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Liquid Crystals

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LIQUID CRYSTALS, 1997, VOL. 22, NO. 1, 51–60

Liquid crystalline behaviour of hydrogen bonded complexes of a non-mesogenic anil with *p-n*-alkoxybenzoic acids

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Phase diagrams of binary mixtures of the non-mesogenic *N*-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminopyridine with a series of *p*-*n*-alkoxybenzoic acids ranging from methoxy to hexadecyloxy were established using differential scanning calorimetry and polarising optical microscopy. The key results obtained are: (1) the formation of 1:1 hydrogen bonded complexes between the pyridine derivative and the alkoxybenzoic acids, (2) the stability of the alkoxybenzoic acid mesophases over a wide range of compositions (up to slightly over 50 mol % of the pyridine derivative), (3) the absence of additional mesophases corresponding specifically to the 1:1 complexes, and (4) the complete miscibility of the acids with the complexes in the mesomorphic state. With alkoxy chains from methoxy to heptyloxy, mixtures produce only nematic phases; they produce both nematic and smectic phases with chains from octyloxy to dodecyloxy, and only smectic phases with chains from tetradecyloxy to hexadecyloxy. The formation of hydrogen bonded complexes was investigated at various temperatures using FTIR spectroscopy. Molecular ordering was studied by X-ray diffraction as a function of temperature and composition both for the crystalline and the mesomorphic states.

1. Introduction

It is only recently that hydrogen bonding has started to be extensively used in several laboratories as a tool for the formation of monomeric and polymeric liquid crystals. Many papers in the literature deal with the formation of liquid crystals from aromatic acids, amphiphilic carbohydrates, multihydroxy amphiphiles and bola-amphiphiles, as well as from mixtures of unlike molecules interacting through intermolecular hydrogen bonding. Most of the papers published up to early 1995 are summarized in two review papers, one treating the subject in a general manner [1], the other focusing specifically on the case of carbohydrates [2]. Examples of more recent papers are quoted in references [3–13].

Mixtures of unlike hydrogen bonded molecules producing liquid crystals frequently involve donor molecules derived from carboxylic acids and acceptor molecules derived from pyridine, 4,4′-bipyridine or stilbazole. Inspection of the literature shows that such donor and acceptor molecules are not always mesogenic by themselves. If neither of the two molecules is mesogenic, then the formation of liquid crystals in binary mixtures can be attributed without ambiguity to hydrogen bonding, especially when the thermal stability of the induced mesophases goes through a maximum at a stoichiometric composition. On the other hand, if at least one of the two interacting molecules happens itself to be mesogenic, then of course the rôle of hydrogen bonding in the formation of liquids crystals is questionable, particularly when the hydrogen bonding is known not to be very strong and when the thermal stability of the liquid crystals presents no maximum as a function of composition.

In a recent preliminary paper [14], equimolar mixtures of *N*-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminopyridine (indicated in the following text as the anil), used as an acceptor of hydrogen bonds, with several *p*-*n*-alkoxybenzoic acids, used as donors were investigated. They were found to produce smectic and nematic phases at temperatures above the melting points of the components. In the present paper, the anil/alkoxybenzoic acid complexation is studied systematically as a function of temperature and length of the alkyl chain of the alkoxybenzoic acid molecules (from hexyloxy to hexadecyloxy), and as a function of the composition of the binary mixtures. The hydrogen bonding is also investigated by FTIR spectroscopy, and the molecular ordering is analysed using X-ray diffraction.

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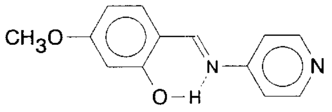
*Authors for correspondence.

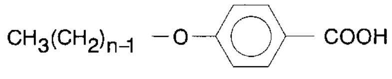
2. Materials

The *N*-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminopyridine used in the present work:



was synthesized as described previously [14]. The hydrolysis of the azomethine bond, generally rather easy, is slowed down here by the intramolecular hydrogen bonding of the nitrogen atom with the *o*-hydroxy group of the benzylidene ring. Incapable of producing liquid crystals by itself, the anil passes on heating directly into the isotropic liquid state, at ~121°C.

Binary mixtures of the anil with a series of *p*-*n*-alkoxybenzoic acids (Aldrich):



$n = 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16$

were prepared by simple mechanical stirring of the components at a temperature above the melting points. In the pure state, the *p*-*n*-alkoxybenzoic acids used produce liquid crystals defined by the following polymorphic schemes [15, 16]:

$n=1$ Cr 184 (N 156) I
$n=2$ Cr 196 (N 165) I
$n=3$ Cr 145 (N 154) I
$n=4$ Cr 147 (N 160) I
$n=5$ Cr 124 (N 151) I
$n=6$ Cr 105 (N 153) I
$n=7$ Cr 92 Sc 98 (N 146) I
$n=8$ Cr 101 Sc 108 (N 147) I
$n=9$ Cr 94 Sc 117 (N 143) I
$n=10$ Cr 97 Sc 122 (N 142) I
$n=12$ Cr 95 Sc 129 (N 137) I
$n=14$ Cr 97·5 Sc 139·51
$n=16$ Cr 85 Sc 132·5 I

With the exception of the methoxy and ethoxy derivatives, which exhibit only a monotropic nematic phase, the members of the series show enantiotropic liquid crystal phases over a wide range of temperatures: only nematic phases occur for the alkoxybenzoic acids from propoxy to hexyloxy, both smectic and nematic phases for the acids from heptyloxy to dodecyloxy, and only the smectic phase for the others.

3. Phase diagrams

The liquid crystal behaviour of the binary mixtures was studied by differential scanning calorimetry (Perkin-Elmer DSC7, heating/cooling rates of 5°C min^{-1}) and polarizing optical microscopy (Leitz Orthoplan microscope equipped with a Mettler FP82 hot-stage).

