C(7)-O(3)-C(10)	115.9(4)	119.0(2)	118.5(2)	119.0(3)	128.9(14)
O(3)-C(10)-C(11)	106.7(5)	106.5(2)	107.9(2)	104.0(3)	109.0(16)
C(10)-C(11)-C(12)	—	112.3(3)	112.4(3)	113.7(4)	113.7(17)
C(11)-C(12)-C(13)	—	112.7(3)	113.8(3)	110.5(5)	115.3(19)
C(12)-C(13)-C(14)	—	—	—	114.0(5)	114.8(18)
C(13)-C(14)-C(15)	—	—	—	113.8(5)	109.3(19)
C(14)-C(15)-C(16)	—	—	—	—	109.9(18)
C(15)-C(16)-C(17)	—	—	—	—	113.1(24)

TABLE VIII

Equations of selected least-squares mean planes

Compound	Plane	*a*	*b*	*c*	*d*	Δ_{ave}	Δ_{max}
2OCAC	1	−0.51310	0.07928	0.85466	−0.02069	0.001	0.003
	2	−0.47323	0.05484	0.87923	−0.01653	0.002	0.002
	3	−0.49939	0.05617	0.86455	−0.12197	0.002	0.004
	[a]4	−0.49728	0.04198	0.86657	−0.21828	—	—
	5	−0.49734	0.06545	0.86508	−0.04454	0.019	0.045
4OCAC (A)	1	−0.67159	−0.51638	0.53134	1.02171	0.002	0.004
	2	−0.66946	−0.57205	0.47390	0.89960	0.010	0.012
	3	−0.65608	−0.63026	0.41513	0.96302	0.000	0.000
	4	−0.70131	−0.58355	0.40944	0.15971	0.010	0.010
(B)	1	−0.69992	−0.52242	0.48702	0.76034	0.002	0.003
	2	−0.70153	−0.50548	0.50234	0.80699	0.000	0.000
	3	−0.68260	−0.44197	0.58199	1.09323	0.001	0.001
	4	−0.68946	−0.55426	0.46630	0.48850	0.024	0.024
	[b]5	−0.68870	−0.55951	0.46112	0.55803	0.135	0.307
6OCAC	1	0.35952	−0.84310	0.39991	0.05843	0.004	0.009
	2	0.29008	−0.88544	0.36310	0.11502	0.007	0.008
	3	0.29880	−0.88057	0.36785	0.07884	0.002	0.003
	4	0.29439	−0.88144	0.36933	0.08795	0.011	0.021
	5	0.30228	−0.87261	0.38364	0.11763	0.021	0.093
8OCAC	1	−0.98050	−0.08282	0.17820	−0.08895	0.013	0.026
	2	−0.97371	−0.09452	0.20724	−0.08305	0.022	0.023
	3	−0.95829	−0.08671	0.27231	0.21317	0.017	0.028
	4	−0.94431	−0.03755	0.32691	1.00584	0.038	0.085
	5	−0.96644	−0.03711	0.25421	0.25319	0.136	0.280

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 unit cell origin. The conversion matrices are:

2OCAC:	9.11100	0.00000	0.00000	*4OCAC:*	14.68620	0.00000	0.00000
	−0.76897	7.64402	0.00000		−4.86524	10.66872	0.00000
	−0.31061	−1.01740	7.20348		−1.26286	−0.57921	7.63786
6OCAC:	25.86500	0.00000	0.00000	*8OCAC:*	20.19850	0.00000	0.00000
	0.00000	7.49900	0.00000		−1.31001	7.56451	0.00000
	−2.82953	0.00000	14.88627		−1.53068	−1.12886	5.33800

The planes are as follows:

(1) O(1), O(2), C(1), C(2)
(2) C(1), C(2), C(3), C(4)
(3) C(4), C(5), C(6), C(7), C(8), C(9)
(4) The atoms of the chain excluding O(3)
(5) The complete monomer

[a] Includes O(3).

