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Molecular Arrangement in Mesophases of Some *p*-*n*-Alkoxybenzoic Acids

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The properties of an even homologous series of alkoxy benzoic acids have been investigated in the crystalline and mesomorphic states by means of thermal microscopy, x-ray scattering and dilatometry.

Structural parameters such as inter-lamellar distance d, and the molar volume V_m were studied as a function of the number n of methylene units of the alcoxy radical.

In the crystalline state and the smectic C state the variation of d and of V_m with n is perfectly linear. The angle of tilt of the paraffinic chains α' and of the aromatic stems ϕ was determined in the crystalline state. It was found that both moieties have the same magnitude of the tilt. In the smectic C state the value of α' was found to be 25° as compared to 60.7° in the crystalline state indicating a "pulling up" of hydrocarbon tails when passing from the crystalline state to the smectic state. The passage from crystalline into the smectic state is also accompanied by a strong increase in V_m. Analysis of data indicates that this increase is entirely due to the aromatic part of the molecule while the aliphatic chains have the same V_m as in the crystalline state. It is concluded that while in the crystalline state the cohesion of the phase is insured to a large extent by dimerized, hydrogen bonded molecules, in the smectic C state the cohesion is insured by attraction between extended aliphatic chains. Evidence is also given for the formation of cybotactic groups in the nematic phase of octyloxy benzoic acid.

INTRODUCTION

The mesomorphic properties of *p*-*n*-alkoxybenzoic acids have been investigated by several authors.[1,2] It is known that *p*-*n*-alkoxybenzoic acids containing alkoxy groups with the number of carbon atoms $n > 3$ are characterized by enantiotropic mesophases; nematic for $n < 7$; nematic and smectic for $n \geq 7$. The smectic phases of *p*-*n*-alkoxybenzoic acids are "Smectic C" phases, i.e., with a structure in which molecules, are tilted with respect to the plane of the molecular stratum. In most of the structural studies of such phases the molecular arrangement is considered in terms of dimerized coplanar rigid molecules of *p*-*n*-alkoxybenzoic acid, in which the aromatic and aliphatic moieties are parts of a linear entity tilted about the normal to the stratum by an angle α, Such approach is justified for rod-like, rigid molecules such as, for example the Di-4, 4'azoxycinnamicacidbismethyl ester[3] or 4'-methoxybiphenyl, 4-carboxylic acid.[4] For higher homologues of alkoxybenzoic acids, with two moieties, one rigid, polar and aromatic, the other flexible and non polar, the concept of a linear molecule becomes questionable. In fact, one can expect "a priori" the two moieties, because of varying geometries and interaction forces, to assume different tilts. This has been very recently shown to be the case for the smectic C phases of 4-4'bis(*p*-*n*-alkoxybenzylideneaminobiphenyl) in which the alkoxy chain and the aromatic moiety assume different tilt angles.[5]

In this paper we are discussing some preliminary structural data obtained from low angle X-ray diffraction for a series of alkoxybenzoic acid with an even number of carbon atoms ranging from $n = 8$ to $n = 18$ in the methylene chain.

EXPERIMENTAL

All *n*-alkoxybenzoic acids with the exception of octyloxybenzoic acid were synthesized according to a Schotten–Bauman Procedure and described elsewhere.[7] In all cases alkliodides were condensed with the hydroxybenzoic acid at pH $\simeq 8$ in presence of potassium hydroxide. The products were recrystallized twice from glacial acetic acid, methanol, benzene and acetone respectively. The octyloxybenzoic acid purchased from Frinton Laboratories was purified by customary recrystallizations.

X-ray diffraction patterns were obtained with a flat plate low angle camera (Warhus) provided with a sample heater and mounted on a Norelco generator. (Ni filter, Cu radiation). The sample holder consisted of three brass rings of approximately 2 mm thickness and 1 cm. diameter. One end of the center ring was sealed with mica. The powder was placed in the sealed ring, heated and then cooled. This procedure was repeated until the powder was tightly packed. The other end of the center ring was then sealed with mica. A ring was placed on each side of the center ring and all three rings were tightened by means of screws. The assembled cell was placed in the camera mounted furnace at the desired temperature. The temperature was controlled to within one degree. X-ray data were supplemented by D.S.C., Polarizing microscopy and dilatometry measurements.