Special emphasis was given to mixtures with the pentyloxy- and dodecyloxy-benzoic acids. The DSC thermograms were recorded upon heating and subsequent cooling in the temperature range from 25 to 170°C. First order transitions, running through biphasic regions of temperature and composition, were indicated as usual by the presence of single, fairly symmetrical peaks (T in figure 1, see also figure 2); the width of these peaks increased with the width of the temperature range

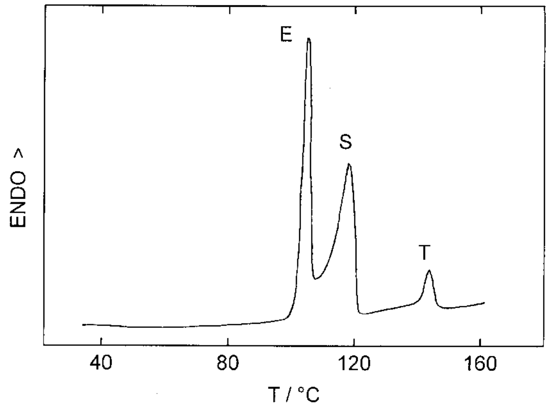


Figure 1. Differential scanning calorimetry curve of the binary mixture of *p*-*n*-pentyloxybenzoic acid with 12·5 mol% of the anil, recorded upon first heating at a rate of 5°C min^{-1}: E eutectic peak, S *solidus* peak, T nematic to isotropic phase transition peak.

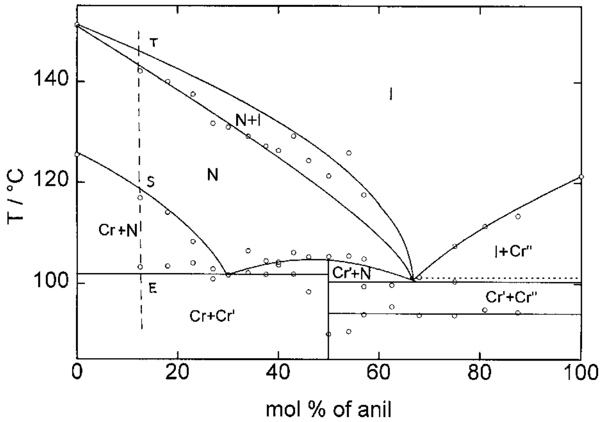


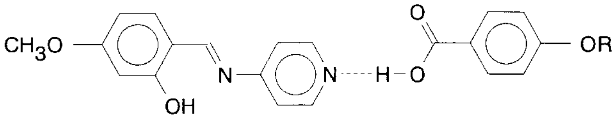
Figure 2. Phase diagram of the binary mixture of *p*-*n*-pentyloxybenzoic acid with the anil. Symbols I and N represent the range of existence of the isotropic liquid and the nematic phase; symbols Cr, Cr′ and Cr″ stand, respectively, for the crystalline phases of pure *p*-*n*-pentyloxybenzoic acid, of the equimolar stoichiometric compound and of pure anil. Experimental points came from DSC measurements, confirmed by optical observations. Dashed vertical line corresponds to the DSC run shown in figure 1; letters E, S, T are defined in figure 1; dotted horizontal line represents the eutectic melting of N and Cr″.

of the transition, that is, with the width of the biphasic region of the transition at the composition considered. On the other hand, eutectic transitions were indicated by the presence (on heating) of two distinct, but connected peaks: a sharp peak (E in figure 1) at the eutectic temperature (independent of composition), revealing a partial melting of the mixture (appearance of a 'liquid' having the eutectic composition, in coexistence with a certain amount of one of the components still in a crystalline state); and an asymmetrical peak (S in figure 1) at the *solidus* temperature (dependent on composition), indicating the completion of the melting process. Extending down to the eutectic temperature, the left wing of the peak S reflects the progress of the melting as a function of increasing temperature between the eutectic and *solidus* temperatures. The separation of the two peaks decreases and the height of the peak E grows linearly as the binary mixture approaches the eutectic composition. Such a behaviour makes it easier first to establish the existence of a eutectic melting and secondly to determine experimentally its coordinates in a phase diagram.

The optical textures observed upon slow cooling from the isotropic melt showed clearly the existence of two distinct liquid crystal phases: focal conic and fine four-brush schlieren textures indicated the presence of smectic C phases, and large four- and two-brush schlieren textures that of nematic phases. They also showed that, in certain temperature and composition intervals, either the two phases coexist, or else each of them coexists in equilibrium with the isotropic melt or a crystalline phase. Finally, in the case of phase separation, the optical textures allowed us to estimate, at least qualitatively, the relative amounts of the two phases present in the mixtures and hence the widths of the biphasic regions in the phase diagrams.

These observations may be summarized in the phase diagrams shown in figures 2 and 3, concerning the binary mixtures of the anil with pentyloxy- and dodecyloxy-benzoic acid. The diagrams were established from thermodynamic information obtained by considering the continuous evolution of the DSC peaks with concentration and by analysing the textures observed. It is worth noting that the biphasic regions involving two liquid crystal phases or a liquid crystal phase coexisting with the isotropic melt were not easy to define accurately. This was probably due to the small enthalpy changes involved for the corresponding phase transitions, to the spreading of the DSC peaks, and also to the fuzziness of the textures near the transition boundaries. By contrast, the precise delineation of the biphasic regions between crystals and liquid crystals was straightforward.

Inspection of the above results gives rise to the following comments. It is clear in the first place that no extra liquid crystal phases appear in the mixtures with reference to those presented by the alkoxybenzoic acids taken in the pure state. The extension of the existence range of these latter phases as a function of composition is rather important, slightly exceeding anil concentrations of about 50 mol %; this shows that the anil incorporated in the mixtures does not play a simple rôle of diluent, but rather participates actively in the formation of the liquid crystal structures. However, the absence of an 'azeotropic' maximum for the smectic and nematic mixtures suggests that the interactions between the dimerized alkoxybenzoic acid and the hydrogen bonded 1:1 stoichiometric compound (the presence of such species will be discussed in §4) are not particularly stronger in the mesomorphic than they are in the isotropic liquid state. On the contrary, the presence of a melting maximum for the crystalline mixtures containing 50 mol % of anil proves without any possible doubt that a well defined 1:1 stoichiometric compound is formed, resulting from the hydrogen bonding of one anil with one alkoxybenzoic acid molecule:



To generalize these observations, optical microscopy experiments were carried out with equimolar (50 mol %) mixtures of the anil with a series of alkoxybenzoic acids. With acids from methoxy to heptyloxy, the mixtures were found to exhibit only nematic phases; with acids from octyloxy to dodecyloxy, they were found to exhibit both nematic and smectic phases; and from tetradecyloxy to hexadecyloxy, only smectic phases were observed. DSC measurements fully confirmed these results. The phase transition temperatures determined are shown in figure 4. Quite clearly, the phases detected in the mixtures are exactly the same as those observed with the corresponding pure alkoxybenzoic acids. The only difference detected is that the nematic phases obtained with the methoxy and ethoxy acids are no longer metastable (monotropic), but instead are perfectly stable (enantiotropic), probably due to the normal thermodynamic depression of the melting temperatures of crystals in the presence of additives, which, of course, disfavours the crystal to the benefit of the underlying nematic phase.