[b] Plane of the dimer.

angles C(2)–C(3)–C(4) are markedly greater than 120°, with a mean value of 127.6(6)°. This opening is again characteristic of cinnamic acid derivatives and is due, in part, to repulsions between H(2) and H(5). The repulsion is particularly severe for the mesogenic cinnamic acids thus far studied, where there is only a small angle between the planes of the ethylenic groups and those of the phenyl rings, but it is also present in systems where that dihedral angle is much larger.[11] The plane of the ethylene group makes angles of +3.0, +4.6, +1.3, +5.1, and +1.9° with the plane of the carboxy group in 2OCAC, 4OCAC (A and B), 6OCAC, and 8OCAC, respectively. The angles between the ethylene plane and the phenyl ring planes for the same sequence are +1.7, −4.8, −5.9, +0.7, and −3.9°, yielding angles between the carboxy and phenyl planes of −1.7, −9.4, −5.9, −0.7, and +3.9°. The angle between the two carboxy planes in 4OCAC is 3.0°, between the two ethylenic planes 4.5°, and between the two phenyl planes 14.5°.

(*c*) *Phenyl rings* In the three accurately determined structures, and even in the less accurately determined 8OCAC, the shortest of the ring bonds, by a significant margin in most cases, is C(5)–C(6). This contraction is found in other alkoxyphenyl systems,[2] and is associated with the presence of the ether oxygen at C(7). An explanation in terms of inductive effects has been offered by Colapietro *et al.*,[13] which may also be invoked to account for the contraction of the endocyclic valence angle at C(4) from 120°. The rings are planar within the limits of error in each case.

(*d*) *Alkyl chains* The accuracy of determination of atomic positions in the chains is adversely affected in 6OCAC and 8OCAC by the very pronounced thermal vibrations of the chains in those two compounds, which are discussed below. The chain carbon atoms in 2OCAC are coplanar with the phenyl ring, and in the other acids they are in the all-*trans* extended conformation normally found in the solid state. In each case the plane of the chain carbon atoms makes only a small angle with the phenyl ring plane. These angles are +3.7° and +9.3° for monomers A and B of a 4OCAC, −0.2° for 6OCAC, and −4.3° for 8OCAC. The two alkyl planes in 4OCAC are inclined to one another at 3.7°. The overall coplanarity of chain and core residues in this series of acids is in sharp contrast to the *gauche* conformation about the $C(\alpha)-C(\beta)$ bond of the chain found for the *p*-n-alkoxybenzoic acids in the solid state[2] and in the smectic mesophase.[14]

(*e*) *Ether linkages* In 4OCAC and 6OCAC these show the normal pattern of O—C bond distances with O(3)—C(7) having a mean value of 1.360(8) Å and O(3)—C(10) a mean of 1.430(14) Å, both values typical of those found in other alkoxy systems. The reversal of this pattern in 8OCAC is without significance given the low accuracy of determination in that case, but the same reversal in 2OCAC, where the formal accuracy is much greater, is anomalous. The effect seems to be real and not simply due to a false minimum in the least-squares refinement as correction of the position of O(3) to produce the expected geometry is undone upon further refinement. There is an additional anomaly in that the equivalent isotropic B value of C(10) is greater than that for C(11), whereas the terminal atom would normally be expected to have the larger thermal motion. The presence of a 0.5 e peak in the final difference electron-density map, midway between C(8) and C(10) has already been mentioned, and the accumulation of these anomalies suggests the presence of some form of disorder in this part of the structure. Thin layer chromatography of the original sample fails to reveal any impurity present in sufficient quantity to account for the residual density and there is no evidence of translational disordering of the molecule in a direction parallel to its long axis, so that some form of radiation damage to the crystal seems to be the most probable explanation of these effects. Despite these anomalies, the expected distortions in the angles O(3)–C(7)–C(6) and O(3)–C(7)–C(8), caused by steric interactions between H(8) and the C(10) methylene protons, are present in this acid as in the other (excluding 8OCAC). The mean values for these two angles in the three crystals are 114.7(14)° and 125.5(9)°, comparable to those found in other alkoxyphenyl systems.[2]

