X-ray investigation of the nematic and reentrant nematic phases of N-[(4-n-octyloxybenzoyloxy)-salicilidene]-4'-cyanoaniline

B. I. Ostrovskii[a]; B. M. Bolotin[ab]; M. A. Saidachmetov[a]

[a] Institute of Crystallography, U. S. S. R. Academy of Sciences, Moscow, U.S.S.R. [b] Organic Intermediates and Dyes Institute, Moscow, U.S.S.R.

PLEASE SCROLL DOWN FOR ARTICLE

X-ray investigation of the nematic and reentrant nematic phases of N-[(4-n-octyloxybenzoyloxy)-salicilidene]-4'-cyanoaniline

by B. I. OSTROVSKII, B. M. BOLOTIN† and M. A. SAIDACHMETOV

Institute of Crystallography, U.S.S.R. Academy of Sciences, Leninsky prospekt 59, Moscow 117333, U.S.S.R.

We have performed an X-ray scattering study of the nematic–smectic A and reentrant nematic–smectic A phase transitions in N-[(4-n-octyloxybenzoyloxy)-salicilidene]-4'-cyanoaniline (OOBOSCA). A diffractometer with a linear position sensitive detector was used. The results show that the smectic phase in OOBOSCA is of the A_d type with an interlayer spacing incommensurate with the molecular length L; $d \approx 1 \cdot 2L$. In the reentrant nematic phase two types of fluctuation modes were found. One of them corresponds to the monolayer wavevector $q_1 \approx 2\pi/L$, and the other is due to the partial bilayer fluctuations with the wavevector $q_2 \approx 0 \cdot 8q_1$. The temperature dependences of the interlayer spacing, X-ray scattering intensity and longitudinal correlation length for both types of layering in the reentrant nematic phase are presented. The change of the fluctuation regime from S_{A_d} to S_{C_d} type with decreasing temperature in the reentrant nematic phase of OOBOSCA was found. The results are discussed on the basis of models with competing order parameters. The influence of alkyl chain flexibility on the stability of a partial bilayer smectic phase is also considered.

1. Introduction

The existence of reentrant phases, that is phases with higher symmetry at lower temperature, is a well known phenomenon for liquid-crystalline systems. Beginning in 1975, when the first report of an unusual phase sequence nematic–smectic A-reentrant nematic was published [1]; there have been many such examples among liquid crystals of different chemical classes [2, 3]. It is now clear that the reentrant behaviour of liquid crystals is caused mainly by the effects of intermolecular association; these are especially pronounced in compounds consisting of molecules with a large terminal dipole moment. Such effects are also typical of mixtures of strongly polar liquid crystals as well as strongly polar compounds with weakly polar compounds. In addition to the monolayer smectic A_1 phase with an interlayer distance equal to the molecular length, $d \approx L$, in such systems bilayer smectic A_2 with $d \approx 2L$ and partial bilayer smectic A_d phases whose period is incommensurate with the molecular length, $L < d < 2L$ are observed [1–4]. The reentrant behaviour can be understood in terms of a monomer-dimer equilibrium to account for the antiparallel dipole correlation, in combination with van der Waals attraction, intermolecular steric hindrance and packing effects which determine the stability of the smectic phase [5]. The multiple reentrant phenomena in liquid crystals was reproduced with the frustrated spin-gas model [6], in which the dipolar frustration of molecules play an important role. The flexibility of the terminal alkyl chain also affects the stability of nematic and smectic A phases [7].

† Organic Intermediates and Dyes Institute, B. Sadovaya 1-4, Moscow 103787, U.S.S.R.