4. Hydrogen bonding

To evaluate the importance of hydrogen bonding in the formation of the liquid crystals investigated in the present work, binary mixtures of the anil with alkoxybenzoic acids, mainly pentyloxy- and dodecyloxy-benzoic acids, were studied systematically by infrared spectroscopy (Nicolet Magna 550 FTIR spectrometer, reso-

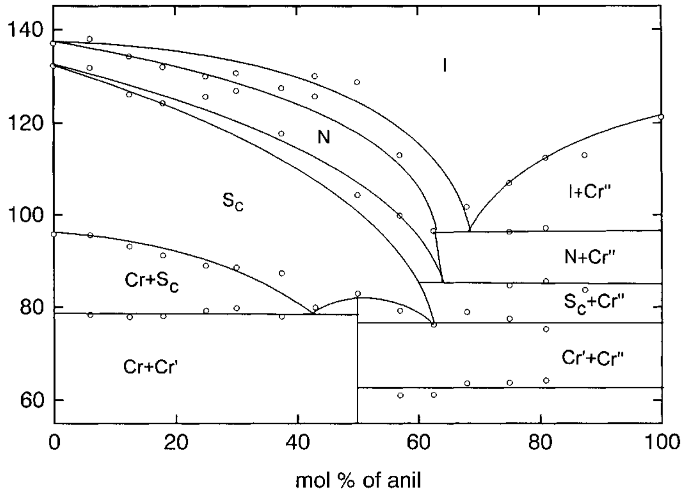


Figure 3. Phase diagram of the binary mixture of *p*-*n*-dodecyloxybenzoic acid with the anil. Symbols I, N and S_C represent the range of existence of the isotropic liquid, the nematic and the smectic C phase; symbols Cr, Cr′ and Cr″ stand, respectively, for the crystalline phases of pure *p*-*n*-dodecyloxybenzoic acid, of the equimolar stoichiometric compound and of the pure anil. Experimental points come from DSC measurements, confirmed by optical observations.

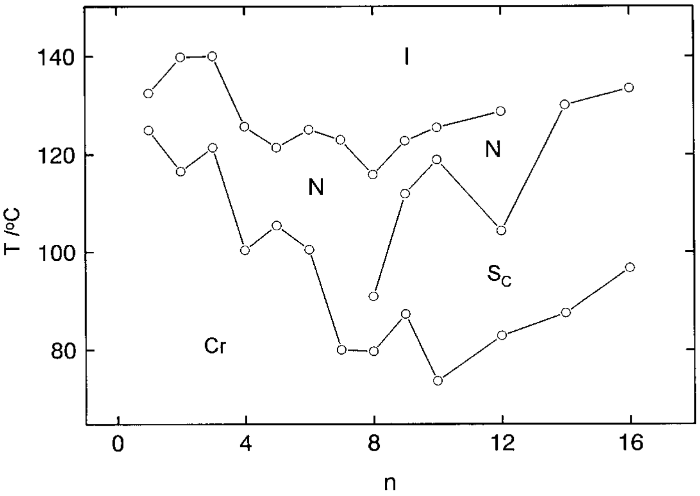
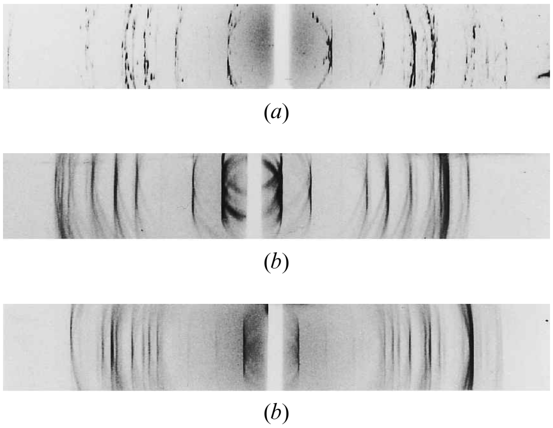


Figure 4. Thermotropic polymorphic behaviour of equimolar binary mixtures of the anil with *p*-*n*-alkoxybenzoic acids as a function of the number *n* of carbon atoms in the alkoxy chains. Symbols I, N, S_C, and Cr stand for isotropic liquid, nematic, smectic C, and crystal phases.

lution of 4 cm^{-1}). Spectra were recorded at various temperatures, ranging from ambient to about 150°C, that is above the nematic to isotropic phase transition.

At room temperature, the infrared spectra of the crystalline mixtures proved not to result from a weighted superposition of the spectra of the pure components, but instead presented distinct features and changes depending on composition. On increasing the anil concentration of the mixtures, starting from pure acid, two additional broad bands (at ~1935 and 2450 cm^{-1}) appear in the spectra, indicating strong hydrogen bonding of the pyridine rings with the carboxyl groups of the acids [17–20]. Their intensity passes through a maximum for concentrations of 50 mol % of anil, pointing to the formation of a 1∶1 complex between the anil and the benzoic acid. At the same time, the two bands at 2665 and ~2560 cm^{-1} [20–22], along with the very broad and strong OH band at ~3000 cm^{-1}, all three of which characterize the acid dimers, decrease in intensity to vanish completely beyond 50 mol % of anil. Finally, in the 1∶1 stoichiometric mixtures, the C–O stretching band of the pure acid dimer at 1678 cm^{-1} is replaced by a doublet (at ~1685 and ~1695 cm^{-1}), suggesting the formation of hydrogen bonds with a double minimum energy potential [18, 23]. Clearly, the alkoxybenzoic acid present in the mixtures is engaged entirely in the formation of a stoichiometric 1∶1 complex, in perfect agreement with the phase diagrams established in § 3.