Phase transition temperatures were determined by means of differential scanning calorimetry (Perkins Elmer DSC-1B) and hot stage polarizing microscopy (Leitz–Ortholux Microscope with a Mettler hot stage).

The dilatometric measurements were obtained as described in Ref. 5.

RESULTS AND DISCUSSION

Table I and Figure 1 give the transition temperatures as a function of n, obtained by D.S.C. in agreement with thermal microscopy. The transition temperatures for $n = 6$ and $n = 7$ have been taken from Ref. 6 and plotted on Figure 1 together with our data. The existence of a narrow range nematic phase for $n = 14$ which can be anticipated from Figure 1, has not been confirmed experimentally and is therefore absent in Table I.

TABLE I

DSC phase transition temperatures of p-n-alkoxybenzoic acids

	Transition temp. °C			
Alkoxybenzoic acid	Cr/Sm	Sm/Ne	Ne/Is	Sm/Is
Octyloxy B.A.	99	105	148	—
Decyloxy B.A.	94.5	123.5	144	—
Dodecyloxy B.A.	90.5	132	140	—
Tetradecyloxy B.A.	96	—	—	136
Cetyloxy B.A.	98	—	—	133
Octadecyloxy B.A.	102	—	—	130

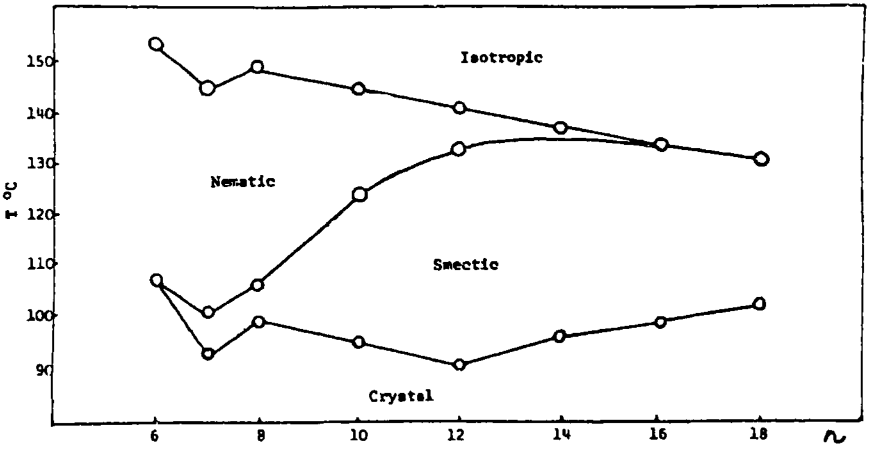


FIGURE 1 Transition temperatures vs. no. of carbon atoms of the paraffinic moiety in p-n-alkoxybenzoic acids.

A typical dilatometric curve is given in Figure 2. Good agreement was found between the transition temperatures obtained by different techniques.

The combination of data on interlamellar distance d (obtained directly from x-ray scattering) and of the molar volume V_m (obtained from dilatometry) gives the average area occupied by a dimerized molecule:

$$S = 2V_m/N_A d \tag{1}$$

where N_A is Avogadro's number.