Reentrant behaviour is well described by a phenomenological model which involves two competing lengths, namely, the molecular length, L, and the length of the anti-parallel dipolar pairs, L', $L < L' < 2L$ [8]. The two wavevectors $q_1 = 2\pi/L$ and $q_2 = 2\pi/L'$ correspond to the density and local molecular polarization waves. Smectic phases with two incommensurate periods are stable only in some limited range of model parameters [8]. As a rule, the mode competition leads to frustration and formation of smectic layers of a certain type, A_1, A_2 or A_d. In those cases, when the free energies of the states $F(q_1)$ and $F(q_2)$ are of the same order of magnitude the fluctuations of the corresponding density waves blur the smectic phase resulting in the formation of the nematic phase. It is confirmed by the fact, that, as a rule, the stability ranges of the smectic A_1 and A_d phases are separated by the nematic [9, 10]. In those few cases, when the $S_{A_1} \leftrightarrow S_{A_d}$ line still exists in the phase diagram it rapidly terminates at the bicritical $NS_{A_1}S_{A_d}$ point, at a critical point similar to the gas-liquid critical point [11], or finishes with an island of the nematic phase [9].
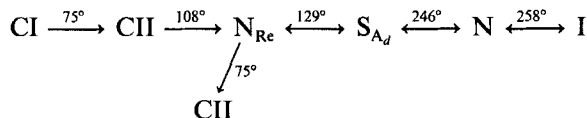
Thus, to obtain a better understanding of reentrant behaviour in liquid crystals it is important to study the nature of the associated states and the corresponding forms of lamellar packing. X-ray scattering is sensitive to changes in both the kind and period of the layer packing. The scattering spectra from the nematic phase give information on what type of structural units (monomers or dimers) and what type of lamellar packing are thermodynamically stable in the neighbouring smectic phase. In order to study the correlation between the reentrant behaviour of liquid crystals and the effects of intermolecular association we have carried out an X-ray investigation of reentrant polymorphism in N-[(4-n-octyloxybenzoyloxy)-salicilidene]-4′-cyano-aniline (OOBOSCA).

2. Experimental technique

The three ring compound N-(4-n-octyloxybenzoyloxy)-benzilidene-4′-cyano-aniline (1) shows the phase sequence [12]

$$C \rightarrow N_{Re} \leftrightarrow S_A \leftrightarrow N \leftrightarrow I.$$
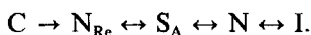
Mesogenic salicilideneanilines exhibiting a smectic C phase have also been described [13] although among these no reentrant mesogen has been reported. It was of interest therefore to synthesise a salicilidene-type analogue of compound (1) where reentrant polymorphism would include a smectic C phase. The chemical formulae of such an analogue is shown in figure 1. The transition temperatures were measured using a differential scanning calorimeter DSC-111 (SETARAM), optical microscopy and certain features of the X-ray scattering patterns. The phase sequence for OOBOSCA is

$$CI \xrightarrow{75°} CII \xrightarrow{108°} N_{Re} \xleftrightarrow{129°} S_{A_d} \xleftrightarrow{246°} N \xleftrightarrow{258°} I$$
$$\Big\downarrow 75°$$
$$CII$$

As is typical of many three ring compounds this is rather unstable chemically, especially when heated to 200°C. After some heating-cooling cycles the transition temperatures are reduced. At 75°C OOBOSCA reveals a phase transition between two

$$H_{17}C_8O\!-\!\langle\bigcirc\rangle\!-\!CO.O\!-\!\langle\bigcirc\rangle\!-\!CH\!=\!N\!-\!\langle\bigcirc\rangle\!-\!CN$$
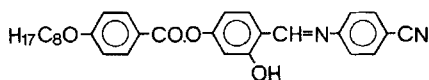$$OH$$

Figure 1. Molecular structure of OOBOSCA.

crystal modifications. In both crystalline phases wide angle X-ray patterns show a number of sharp reflections indicating long range positional order in the layer plane. The transition temperatures between smectic and nematic phases were determined by observing the broadening of the diffraction peaks centred about the wavenumber $q_0 = 2\pi/d$ corresponding to a smectic lattice spacing d.

To identify correctly a smectic phase (S_A or S_C) in OOBOSCA the following experiments were carried out.

(*a*) A study of the Freedericks transition in a planar oriented cell. The threshold of the transition in the nematic phase was shown to be typical of cyano derivatives with positive dielectric anisotropy, $U_{th.} \approx 3$ V. In the smectic phase, no Freedericks transition was observed for voltages up to 30 V. Thus, this is an orthogonal smectic phase [14, 15].

(*b*) A study of the linear electro-optical effect and the pyro-effect in a sample of OOBOSCA doped with a small amount of a chiral dipolar additive with a similar molecular structure. In the smectic C phase such an additive would remove an inversion centre resulting in the chiral ferroelectric smectic C* phase [16]. For OOBOSCA neither a linear electro-optic effect nor a pyro-effect were observed. Thus the smectic phase has to be referred to as S_A.