The infrared spectra of the stoichiometric 1∶1 complexes remained totally unchanged upon heating up to temperatures of about 140 and 100°C for the mixtures with pentyloxy- and dodecyloxy-benzoic acid, respectively. However, at higher temperatures several changes were seen, suggesting a gradual dissociation of the complexes with release of free alkoxybenzoic acid in a strongly dimerized form. Indeed, the bands characteristic of the stoichiometric 1∶1 compound started to widen and to diminish in intensity, remaining nevertheless perfectly visible even at temperatures as high as 150°C, well into the stability range of the isotropic melt. On the other hand, the characteristic bands of the acid dimers, along with a faint band at 1732 cm^{-1}, characteristic of the acid in a monomeric form, started to appear in the spectra. Clearly, the hydrogen bonding of the pyridine with the carboxyl groups, even though broken to some extent, does persist in the isotropic liquid state, the small amount of liberated acid being essentially in a dimeric form. Note that the dissociation of the 1:1 complex starts at slightly lower temperatures with the dodecyloxy (in the nematic state) than it does with the pentyloxybenzoic acid complex (in the isotropic state). It is of interest to add that the alkoxybenzoic acids in the pure state are completely dimerized at room temperature and start to dissociate into single molecules only when heated to relatively high temperatures, essentially in the isotropic state.


(*a*)

(*b*)

(*b*)

Figure 5. Typical X-ray diffraction patterns at room temperature of (*a*) pure anil, (*b*) pure *p*-*n*-dodecyloxybenzoic acid, and (*c*) the equimolar mixture of anil with *p*-*n*-pentyloxybenzoic acid. Patterns of the pure anil look granular because of the unavoidable formation of large crystals with this compound.

5. Molecular ordering

The structure of the mixtures was then investigated by X-ray diffraction. Patterns of powder samples were recorded either photographically or using a curved position-sensitive detector (INEL-CPS 120) (Guinier focusing cameras, bent quartz monochromator, Cu-Kα_1). Patterns of magnetically oriented samples (submitted to a magnetic field of 1·4 T during the X-ray experiment at high temperature) were recorded photographically with a home-made pinhole camera using Ni-filtered copper radiation.

5.1. *Crystalline state*

At room temperature, the diffraction patterns recorded with a variety of binary mixtures were all in perfect agreement with the phase diagrams and infrared spectroscopy results quoted in §3 and 4. The patterns of the pure anil (figure 5 (*a*)) give evidence of a three-dimensional crystalline structure with a lamellar period of 13·8 Å. The length of the rod-like anil molecules (~13·8 Å as estimated by molecular modelling using Biosym software) is identical to the lamellar spacing measured experimentally; molecules in the crystal must therefore be arranged in single layers and oriented perpendicular to the layer planes.

The X-ray patterns of the pure alkoxybenzoic acids (figure 5 (*b*)) contain a set of equidistant Bragg reflections in the small-angle region, indicative of a lamellar structure, and a series of sharp reflections in the wide-angle region, indicative of a three-dimensional crystalline packing of the molecules. In perfect agreement with results reported in the literature by Blumstein and Patel [24], the lamellar period is smaller than twice the molecular length† and grows linearly with the number n of carbon atoms in the alkoxy group, according to the equation: $d\,(\text{Å}) = 8{\cdot}54 + 1{\cdot}244n$ (estimated by a least-squares fit method). From a simple comparison of the Y-intercept of the corresponding straight line (i.e. 8·54 Å, representing the thickness of the aromatic sub-layers in the lamellar structure) with the length of the dimerized aromatic cores of the molecules (17·4 Å)†, one may immediately conclude that the aromatic cores, dimerized by hydrogen bonding, are arranged in double layers and tilted away from the layer normals by an angle of $\cos^{-1}(8{\cdot}54/17{\cdot}4) = 60{\cdot}6$ degrees. Similarly, by comparing the slope of the d versus n straight line (1·244 Å) with the slope of $_{2}L_{\mathrm{A}}$ versus n (2·54 Å)†, one might conclude, as suggested by Blumstein and Patel [25], that the fully extended alkyl chains are arranged in exactly the same way, that is, in double layers with a tilt of $\cos^{-1}(1{\cdot}244/2{\cdot}54) = 60{\cdot}7$ degrees. However, the two slopes being in the ratio 1:2, one should be careful not to discard a possibility that the alkyl chains are interdigitated in a single layer pattern and oriented normal to the layer planes. Actually, both structures have been established experimentally by X-ray studies with single crystals of alkoxybenzoic acids [25].

The diffraction patterns of the 1:1 binary mixtures at room temperature (figure 5 (*c*)) are similar to, but not identical with, those of the pure components taken

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†The overall length of the alkoxybenzoic acid dimers in a fully extended conformation may be approximated by molecular modelling (using Biosym software) as: $_{2}L_{\mathrm{A}}\,(\text{Å}) = 17{\cdot}4 + 2{\cdot}54n$, where n is the number of carbon atoms in the alkoxy chains. For $n=0$, the value of $_{2}L_{\mathrm{A}}$ ($=17{\cdot}4$ Å) represents the length of the aromatic core of the dimers.

separately. They are characterized by different lamellar spacings and different sequences of wide-angle reflections. Quite clearly, in compliance with the phase diagrams and the infrared spectroscopic data given above, the mixtures form well defined stoichiometric compounds having distinct lamellar structures and specific structural parameters. With mixtures of intermediate compositions, the patterns result from the weighted superposition of the pattern of the stoichiometric 1:1 compound either with that of the pure alkoxybenzoic acid or with that of the pure anil, depending upon whether the composition of the mixture is in the range from 0 to 50, or from 50 to 100 mol % of anil.

Figure 6 shows the variation of the lamellar period of the crystalline 1:1 stoichiometric complexes as a function of the number n of carbon atoms in the alkoxy chains. In spite of a narrow dispersion of the data, this period appears to grow linearly with the size of the molecules, according to the equation: $d(\text{Å})=8{\cdot}78+0{\cdot}934n$ (estimated by a least-squares fit method). In such a situation, one is quite commonly tempted to conclude that the members of the series of compounds studied all have a similar structure, more precisely that the tilt of the aromatic cores and the alkoxy chains with respect to the layer normal are both kept unchanged. Moreover, one is tempted to calculate‡ the respective tilts of the aromatic cores and the alkoxy chains from a comparison of the slopes and Y-intercepts of the two straight lines describing the n-dependence of the lamellar period and of the length of the molecules in a fully extended conformation: ${}_1L_c\,(\text{Å})=22{\cdot}5+1{\cdot}27n$ (estimated by molecular modelling). In the present case, however, such an approach is totally unfounded, for it leads to values of the tilt angles that are incompatible with one another§. The tilt of the aromatic cores and paraffin chains varies therefore with the length of the molecules considered. The simplest and most plausible way to describe the crystal structure of the 1:1 complexes is then to say that the molecules are fully elongated and arranged in simple rather than double layers. They are fully elongated in order to avoid the energy penalty that would be caused by a bending of the molecules between the stereochemically coupled aromatic cores and paraffin chains. They are arranged in simple rather than in double layers in order to avoid excessive tilt angles with respect to the layer normals. At any rate, the structural model proposed in this work, though quite reasonable, remains still to be confirmed by a complete X-ray crystallographic study of single crystals.