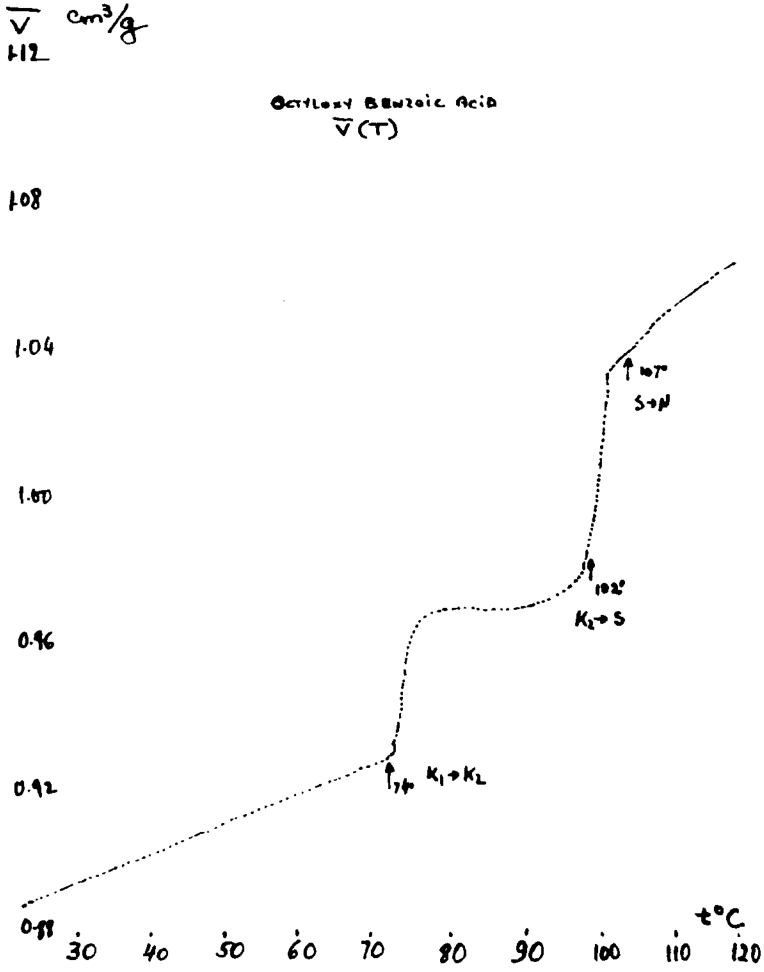


FIGURE 2 A typical dilatometric curve v versus t °C (for the octyloxybenzoic acid).

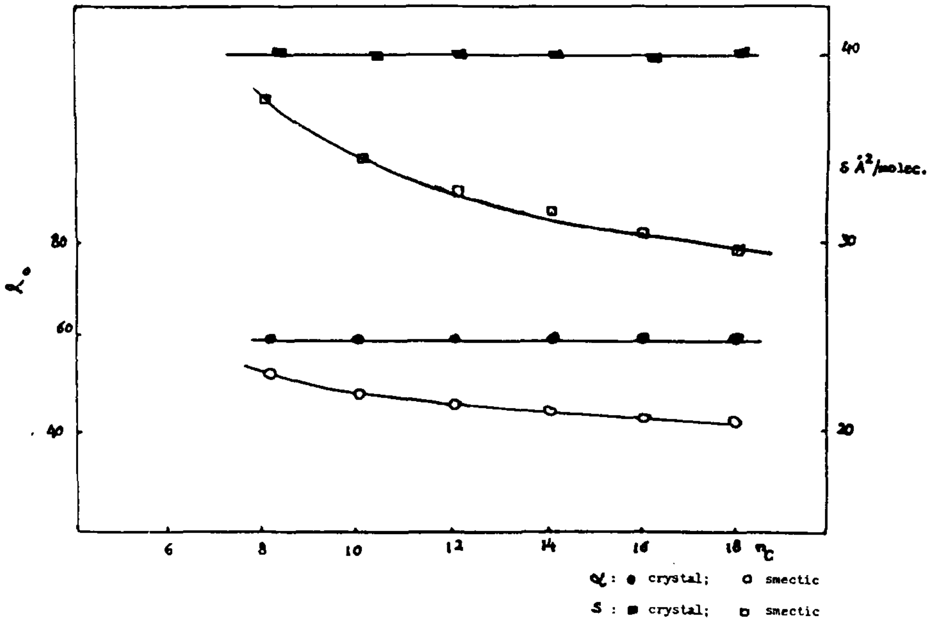


FIGURE 3 The overall tilt α and molecular areas *S* versus the number of carbon atoms of the paraffinic moiety.

Figure 3 illustrates the variation of α the overall tilt which is given by $d = 1 \cos \alpha$ (where l is the overall length of a dimerized molecule of alcoxybenzoic acid in which the aliphatic chain is in the extended planar zig-zag conformation). Figure 3 also illustrates the variation of *S* as a function of *n*. It can be seen that in the crystalline state (25°C) α and *S* do not change with *n*. In contrast in the smectic state both α and *S* decrease as *n* increases.