Molecular packing

Despite the differences in unit cell sizes and shapes, the molecular packing arrangement in the four crystals is fundamentally the same, and of a type conducive to formation of a nematic phase on heating. Thus, in all four crystals the highly formanisotropic dimers are arranged in head-to-tail fashion in parallel staggered rows, and the efficiency of the molecular packing diminishes with increasing chain length in the same way as is found for the nematogenic members of the homologous series of *p*-n-alkoxybenzoic acids.[2] This drops in packing efficiency, which is presumably related to the fall in C → N transition temperature and enthalpy as the series is ascended, is seen in two ways. The first evidence is provided by the increment in crystal volume per CH_2 group as the chain length increases. In close-packed normal paraffins and aliphatic carboxylic acids the volume increment per additional CH_2 group in the crystal is about 23.4 $Å^3$,[15] and in the close-packed smectogenic *p*-n-alkoxybenzoic acids it is about 23.7 $Å^3$.[2] By contrast, the average increment per CH_2 group in this series is 27.3 $Å^3$. The individual increments are: $n = 2 \rightarrow 4$, 24.1 $Å^3$; $4 \rightarrow 6$, 30.8 $Å^3$; and $6 \rightarrow 8$, 23.4 $Å^3$; showing that the problem of accommodation the sterically disparate cores and chains becomes most acute at a chain length of six carbon atoms in this series, as compared to four in the *p*-n-alkoxybenzoic acids.[2] The second piece of evidence comes from the increasingly high amplitudes of thermal vibration executed by the chain atoms as chain length increases. The individual monomeric units of 2OCAC and 4OCAC (rather than the dimers) vibrate as essentially rigid bodies,[16] with fairly normal increases in vibrational amplitudes towards the extremities of the molecule. The major principal axes of the thermal ellipsoids are more or less normal to the molecular plane, the median axes in the plane and normal to the molecular long axis. The chain vibrational amplitudes for 6OCAC and 8OCAC, however, are abnormally large and do not show a regular increase from one end of the chain to the other, but rather behave as though one side of each chain was less tightly packed than the other. These disproportionately large thermal motions of the chains may be seen from Figures 1(c) and (d), where the atomic envelopes are drawn to indicate a 50% probability of containing the atomic center at any given instant. The envelopes for 8OCAC are sufficiently large that some disorder in the positions of the chain atoms may be present, although all the chain atoms appear as single peaks in an appropriate difference electron-density map. A closer analysis of the packing modes shows that what is evidently a highly favorable mode of side-by side packing of the cores is preserved to quite large chain length at the expense of very poor chain-chain interactions.

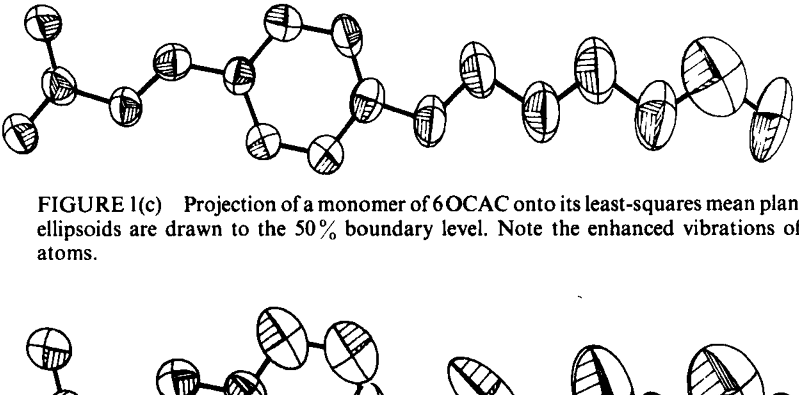

FIGURE 1(c) Projection of a monomer of 6OCAC onto its least-squares mean plane. Thermal ellipsoids are drawn to the 50% boundary level. Note the enhanced vibrations of the chain atoms.