Our X-ray study in the small angle region was performed using a diffractometer with a linear, position sensitive detector and CuKα radiation. Details of the X-ray experiment were reported earlier [17, 18]. A window of the detector was placed in the detection plane in such a manner that we can take the picture of the scattering intensities corresponding to the cross-section of the reciprocal lattice along the $q_\parallel$ coordinate, that is parallel to the director **n**. In the experiments the position, intensity and angular width (in the nematic phases) were determined. Samples with dimensions $1 \cdot 5 \times 1 \cdot 5 \times 2$ mm^3 were placed between plane electrodes in a thermostat. The orientation of the liquid crystal was induced by an A.C. electric field of strength 1 kV cm^{-1} and frequency 3 kHz. The temperature was measured with a calibrated thermistor and thermocouple. The accuracy of maintaining and measuring the temperature was about $0 \cdot 01$ K.

Two dimensional diffraction patterns were studied by a standard photo technique using an X-ray tube with a point collimation of radiation.

3. Experimental results

Figure 2 shows typical small angle scattering patterns for OOBOSCA in the nematic, smectic A and reentrant nematic phases. The temperature dependence of the interlayer distance near the N $\leftrightarrow$ S$_{A_d}$ and N$_{Re}$ $\leftrightarrow$ S$_{A_d}$ phase transitions is shown in figure 3. In both the high temperature nematic N and the smectic A phases we can observe scattering in the vicinity of the wavevector q_2 corresponding to the smectic A$_d$ phase with a layer period $d_2 = 1 \cdot 2L$ ($L = 32$ Å). The scattering intensity in the nematic phase increases anomalously when the transition into the smectic A$_d$ phase is approached. In the reentrant nematic phase scattering in the vicinity of two vectors of reciprocal space, q_1 and q_2 with corresponding periods $d_1 \approx L$ and $L < d_2 < 2L$ is observed. The scattering intensity near the vector q_2 increases anomalously as the transition into the S$_{A_d}$ phase is approached while the intensity $I(q_1)$ is almost independent of temperature, (see figure 4). With decreasing temperature down to $|T - T_c| > 30°$C (the N$_{Re}$ phase is easily supercooled down to 75°C where crystallization occurs), the scattering by the monomeric density wave begins to dominate,
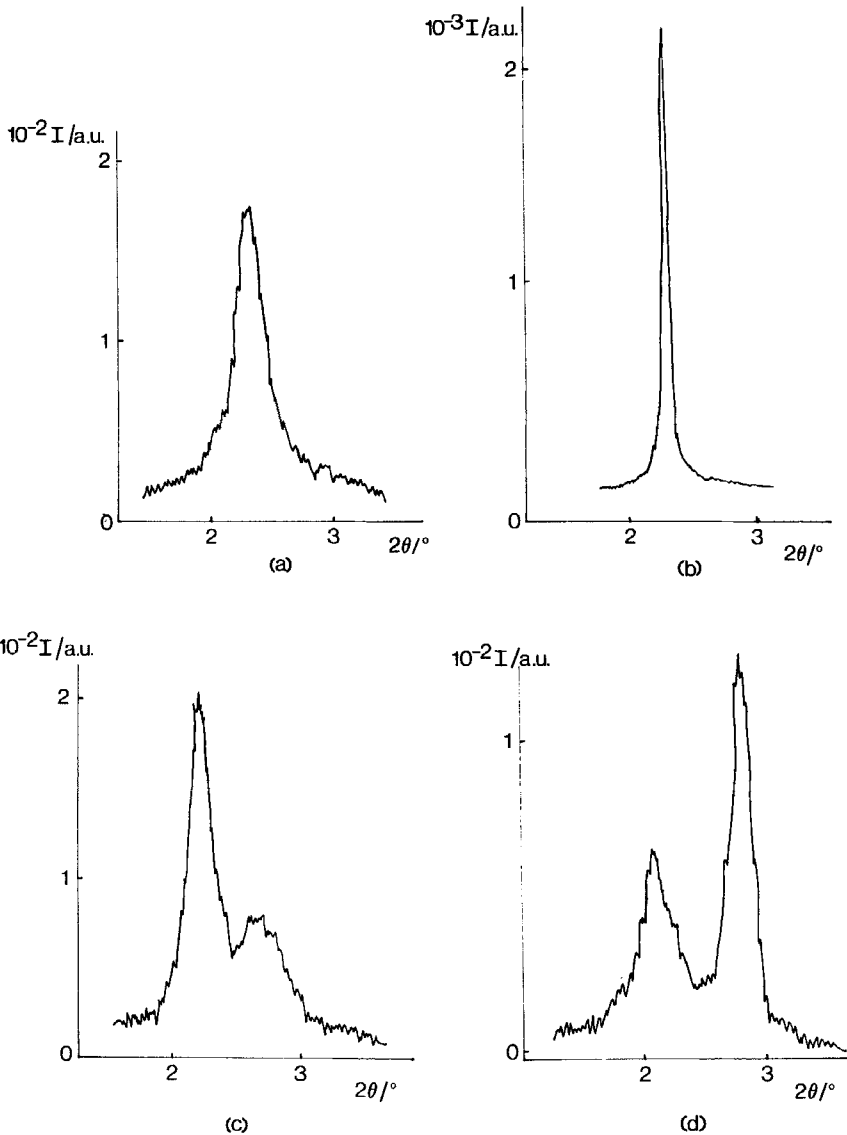
Figure 2. Small angle X-ray diffraction patterns for OOBOSCA; (a) nematic phase, $T - T_{S_A N} = 3°C$; (b) smectic A_d phase; (c) reentrant nematic phase, $T_{S_A N} - T = 15°C$; (d) reentrant nematic phase, $T_{S_A N} - T = 40°C$.