Crystalline state

Figure 4 gives the variation of the lamellar thickness *d* with the number of carbon atoms in the aliphatic chain of the *n*-alcoxybenzoic acid. One can see that in the crystalline state the data fit a perfect straight line. The extrapolation to $n = 0$ of this line gives the portion of the interlamellar spacing due to the rigid dimerized aromatic moieties $d^{(n=0)}$. This value is $d^{(n=0)} =$ 8,5 Å, Table II gives the important characteristics of the alcoxybenzoic acids in the crystalline state at 25°C. The average area per molecule *S* given in column 5 is constant and so is the overall tilt angle α. The crossectional area per molecule $Sc = S \cos \alpha$ (column 7, Table II) is 20 Å^2 a value very close to the crossection of an extended hydrocarbon chain. The linear variation of

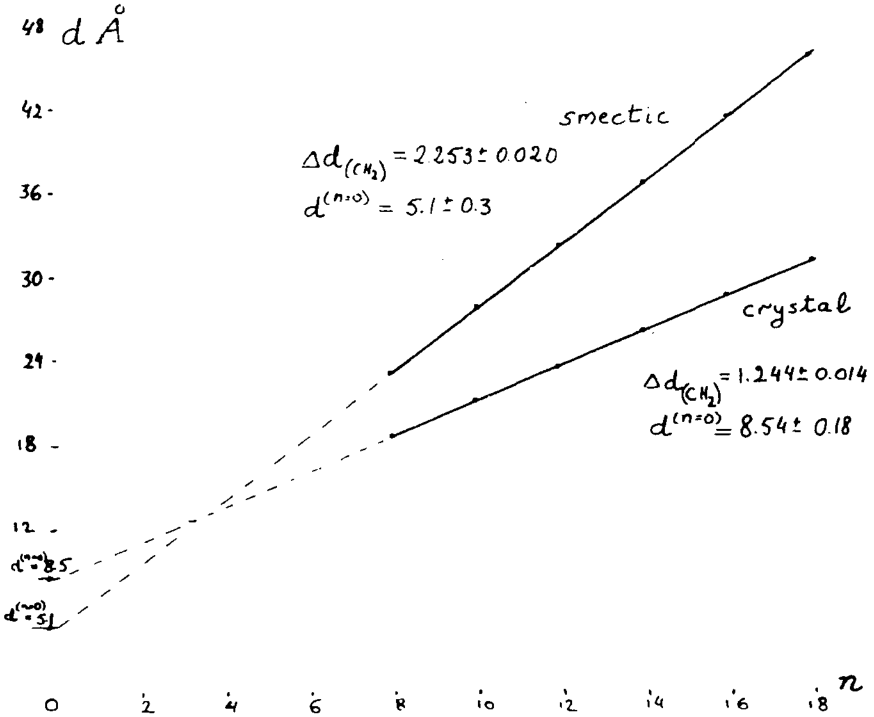


FIGURE 4 The low angle X-ray spacing d as a function of the number of methylene groups in the alcoxybenzoic acids.

TABLE II

Structural parameters of n-alcoxybenzoic acids in the crystalline state

1	2	3	4	5	6	7
n	d, Å ± 0.1	$\bar{V}\ \frac{\text{cm}^3}{\text{g}}$	$V_m\ \frac{\text{cm}^3}{\text{mole}}$	S Å^2 ± 0.2	α	Sc, Å^2 ± 0.2
8	18.5	0.89	223	40	59.8	20.1
10	21.1	0.908	253	40	59.5	20.1
12	23.4	0.910	282	40	59.8	20.1
14	25.8	0.934	312	40	60.0	20.0
16	28.5	0.946	342	40	59.8	20.1
18	31.0	0.953	372	40	59.8	20.2
0	$d_{n=0} = 8.44$		103.8			

$d(n)$ (Figure 4) allows for the calculation of the tilt of the paraffinic tails and of the aromatic stems ϕ with respect to the normal to the layers. From the slope of $d(n)$ (1.24 Å) and the known length of one zig-zag (2.54 Å) in paraffin chain, one can get $\cos \alpha' = 1.24/2.54 = 0.49 \pm 0.01$ and $\alpha' = 60.7 \pm 1°$. The tilt of the aromatic moiety ϕ can be obtained similarly by dividing $d_{n=0}$ by the length of the dimerized aromatic part $l_a \approx 16.4$ Å (calculated from interatomic distances and bond angles). $\cos \phi = 8.54/16.4 = 0.521$, making $\phi = 58.6 \pm 1°$.

The magnitude of the tilt is therefore very similar for both moieties in the crystalline state.

The smectic phase

Table III gives the structural properties and conformational parameters of alcoxybenzoic acids in the smectic state. It is considered here that the dispersion of the temperatures in the smectic phases (see column 2 Table III) does not significantly affect the value of d.