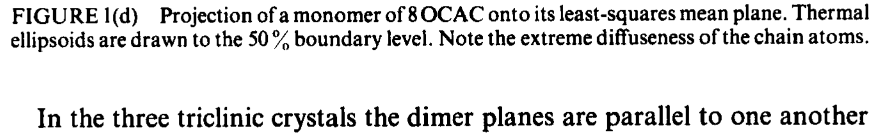

FIGURE 1(d) Projection of a monomer of 8OCAC onto its least-squares mean plane. Thermal ellipsoids are drawn to the 50% boundary level. Note the extreme diffuseness of the chain atoms.

In the three triclinic crystals the dimer planes are parallel to one another by the requirements of crystallographic symmetry, and in the monoclinic crystal of 6OCAC they make an angle of ±29.2° with the $y = 0$ plane. By viewing the molecular packing arrangement in projection onto the dimer planes the remarkable similarity in the side-to-side packing in all four crystals becomes apparent, with the centers of dimers in adjacent rows (alternate rows in 4OCAC) having almost the same vector relation in each case. Dimers related in this way form stepped-sheet elements in the triclinic crystals and form a pleated sheet element in 6OCAC. What is meant by a stepped-sheet element is best understood in terms of the detailed descriptions of the molecular packing given below. In simple terms, if the molecules are viewed in projection normal to their least-squares mean plane, they form a sheet in which the rows of dimers are arranged as a set of steps. The major differences in packing between the various crystals then lie in the way in which these sheets are stacked atop one another. In 2OCAC, 4OCAC, and 6OCAC the sheet elements are stacked so as to bring the chain ends of dimers in one sheet into contact with the hydrogen-bonded carboxy groups of dimers in the next. In 8OCAC, on the other hand, the phenyl rings of dimers in one sheet lie above the carboxy groups of dimers in the next and a degree of interdigitated three-dimensional chain packing emerges, albeit of a very loose type.

The various arrangements are shown in Figure 2–7. Figures 2, 3, and 7 are projections onto the least-squares mean planes of the dimers whereas the other figures are normal axial projections or partial projections.

2OCAC The arrangement of parallel staggered rows of dimers in a stepped-sheet element in this crystal is shown in Figure 2. Within a row dimers are related by centers of symmetry at translational displacements of 2*a*, 3*b*, *c*. The vertical displacement from the center of one dimer to that of the next along a row is 0.12 Å, the center to center distance being 27.85 Å. The centers of dimers in adjacent rows are related by unit translation in *b*. For purposes of comparison it is useful to express this row-to-row displacement in terms of components with respect to the molecular axes. The centers are separated by 5.5 Å in a direction parallel to the row axes (longitudinally), by 5.1 Å in a direction normal to the row axes (laterally), and by 0.9 Å in a direction normal to the dimer planes (vertically). The gaps between the chain ends of neighboring dimers within a row have an approximate steric equivalence with the hydrogen-bonded carboxy groups, in the way in which they both flank phenyl groups in adjacent rows.

Identical stepped-sheet elements are stacked atop one another by unit translations in both *a* and *b* to give a perpendicular separation of dimer planes of 3.52 Å, comparable to that found in *p*-methoxycinnamic acid and 0.1 Å greater than the minimum van der Waals separation of pair of phenyl rings. A dimer in a lower layer is indicated in Figure 2 in the upper left-hand corner. The sterically thickest ethyl residues ($r = 2.0$ Å) are placed directly above the sterically thinnest hydrogen-bonded carboxy residues ($r = 1.4$ Å) and the phenyl rings are superimposed above and below the ethylenic