5.2. *Mesomorphic state*

At high temperature, the X-ray patterns recorded with a wide variety of mixtures were again in perfect compliance with the phase diagrams reported in § 3, showing the presence of smectic and nematic phases. On the one hand, patterns of the smectic phases (figure 7 (*a*)) contain a sharp Bragg reflection in the small-angle region, related to the smectic layering; and a broad band in the wide-angle region, related to the lateral liquid-like correlations of the molecules within the layers and to the disordered conformation of the alkoxy chains. On the other hand, patterns of the nematic phases (figure 7 (*b*)), though resembling in many respects the patterns of the smectic phases, are devoid of sharp reflections, as expected from the fact that long-range positional correlations between the molecules do not exist; the broad peak that appears in the small-angle region of the patterns, in place of the sharp reflections of the smectic phases, is related to the presence of 'cybotactic groups' [28], that is, to the presence of smectic fluctuations.

The smectic periods deduced from the position of the small-angle Bragg reflections turned out to be practically independent of temperature. Such a behaviour is quite natural since the smectic phases studied fall into the

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‡ The lamellar spacing measured reflects the thickness of one aromatic and one paraffin sublayer superposed: $d=d_{\text{arom}}+d_{\text{paraf}}$. Thus $d=\varepsilon_{\text{arom}}\,L_{\text{arom}}\cos\phi_{\text{arom}}+\varepsilon_{\text{paraf}}L_{\text{paraf}}\cos\phi_{\text{paraf}}$, where the Ls and ϕs represent the length and tilt of the aromatic and paraffin moieties, respectively, and where the εs are equal to 1 or 2, depending on whether the corresponding moieties are arranged in mono- or bi-layers. When the ϕs are maintained constant, d grows linearly with L_{paraf}, that is, with the number n of carbon atoms in the extended paraffin chains. By comparing the Y-intercept of d versus n, $d(n=0)=8{\cdot}78$ Å, with the length of the aromatic core, ${}_1L_c\,(n=0)=22{\cdot}5$ Å, one may calculate at once $\cos{}_1\phi_{\text{arom}}=8{\cdot}78\div22{\cdot}5=0{\cdot}39$ and $\cos{}_2\phi_{\text{arom}}=8{\cdot}78\div(2\times22{\cdot}5)=0{\cdot}20$, corresponding to the tilts when the aromatic cores are arranged in mono- and bi-layers, respectively. Likewise, by comparing the slope of d versus n, i.e. 0·934, with the slope of ${}_1L_c$ versus n, i.e. 1·27, one easily deduces $\cos{}_1\phi_{\text{paraf}}=0{\cdot}934\div1{\cdot}27=0{\cdot}74$ and $\cos{}_2\phi_{\text{paraf}}=0{\cdot}934\div(2\times1{\cdot}27)=0{\cdot}37$, corresponding to the tilts when the paraffin chains are arranged in mono- or bi-layers, respectively.

§ To convince oneself of this, it is useful to remember that the aromatic cores of common calamitic mesogens and the extended paraffin chains in the crystal happen to have cross-sectional areas that are very close to one another ($\sigma_{\text{arom}}\approx\sigma_{\text{paraf}}\approx20\,\text{Å}^2$ [26, 27]). Thus, if arranged similarly, that is, both in single or both in double layers, then the two moieties must be tilted equally with respect to the layer normals. Otherwise, those moieties that are arranged in double layers must be tilted more than the others: ${}_2\phi>{}_1\phi$. This is simply because the junctions of the aromatic cores with the paraffin chains cover necessarily the same area on both sides of the interfaces between the aromatic and paraffin sublayers: $S=\sigma/\cos{}_1\phi=2\sigma/\cos{}_2\phi$. Obviously such is not the case here, since $\cos{}_1\phi_{\text{arom}}\neq\cos{}_1\phi_{\text{paraf}}$, $\cos{}_2\phi_{\text{arom}}\neq\cos{}_2\phi_{\text{paraf}}$, $\cos{}_1\phi_{\text{arom}}\neq2\times\cos{}_2\phi_{\text{paraf}}$, and $2\times\cos{}_2\phi_{\text{arom}}\neq\cos{}_1\phi_{\text{paraf}}$.