One can see in Table III that in contrast to the crystalline state, in the smectic state the overall angle of tilt defined by $d = l \cos \alpha$ (where l is the Van der Waals length of the dimerized molecule) changes from 51.5° for $n = 8$ to 42.4° for $n = 18$. While the overall area per dimerized molecule S (column 6) decreases from 37.6 Å^2 to 29.8 Å^2. The crossectional area per dimerized molecule $S_c = S \cos \alpha$ (column 10) remains constant as it should. This does not mean necessarily that the angles α' and ϕ of the aliphatic and aromatic moieties do vary with n since from purely geometrical considerations, one would expect α to decrease when the length of the paraffinic moiety increases (Figure 5). This suggests, however, that unlike in the crystalline state, α' and ϕ assume different values.

TABLE III

Structural parameters of n-alcoxybenzoic acids in the smectic C state

1	2	3	4	5	6	7	8
n	t, °C	d, Å ±.5	$\bar{V}\ \frac{\text{cm}^3}{\text{g}}$	$V_m\ \frac{\text{cm}^3}{\text{mole}}$	S Å^2 ±1	$\alpha°$ ±3	Sc, Å^2 ±1
8	105	22.9	1.04	260	37.6	51.5	23.5
10	100	27.8	1.046	291	34.5	48.0	23.5
12	98	32.3	1.046	320	32.8	46.2	22.7
14	104	36.6	1.047	350	31.7	44.8	22.5
16	104	41.1	1.051	380.5	30.6	43.5	22.5
18	108	45.6	1.057	410.0	29.8	42.4	22.5
0		$d_{n=0} = 5.1$		140.5			

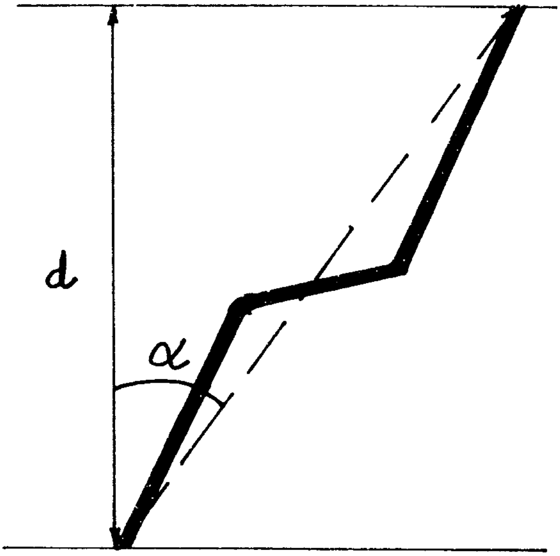


FIGURE 5 Schematic sketch defining the "overall tilt angle α" in the smectic state.

We can also see from figure 4 that d is a perfectly linear function of n with $d^{(n=0)} = 5.1 \pm 0.3$ Å and slope 2.25 ± 0.02 Å and so is $V_m(n)$ (Table III, Figure 6) with $V_m^{(n=0)} = 140.5 \pm 0.7$ cm^3/mole.

This remarkable linearity of both $V_m(n)$ and $d(n)$ in the smectic state allows a meaningful extrapolation to $n = 0$, (see Figures 4, 6 and Column 3 and 5, Table III). One should notice the very significant increase of $V_m^{n=0}$ from 103.8 cm^3/mole in the crystalline state to 140.5 cm^3/mole in the smectic state.

The smaller value of $d^{(n=0)}$ of 5.1 Å than the corresponding value in the crystalline state of 8.5 Å suggests a stronger tilt of the aromatic stems in the smectic state. This will be considered in more detail below.

Table IV and Figure 6 give the molar volumes of the aliphatic moiety in the crystalline and smectic states as a function of n. One can see that the molar volumes of the aliphatic moiety is, within the experimental error, the same in the crystalline as in the smectic state. This indicates that the conformation of the paraffinic tails does not significantly differ in both states. One can also see (Table III, column 8) that the value of the molecular crossection S_c is only slightly larger in the smectic state than in the crystalline state (22.5 Å^2 vs. 20.0 Å^2). It is, therefore, not unreasonable to expect the paraffinic chains of the alkoxybenzoic acids to assume extended conformations in the smectic C state. This is in agreement with literature in which extended conformations of paraffinic tails in smectic phases have been described for thallium stearate[8] and for 4-heptyloxybenzal, 4'ethylaniline.[9]