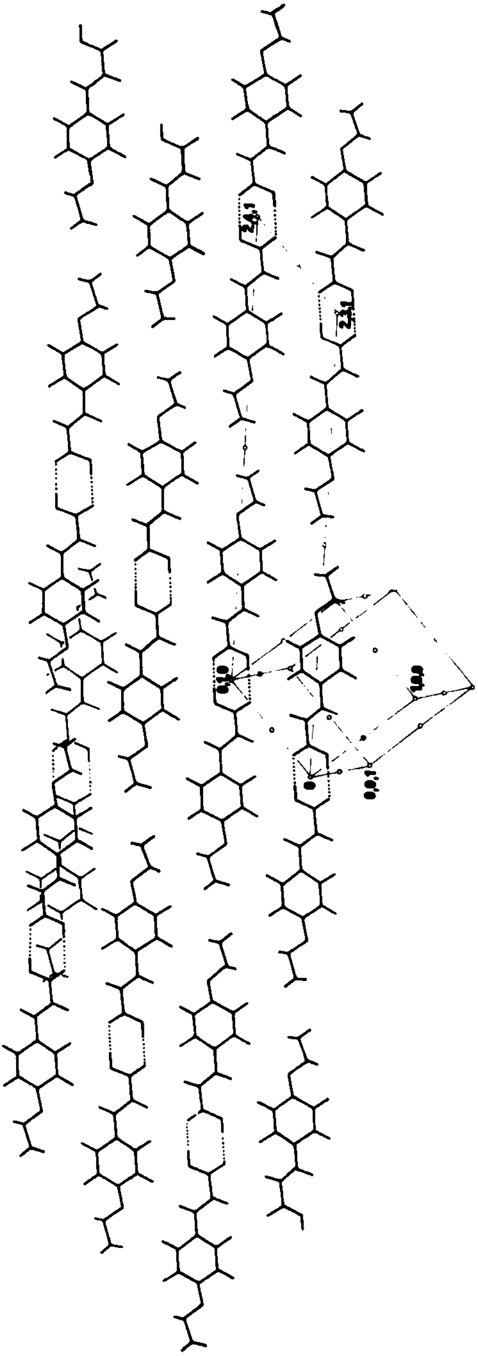

FIGURE 2 A stepped-sheet element in the crystal of 2OCAC seen in partial projection onto the dimer least-squares mean plane.

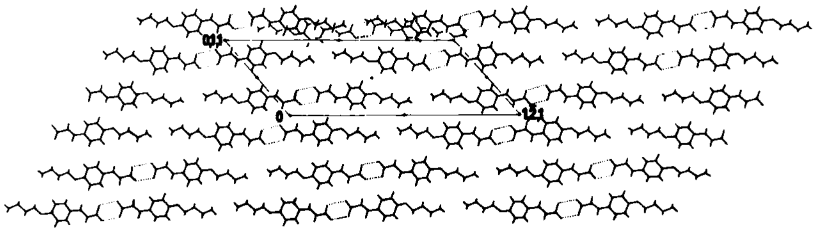

FIGURE 3 A stepped-sheet element in the crystal of 4OCAC seen in partial projection onto the dimer least-squares mean plane.

residues of neighbors. The high overall packing efficiency in this crystal is attested to by the high C → N transition temperature of 467 K.

4OCAC Dimers within a given row in this crystal succeed one another by translational displacements a, $-2b$, c yielding a repeat distance of 32.8 Å, with a vertical displacement from the plane of one dimer to the next along the row of 0.4 Å. The dimers themselves have no formal symmetry, though they approximate a centrosymmetric shape. Pairs of dimers are related by the space group centers of symmetry at 0, 0, 0 and 0, $\frac{1}{2}$, $\frac{1}{2}$ to complete the stepped-sheet element shown in Figure 3. The mutual arrangement of rows related by the first of these centers of symmetry is very similar to that found in 2OCAC. The longitudinal displacement of dimer centers in these adjacent rows is 4.8 Å, the lateral displacement 5.5 Å, and the vertical displacement 1.1 Å. For rows related by the second set of centers these displacements are 14.2, 4.6, and 1.3 Å, respectively. The relationship of a dimer in a lower sheet to those in the main sheet is shown at the top of Figure 3. The sheets are related by unit translation in b.