$I(q_1) > I(q_2)$. In the same temperature range, the small angle reflection corresponding to the dimeric wave (q_2) begins to split, going out of the meridional plane, (see figure 5). The latter is characteristic of a tilted lamellar structure observed in the pretransition region near the smectic C phase [19–21].

4. Discussion

The scattering intensity in the nematic phase consisting even partly of polar molecules involves three terms

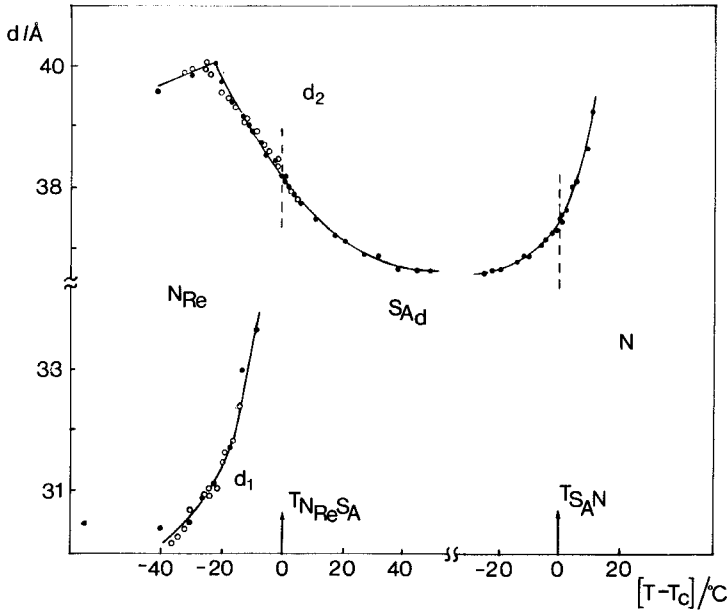$$I(\mathbf{q}) = I_N(\mathbf{q}) + I_{Sm_1}(\mathbf{q}) + I_{Sm_d}(\mathbf{q}). \tag{1}$$

Figure 3. Variation of the layer spacing d at the monolayer (d_1) and partial bilayer (d_2) density waves in nematic, smectic A_d and reentrant nematic phases for OOBOSCA; O, ● denote different series of measurements.

The first, pure nematic, is predetermined by the long range orientational order of the long molecular axes and by the short range order of the molecular centres of gravity. In small angle diffraction patterns this scattering is centred near the vectors $q_i = 2\pi/l_i$ related to the length of the molecular units of the medium (i.e. the molecules or their associates). Near the transition into a smectic phase long wavelength positional correlations along the director play an increasing role. The second and third terms in equation (1) correspond to the additional scattering from smectic fluctuations of the S_{A_1} and S_{A_d} types. Their contributions to the scattering are proportional to the correlations

$$I_{Sm_1}(\mathbf{q}) \sim \langle \psi_1^2(\mathbf{q}) \rangle; \quad I_{Sm_d}(\mathbf{q}) \sim \langle \psi_2^2(\mathbf{q}) \rangle,$$