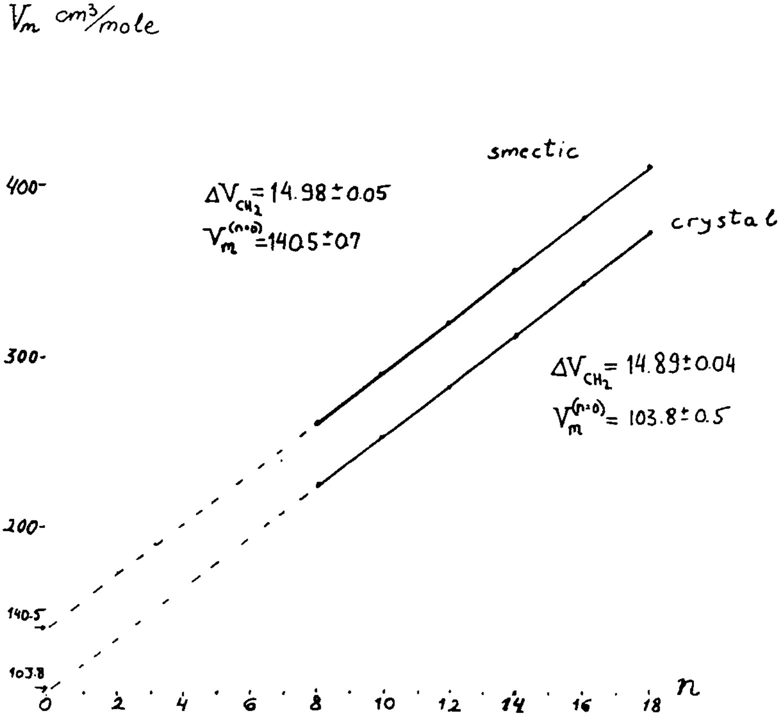


FIGURE 6 Molar volume as a function of the number of methylene groups in the alkoxybenzoic acids.

TABLE IV

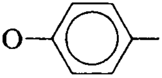
Molar volumes of the aliphatic moiety (n cm³/mole) of alcoxybenzoic acids in the crystalline and the smectic states

	Crystalline state			Smectic state		
n	V_m	$(V_m - V_m^{n=0})$	$(V_m)_{CH_2}$	V_m	$V_m - V_m^{n=0}$	$(V_m)_{CH_2}$
8	223	119.2	14.90	260	119.5	14.94
10	253	149.2	14.92	291	150.5	15.00
12	282	178.2	14.85	320	179.5	14.96
14	312	208.2	14.87	350	209.5	14.96
16	342	238.2	14.89	380.5	240.0	15.00
18	372	268.2	14.90	410.0	269.5	14.97
0	103.8			140.5		

The calculated value of the contribution to the molar volume of paraffinic chains composed of methylene units is 15 cm^3/mole of methylene units. This value is somewhat lower than the value of 16.1–16.5 cm^3/mole of methylene units given for liquid paraffins in the literature of Ref. 10. The molar volume of the aromatic stem $V_m^{(n=0)}$ passes from 103.8 cm^3/mole in the crystalline state to 140.5 cm^3/mole in the smectic C state. The increase of 36.7 cm^3/mole suggests a dramatic gain of mobility of the aromatic moiety in the smectic state. This result is difficult to reconcile with the concept of a rigid hydrogen bonded "three-ring" structure adopted widely for smectic phases of alcoxybenzoic acids. It suggests a rather considerable weakening of the hydrogen bonded dimerized structure. In a recent publication, Ikeda and Hatakayama[11] have reported a drastic decrease in hydrogen bonding of *p,n*-octyloxybenzoic acid in the smectic C state. These authors claim (on the basis of analysis of IR spectra) that 75% of hydrogen bonds, prevalent in the crystalline state, are destroyed in the smectic C state. These findings, like ours, seem to point in the direction of a profound change in the conformational state of the aromatic stem in the smectic state. This does not mean, however, that the concept of lamellar double layers of molecules of alcoxybenzoic acid is not correct. Residual hydrogen bonding and dipolar forces may still provide sufficient cohesion to consider the aromatic part of the double layer as one stem.