6OCAC A sheet of molecules related by the space group c-glide operation in the plane at $y = 0$ is seen in b-axis projection in Figure 4. The dimer long axes, defined arbitrarily as the line C(15)...C(15′) make an angle of 88.7° with b and the dimer planes are inclined at $\pm 29.2°$ to the $y = 0$ plane. Within a given row dimers are related by the space-group two-fold axes at

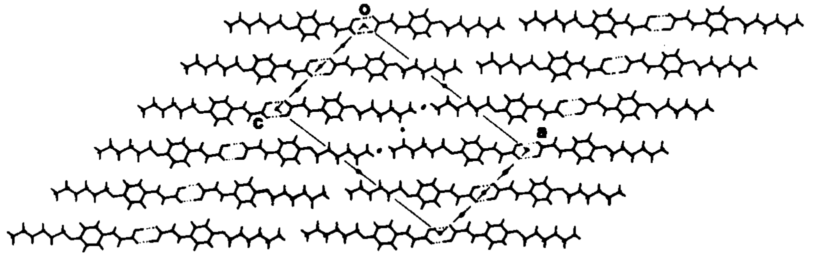

FIGURE 4 A sheet element in the crystal of 6OCAC seen in partial projection down b.

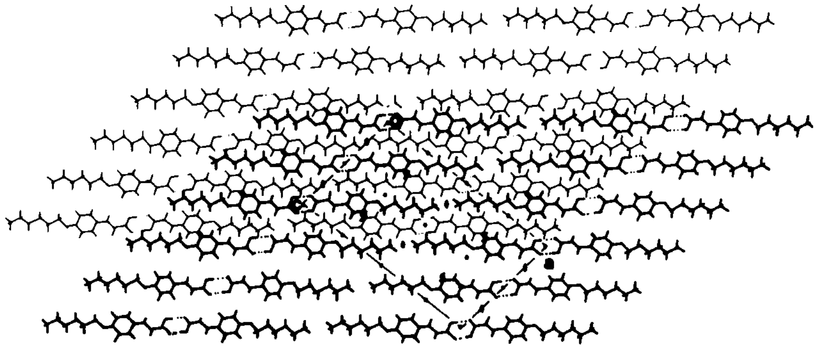

FIGURE 5 Superimposed sheet elements in the crystal of 6OCAC seen in projection down *b*.

a/2, leading to a translational repeat along the row of 37.5 Å. Dimers in adjacent rows are related by the two-fold axes having a *c*/4 component and by the centers of symmetry having an *a*/2 component. With reference to the $y = 0$ plane, the longitudinal displacement of dimer centers in adjacent rows is 5.6 Å, the lateral displacement is 5.1 Å, and the vertical displacement is 0.0 Å. With retention of this center-to-center relation between adjacent dimers and with the extension of the chain to six carbon atoms, there is now a perceptible layering of the dimers within a sheet with a fair amount of chain-chain interactions present. However, as may be seen from Figure 5 which shows the stacking of sheets produced by the *C*-face centering operation of the space group, there is no three-dimensional layering or packing of chains. Instead the *a*/2 component of the centering gives exact head-to-middle staggering of rows parallel to *b*, with the chain ends of the dimers in one sheet being again packed around the hydrogen-bonded carboxy groups of dimers in the neighboring sheets.

8OCAC The packing arrangement in this structure may be seen from Figures 6 and 7. Figure 6 is a projection down the *c*-axis of the triclinic cell

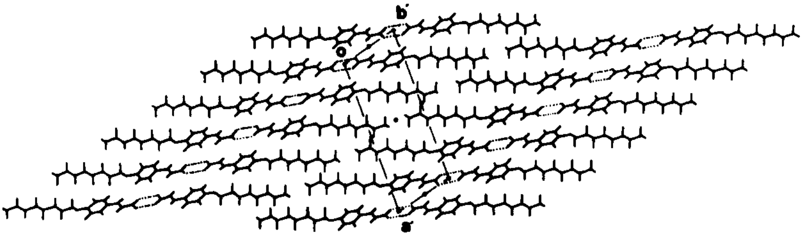

FIGURE 6 Projection of the structure of 8OCAC drawn in *c*-axis projection. Hydrogen atoms have not been located and are drawn in idealized positions.