where ψ_1 and ψ_2 correspond to the order parameters of the S_A phase relating to the modulation of the density (ψ_1) and the local polarization (ψ_2) in a liquid crystal [22]. In the Ornstein–Zernike approximation these correlations have a form $(i = 1, 2)$:

$$\langle \psi_{1,2}^2(\mathbf{q}) \rangle = \frac{kT\chi_i}{1 + \xi_{\parallel i}^2 (q_\parallel - q_{0i})^2 + \xi_{\perp i}^2 q_\perp^2}, \tag{2}$$

where χ_i are generalized susceptibilities, and $\xi_{\parallel i}$, $\xi_{\perp i}$ are correlation lengths parallel and perpendicular to the director. The longitudinal correlation length defines the size of the layered wave-train of either the monomeric or dimeric type in the direction of the long molecular axes. Because of the thermodynamic way we choose to achieve the $S_{A_d} \leftrightarrow N$ or $S_{A_1} \leftrightarrow N$ phase transition lines the critical increase of the scattering occurs for that mode which is thermodynamically stable in the corresponding S_A phase.

In our experiments with a linear position sensitive detector the scattering pattern analysed was determined by the cross-section of a reciprocal lattice node along the
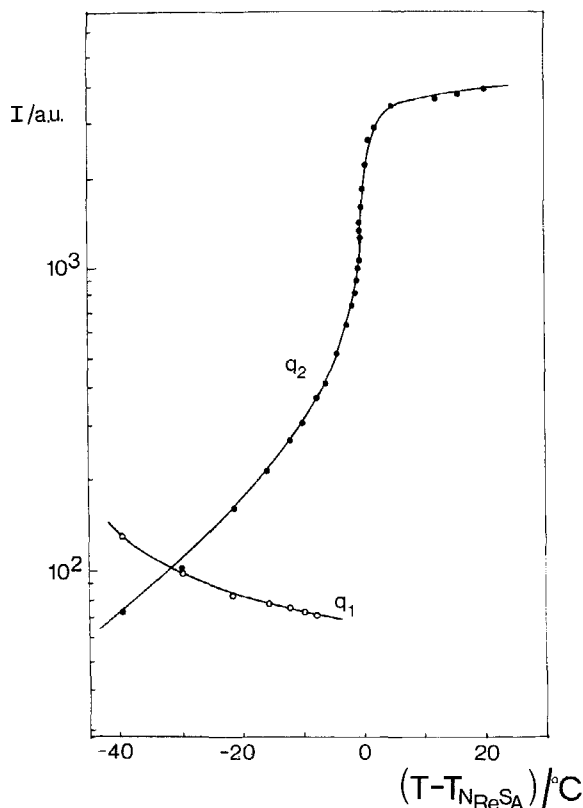
Figure 4. The temperature dependence of the X-ray scattering intensity at the monolayer (q_1) and partial bilayer (q_2) wavenumbers in the reentrant nematic and smectic A_d phases of OOBOSCA.

$q = q_\parallel$ direction. Using equation (2) the longitudinal correlation length $\xi_\parallel \sim \lambda/\Delta(2\theta)$ was calculated from experimental intensity profiles; here $\Delta(2\theta)$ is an angular width at half-height of the scattering curve.

The results obtained show that the smectic phase in OOBOSCA is an S_{A_d}. In the high temperature nematic phase the anomalous scattering results from S_{A_d}-like fluctuations and the temperature dependence of the longitudinal correlation length agrees well with the expression $\xi_{\parallel 2} = \xi_{\parallel 20}\tau^{-v_\parallel}$, see figure 6. The magnitude of the critical exponent, $v_\parallel$, of 0·72 and the bare correlation length, $\xi_{\parallel 20}$, of 8 Å are in accord with those for other nematic phases with similar ranges [17, 23, 24]. Quite another picture is observed for the reentrant nematic phase. True, the longitudinal correlation length $\xi_{\parallel 2}$ for the S_{A_d} fluctuation in the reentrant nematic phase increases anomalously on approaching the $N_{Re} \leftrightarrow S_{A_d}$ phase transition (see figure 7), however, with decreasing temperature there is a tendency to form smectic layers from individual molecules (monomers), see figures 2 and 3.