As in the crystalline state, the linearity of $d(n)$ allows the calculation of the angle of tilt α' of the paraffinic tails in the smectic state from the slope of the $d(n)$. This slope is 2.25 Å and $\cos \alpha' = 2.25/2.54 = 0.885$ giving $\alpha' = 27.6°$. This calculation assumes that a double layer disposition of alcoxybenzoic acid molecules is still preserved in the smectic state. Keeping this assumption, one can also calculate the tilt of the aromatic moiety ϕ. From simple geometric considerations:

$$\cos \phi = \frac{d - n(\Delta d/\Delta n)}{l_a} \tag{2}$$

where l_a is the length of the "aromatic stem" and $(\Delta d/\Delta n)$ the slope of $d(n)$ (Figure 4). In the crystalline state $l_a = 16.4$ Å (Van der Waals length of the dimerized —O——COOH unit).

Using this value in the relation (2) one obtains values of ϕ comprised between 71°–72° (Table V). The correctness of this value is based on the knowledge of "l_a". The value of 16.4 Å is obtained on the basis of the hydrogen bonded dimer concept valid in the crystalline state but as we have shown above, questionable in the smectic state. This means that "l_a" is not known with certitude and correspondingly the value of ϕ is not certain.

TABLE V

Angle of tilt ϕ of the aromatic stem in the smectic state

n	l_p Å	Cos ϕ	$\phi \pm 1°$
8	10	0.287	72.7
10	12.5	0.308	71.2
12	15	0.305	71.2
14	17.5	0.290	72.0
16	20.0	0.299	72.0
18	22.5	0.283	72.1
0	0	$\frac{d^{(n=0)}}{l_n} = \frac{5.1}{16.4} = 0.311$	71.9

Nevertheless, it is likely that in the smectic state ϕ is much larger than α' which decreases from 60.7° in the crystalline state to 24.7° in the smectic state. In the crystalline state the similarity of α' and ϕ seems to indicate that the alcoxy readical is not in its perfectly extended planar zig-zag conformation in which one would expect both moieties to be at an angle of approx. 25°. In the smectic C state such conformation is even less probable because of more frequent rotations around C-C and C-O bonds. Our data indicate both moieties to be at an angle of 44–45°.

The difference in tilt of the aromatic and aliphatic moieties of the molecule of the alcoxybenzoic acid is not surprising. It is known from studies of monolayers and other amphiphyllic lamellar systems that molecules with long aliphatic chains have a tendency to orient normally to the interface. The strong tilt of the benzoic acid moiety can be explained by formation of bonds through coupling between carboxylic groups and benzene rings. Such disposition is represented in Figure 7. It is likely that the overall conformation represents a compromise between these two tendencies.

As pointed out above, the dramatic increase in the molar volume of the aromatic part of the alcoxybenzoic acid molecule does not mean the breakdown of the model of lamellae composed of bimolecular layers. These may be stabilized by residual hydrogen and lateral dipolar bonding allowing for increased rotational motion. A suggested possibility of a lamellar structure composed of molecules of alcoxybenzoic acid with interpenetrating aliphatic tails and a free benzoic acid moiety is contradicted by our data. Because of the similarity of values of V_m of the aliphatic tails in the crystalline and smectic states, one would expect a close packing and a full interpenetration of the aliphatic chains. Such model is incompatible with the rapid increase of d with n which indicates a double aliphatic chain arrangement within a stratum. Other models of bimolecular arrangement cannot be ruled out so easily and the molecular arrangement illustrated in Figure 7 is not intended to provide