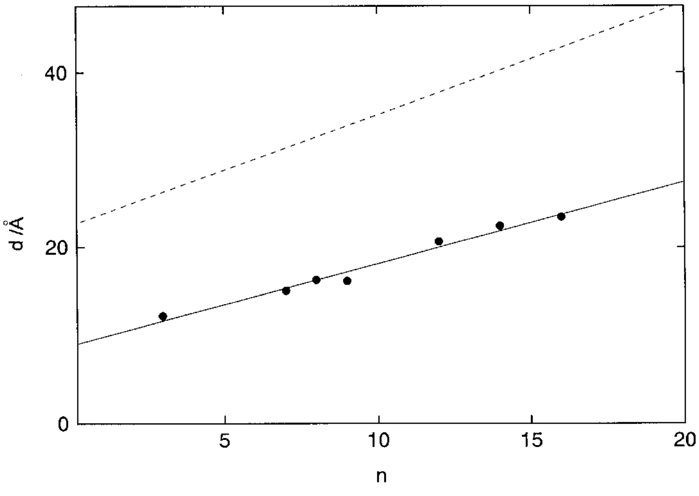
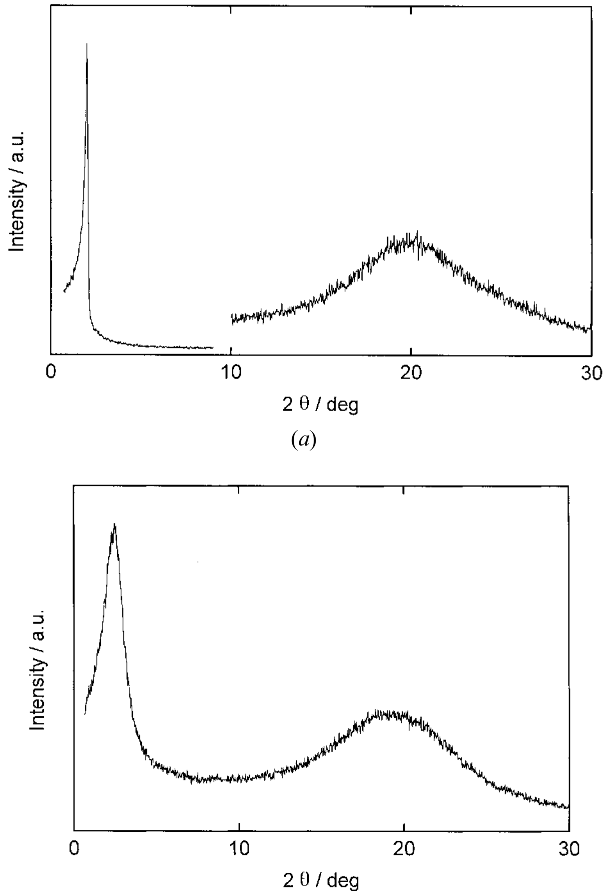


Figure 6. Variation of the lamellar period of the crystalline 1∶1 stoichiometric complexes of anil with alkoxybenzoic acids as a function of the number of carbon atoms in the alkoxy chains: $d(\text{Å})=8{\cdot}78+0{\cdot}934n$. Dashed line represents the n-dependence of the length of the complex molecules in a fully extended conformation: ${}_1L_C$ (Å)$=22{\cdot}5+1{\cdot}27n$.

category of those smectic C phases that are not followed by a smectic A phase on heating. It is also consistent with the fact that the acid dimers and the stoichiometric complexes do not dissociate appreciably in the smectic state (see section 4); such dissociation would, of course, affect the ordering as a result of the formation of extraneous molecular species of different lengths. On the contrary, however, the measured smectic periods were shown to vary significantly with the length of the alkoxybenzoic acids and the composition of the binary mixtures, as will now be discussed.

Figure 8 shows the smectic period of pure alkoxybenzoic acids growing almost linearly with the number of carbon atoms in the alkoxy chains. This period being slightly smaller than twice the molecular length, the molecules (which are completely dimerized by hydrogen



(*a*)

(*b*)

Figure 7. Typical X-ray diffraction patterns of liquid crystalline binary mixtures of *p*-*n*-dodecyloxybenzoic acid with the anil (*a*) in the smectic state (37·5 mol % of anil) (for the sake of clarity, the intensity scattered in the wide-angle region was multiplied by five) and (*b*) in the nematic state (43 mol % of anil).

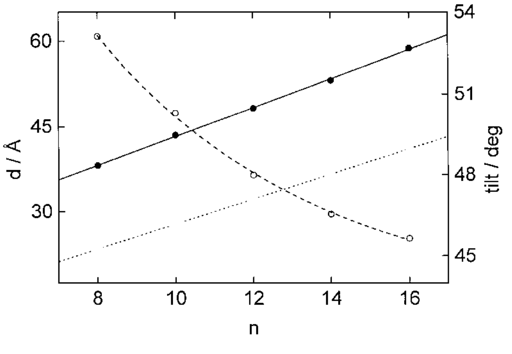


Figure 8. Variation of the smectic period d (solid circles) and the tilt angle (open circles) of the molecules of alkoxybenzoic acids as a function of the number of carbon atoms in the alkoxy chains. The dotted line represents the linear growth of the length of the acid molecules in a fully extended conformation: ${}_1L_A$ (Å)$={}_2L_A/2=8{\cdot}7+1{\cdot}27n$. The dashed curve represents the exponential decay of the tilt: $\phi\,(\text{deg})\approx 43+41\exp(-n/5{\cdot}6)$. Data are in agreement with values quoted in the literature [24].

bonding) must therefore be arranged in double layers, with the paraffin chains in a disordered conformation and the 'aromatic cores' tilted with respect to the layer normals. The molecular tilt may be easily calculated from a simple comparison of the smectic period with the molecular length: $\cos^{-1}(d/{}_2L_{\mathrm{A}})$. By disregarding the effect of the cross-sectional area of the molecules on the thickness of the smectic layers—this area, slightly larger in the smectic phase than in the crystal, leads to some shortening of the paraffin chains (which, being disordered, are allowed to collapse slightly along their axes) [29]—,one may take as the molecular length of the acid dimers the value estimated by molecular modelling for the crystalline state at room temperature. The tilt values found (figure 8) are unusually large, but in perfect agreement (within about one degree) with those measured directly by X-ray diffraction from macroscopically oriented samples (obtained by cooling the nematic phase in a magnetic field) (figure 9). (With such samples, the smectic reflection is resolved into four sharp spots arranged X-wise round the incident beam, and the azimuthal angular position of the spots with respect to the meridian plane provides a measure of the tilt: see figure 12 on p. 305 in ref. [30]). The structural model of a perfectly double-layered, tilted smectic seems therefore perfectly acceptable. It is of interest to add that the molecular tilt was shown to decrease appreciably from 54 to 45 degrees when the molecular length increased from the octyloxy to the hexadecyloxy derivative, as though there were a tendency towards the formation of a smectic A phase. In fact, the tilt angles do not fall to zero, but appear to level off rapidly (with a characteristic length of about $\delta n \approx 5{\cdot}6$), tending asymptotically to values of about 43 degrees (as estimated by an exponential least-squares fit method: $\phi \approx 43 + 41 \exp(-n/5{\cdot}6)$). Such a behaviour reveals the important rôle of the alkoxy chains in the molecular tilting, particularly of the very few methylene groups next to the aromatic core. Probably, but this remains to be further investigated, this is related to the stereochemical geometry of attachment of the alkoxy chains onto the aromatic cores, which determines the molecular arrangement at the interfaces between the aromatic and aliphatic sub-layers.