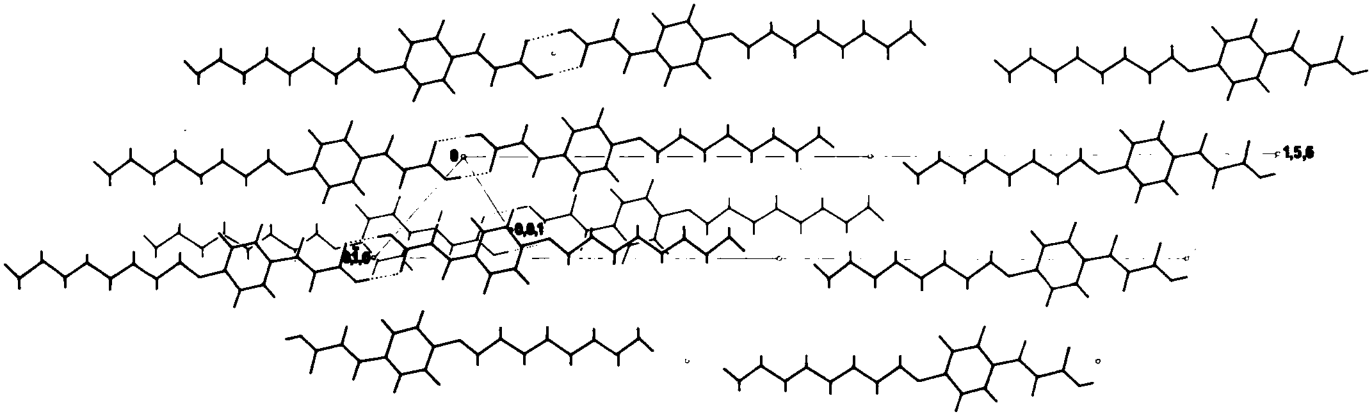

FIGURE 7 A stepped-sheet element of the crystal of 8OCAC seen in partial projection onto the dimer least-squares mean plane. Hydrogen atoms are drawn in idealized positions.

and shows that with the extension of the chain length to eight carbon atoms there is now a recognizable segregation of the dimers into a highly tilted layer structure. Mutual interaction between the dimers in this structure are, however, quite weak as is shown by the generally high thermal parameters for the crystal, particularly for the chain atoms. With the layer being so weakly defined in the crystal, it is not surprising that this crystal passes to a nematic phase rather than a smectic and Figure 7, a projection onto the least-squares mean plane of the dimers, emphasizes the parallel row character of the structure. The degree of staggering of rows, both within and between the stepped sheet elements, is not well marked, however, and it is interesting to note that, in keeping with the progressive tendency towards layering in the crystal structures, the smectic phase in this series makes its first appearance with a chain length of nine carbon atoms, only one more than is present here.

Dimers within a row are related by translations of *a*, 5*b*, and 6*c*, giving a repeat distance between centers of 44.9 Å and a vertical displacement of 0.3 Å. There is an unexpectedly large gap between the ends of dimers within a row, which may be produced by the exigencies of intersheet packing, and there is a wide lateral separation between chains of dimers in the same sheet element. Both these features are consistent with the abnormally large amplitudes of thermal vibration observed for the chain atoms. Dimer centers in adjacent rows within the sheet element are related by unit translations in *b*, corresponding to longitudinal, lateral, and vertical displacements of 5.1, 5.6, and 0.9 Å, respectively. Stacked sheets are related by translation of $-b$, c, giving an interplanar separation of 3.6 Å.

It seems reasonably clear that the particular side-by-side packing of the dimer cores found in these four crystal structures is energetically very favorable, as it is retained with increasing chain length to a point where a considerable sacrifice is being made in terms of chain-chain interactions. One may speculate that with the transition to smectic properties taking place with a chain length of nine carbon atoms, a rather different packing mode may be expected for the higher homologs which will place an increased importance on optimizing chain packing. We have earlier discussed[2] the problems of steric incompatibility between the molecular cores and chains in the alkoxybenzoic acids, and have pointed out that a new type of crystal structure emerges in that series at the point where smectic properties make their appearance. In those structures the problem of packing is resolved by adopting a crystal structure in which chains and cores are segregated in a stratified layer arrangement made possible by adoption of a *gauche*-conformation about the C(α)–C(β) bond of the chain. It is possible that a similar solution is adopted in this series by the higher homologs, which might allow retention of the otherwise favorable side-by-side core packing. Clarification of this point must await the necessary structure determinations.

Acknowledgments

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