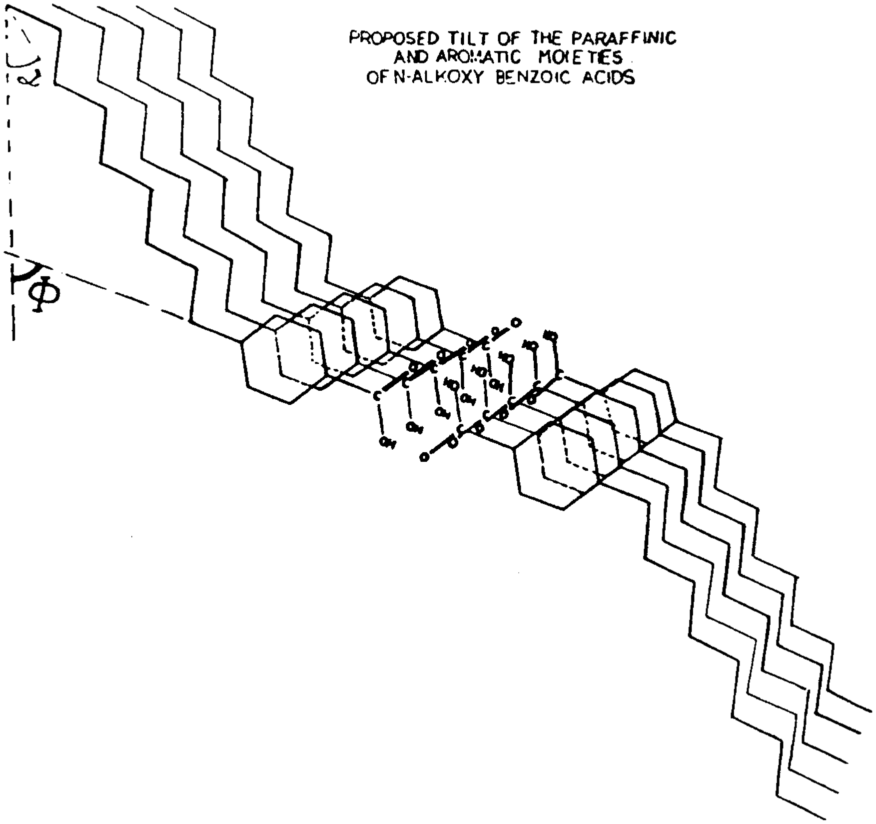


FIGURE 7 Proposed model of tilt and packing for smectic C phases of *p*-*n*-alkoxybenzoic acids.

a detailed conformational model of alcoxybenzoic acids in the smectic C state but merely to show a possibility compatible with our experimental results. The molecular conformations within the aromatic part leading to the observed increase in the molar volume have to be accounted for in any detailed model. Figure 7 also shows the extended aliphatic chains which are likely to provide most of the cohesion responsible for the stability of the smectic phase. This cohesion is so strong that it may persist into the nematic state.

Figures 8a and 8b show typical low angle X-ray patterns for two alkoxybenzoic acids in a smectic and nematic state respectively. A remarkable pattern indicating persistance of organization in the nematic state is obtained when the acid is melted in a thin layer between the two mica windows. This finding is consistent with literature data. As pointed out by DeVries,[12] a nematic structure preserving a "memory" of a smectic order does exist and

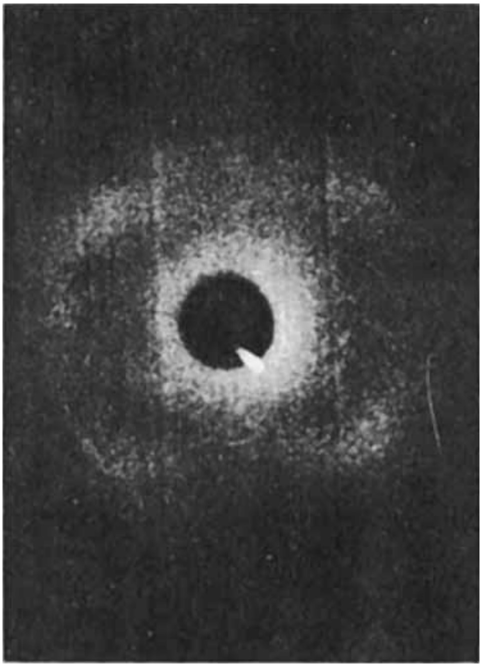


FIGURE 8 (a) X-ray diffraction photograph of a nematic phase of an alkoxybenzoic acid on mica (octyloxybenzoic acid at 113°C).

FIGURE 8 (b) Typical X-ray diffraction photograph of a smectic phase of an alkoxybenzoic acid (dodecyloxybenzoic acid at 98°C).

was reported for the nonyloxybenzoic acid in its nematic state. Some nematic phases, especially when they derive from highly organized smectic arrangements (such as smectic C phases) have been found to consist of small, molecular clusters containing a few thousand molecules. The lamellar, tilted organization of molecules of the "C smectic phases" in each cluster seems to be preserved. They have been designated by DeVries as "cybotactic nematic phases."[13] It is probable that in the case of alkoxybenzoic acids, we deal with such cybotactic nematics.

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