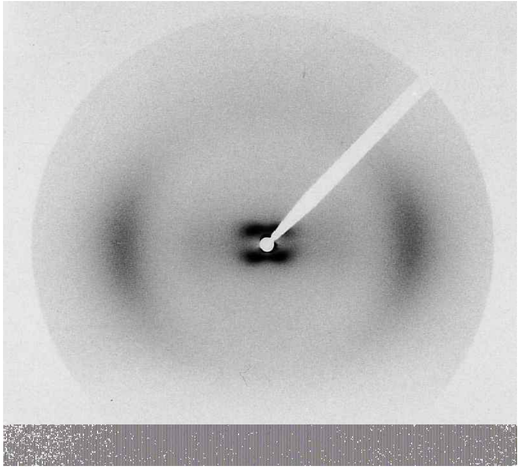


Figure 9. Typical X-ray diffraction pattern of *p*-*n*-dodecylbenzoic acid in the smectic C phase, oriented in a magnetic field.

Figure 10 shows a similar behaviour for the smectic phase observed with mixtures containing 50 mol % of anil, exclusively composed of 1∶1 complex molecules as suggested by infrared spectroscopy (see § 4). The smectic period exceeding the length of the 1∶1 complex molecules, the molecules must, as in the case of pure alkoxybenzoic acids, be arranged in double layers, with the paraffin chains in a disordered conformation and the 'hydrogen bonded aromatic cores' tilted away from the layer normals. The molecular tilt calculated with this assumption—$\cos^{-1}(d/2\,{}_1L_{\mathrm{C}})$, slightly larger than that of pure alkoxybenzoic acids—decreases (also exponentially) from 56 to 53 degrees as the molecular length grows from the octyloxy to the hexadecyloxy derivative: $\phi \approx 53 + 46 \exp(-n/2{\cdot}9)$. It is only fair, however, to stress immediately that this perfectly bilayered smectic model remains still to be demonstrated experimentally. Indeed, all attempts to obtain magnetically oriented samples for a direct measurement of the tilt have so far been unsuccessful. Presumably, the magnetically induced orientation of the nematic phase is destroyed upon cooling through the wide biphasic region of the phase diagram leading from the nematic to the smectic phase.

Figure 11 shows the concentration-dependence of the smectic period in the particular, but typical, case of

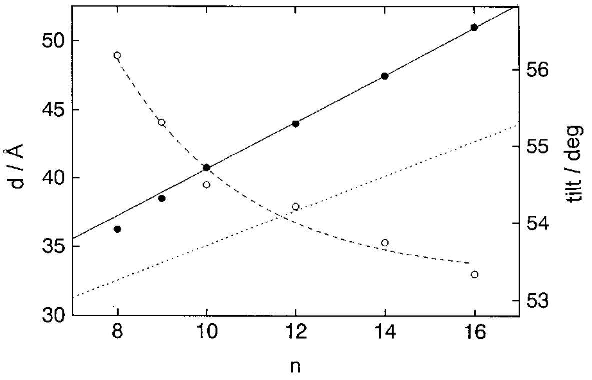


Figure 10. Variation of the smectic period *d* (solid circles) and the tilt angle (open circles) of the 1∶1 complex molecules as a function of the number of carbon atoms in the alkoxy chains. The dotted line represents the linear growth of the length of the complex molecules in a fully extended conformation: ${}_1L_{\mathrm{C}}$ (Å)$=22{\cdot}5+1{\cdot}27n$. The dashed curve represents the exponential decay of the tilt: ϕ (deg)$\approx 53 + 46 \exp(-n/2{\cdot}9)$.

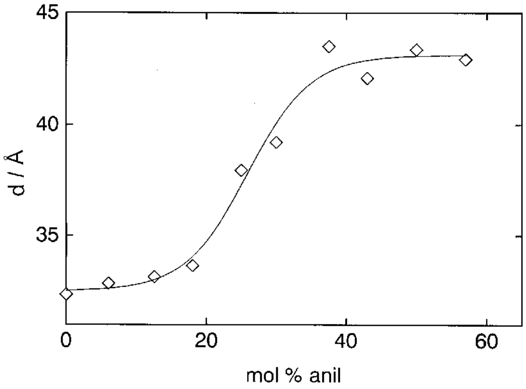


Figure 11. Variation of the smectic period *d* of binary mixtures of the anil with *p-n*-dodecyloxybenzoic acid as a function of molar concentration of anil.

binary mixtures of the anil with dodecyloxybenzoic acid. In spite of a weak dispersion of the experimental data, due to difficulties in controlling the composition of the mixtures accurately, it is clear that the smectic period changes in a continuous manner throughout the whole range of concentrations explored, in agreement with the phase diagram presented above (figure 3). As supported by infrared spectroscopy, the smectic phase is basically formed of a mixture of dodecyloxybenzoic acid dimers and 1:1 complex molecules arranged in layers. The thickness of the smectic layers appears to grow with concentration in a sigmoidal manner between the values corresponding to pure acid and pure 1:1 stoichiometric complex. The Bragg reflections remained very sharp whatever the concentration, this variation can hardly be associated with the presence of concentration inhomogeneities in the mixtures (microsegregation of the components); instead, it may be easily interpreted as resulting from the fact that the two components taken separately have, not only different molecular lengths, but different tilts as well, the tilt angle varying continuously with composition.

6. Concluding remarks

Binary mixtures of the anil with a series of alkoxybenzoic acids were found to produce liquid crystal phases over a wide range of compositions and temperatures. All these corresponded to an extension in the binary mixtures of the same liquid crystal phases produced by the alkoxybenzoic acids in the pure state. The phase diagrams of the particular mixtures of anil with pentyloxy- and dodecyloxy-benzoic acids were drawn in detail. It thus became apparent that the stability range of the liquid crystals as a function of composition is very important, extending slightly beyond anil concentrations of about 50 mol%. The overall features of the phase diagrams imply that, in the mesomorphic state, the 1:1 stoichiometric complex molecules are miscible with the free acid molecules in all proportions; a possible reason for this could be that the 1:1 complex resembles the aromatic part of the acid dimer in polarity as well as in size and is thus able to fit relatively easily into the acid mesophase. It also became apparent that, despite the presence of a stable 1:1 stoichiometric complex, the thermal stability of the liquid crystal phases shows no maximum as a function of concentration; presumably, this is related to the fact that the transition temperatures of the complex are lower than those of the corresponding acids, the pure anil exhibiting no liquid crystalline behaviour.

The hydrogen bonding of the molecules was then studied as a function of temperature using FTIR spectroscopy. In the crystalline state, at low temperature, the alkoxybenzoic acid was found to interact quantitatively with the anil to form a well defined stoichiometric 1:1 complex. This complex proved to resist heating to relatively high temperatures, well into the stability range of the liquid crystalline phases; it started to dissociate perceptibly, with release of alkoxybenzoic acid (dimerizing immediately), only when heated in the isotropic liquid. For all practical purposes, therefore, the liquid crystalline phases observed may conveniently be considered as resulting from a simple mixture of 1:1 complex with fully dimerized acid or anil in excess.

Finally, the structure of the binary mixtures was studied systematically by X-ray diffraction. The presence at low temperature of a well defined, crystalline 1:1 complex could thus be definitely established. Subject to further investigations using X-ray diffraction from single crystals, the lamellar structure of the complex was described as resulting from a single-layered arrangement of fully stretched, rectilinear molecules tilted with respect to the layer normal by an angle depending on the length of the alkoxy chains, and oriented head to tail with the alkoxy chains and the aromatic cores localized in separate sub-layers. The presence at high temperature of a smectic C phase was also confirmed and the thickness of the smectic layers was analysed as a function of the length of the alkoxy chains and the composition of the binary mixtures. Its structure was described as resulting from a double-layered arrangement of 1:1 stoichiometric complex and alkoxybenzoic acid molecules, with the aromatic cores tilted with respect to the layer normals by an angle varying continuously with composition.

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References

[1] Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem. Int. Ed. Engl.*, **34**, 1696.

[2] Prade, H., Miethchen, R., and Vill, V., 1995, *J. Prakt. Chem.*, **337,** 427.

[3] Miethchen, R., Holz, J., Prade, H., and Liptak, A., 1992, *Tetrahedron*, **48,** 3061.

[4] Araki, K., Kato, T., Kumar, U., and Frechet, J. M. J., 1995, *Macromol. Rapid Commun.*, **16,** 733.

[5] Han, H., Roychowdhury, S., and Bhowmik, P. K., 1995, *Polym. Prepr.*, **36,** 126.

[6] Han, H., Molla, A. H., and Bhowmik, P. K., 1995, *Polym. Prepr.*, **36,** 332.

[7] Beginn, U., and Lattermann, G., 1995, *Macromol. Rep.*, **A32** (Suppl. 7), 985.

[8] Wilson, L. M., 1995, *Liq. Cryst.*, **18,** 381.

[9] Hildebrandt, F., Schröter, J. A., Tschierske, C., Festag, R., Kleppinger, R., and Wendorff, J. H., 1995, *Angew. Chem. Int. Ed. Engl.*, **34,** 1631.

[10] Tian, Y., Su, F., Zhao, Y., Luo, X., Tang, X., Zhao, X., and Zhou, E., 1995, *Liq. Cryst.*, **19,** 743.

[11] Kato, T., Fukumasa, M., and Frechet, J. M. J., 1995, *Chem. Mater.*, **7,** 368.

[12] Kato, T., and Frechet, J. M. J., 1995, *Macromol. Symp.*, **98,** 311.

[13] Treybig, A., Dorscheid, C., Weissflog, W., and Kresse, H., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 369.

[14] Sideratou, Z., Paleos, C. M., and Skoulios, A., 1995, *Mol. Cryst. liq. Cryst.*, **265,** 19.

[15] Gray, G. W., and Jones, B., 1954, *J. chem. Soc.*, 1467.

[16] Demus, D., Demus, H., and Zaschke, H., 1974, *Flüssige Kristalle in Tabellen* (Leipzig: VEB Deutcher Verlag für Grundstoffindustrie).

[17] Johnson, S. L., and Rumon, K. A., 1965, *J. phys. Chem.*, **69,** 74.

[18] Odinokov, S. E., and Iogansen, A. V., 1985, *Spectrochim. Acta A*, **32,** 1355.

[19] Kato, T., Frechet, J. M. J., Wilson, P. G., Saito, T., Uryu, T., Fujishima, A., Jin, C., and Kaneuchi, F., 1993, *Chem. Mater.*, **5,** 1094.

[20] Kato, T., Uryu, T., Kaneuchi, F., Jin, C., and Frechet, J. M. J., 1993, *Liq. Cryst.*, **14,** 1311.

[21] Bellamy, L. J., 1972, *The Infra-red Spectra of Complex Molecules*, 2nd edn. (London: John Wiley).

[22] Lee, J. Y., Painter, P. C., and Painter, M. M., 1988, *Macromolecules*, **21,** 346.

[23] Lee, J. Y., Painter, P. C., and Painter, M. M., 1988, *Macromolecules*, **21,** 954.

[24] Blumstein, A., and Patel, L., 1974, *Mol. Cryst. liq. Cryst.*, **48,** 151.

[25] (*a*) Bryan, R. F., Hartley, P., Miller, R. W., and Shen, M.-S., 1980, *Mol. Cryst. liq. Cryst.*, **62,** 281; (*b*) Bryan, R. F., Hartley, P., and Miller, R. W., 1980, *Mol. Cryst. liq. Cryst.*, **62,** 311; (*c*) Bunning, J. D., and Lydon, J. E., 1979, *J. Chem. Soc. Perkin II*, 1621.

[26] Robertson, J. M., 1953, *Organic Crystals and Molecules*, (Ithaca: Cornell University Press).

[27] (*a*) Trotter, T., 1956, *Acta Cryst.*, **14,** 1135; (*b*) Doucet, J., Levelut, A. M., Lambert, M., Liebert, L., and Strzelecki, J., 1975, *J. Physique*, **36-C1,** 1351; (*c*) Doucet, J., Mornon, J. P., Chevalier, P., and Lifchitz, A., 1977, *Acta Cryst.*, **B33,** 1701; (*d*) Seurin, P., Guillon, D., and Skoulios, A., 1981, *Mol. Cryst. liq. Cryst.*, **71,** 51.

[28] De Vries, A., 1975, *J. Physique*, **36-C1,** 1.

[29] Guillon, D., Skoulios, A., and Benattar, 1986, *J. Physique*, **47,** 133.

[30] Leadbetter, A. J., 1979, *The Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (London: Academic Press).