In our experiment we have not been able to observe the monolayer S_{A_1} phase for OOBOSCA, however the scattering from the nematic phase shows the diffuse peaks centred at the monolayer wavevector, q_1. The width of the q_1 scattering curve is indicative of a longitudinal correlation length, $\xi_{\parallel 1}$, of about 300–500 Å; this exceeds the molecular length of OOBOSCA ($L \approx 32$ Å) by approximately an order of
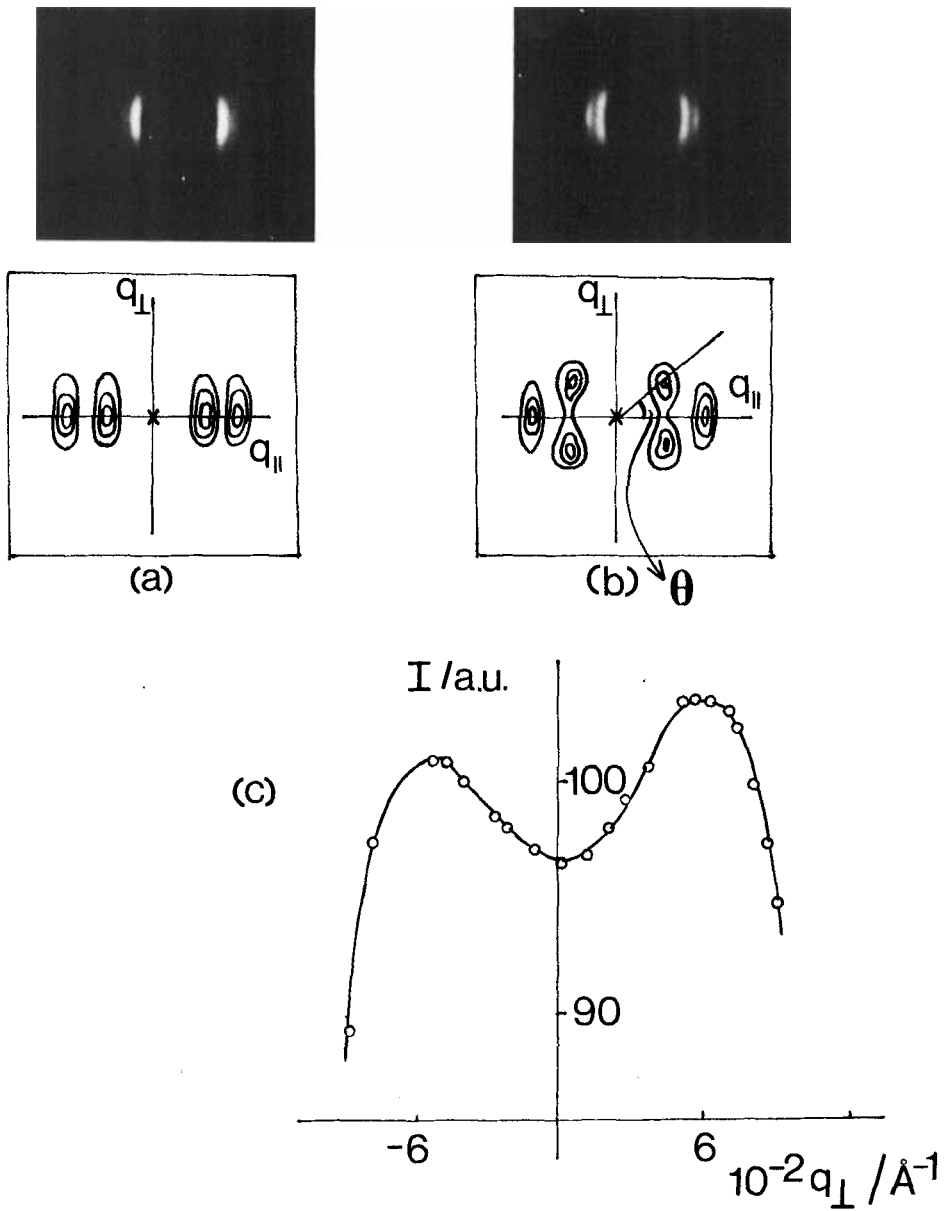
Figure 5. Small angle X-ray diffraction patterns and their schematic representation in a reentrant nematic phase for OOBOSCA; (*a*) X-ray scattering on the fluctuation density waves of S_{A_d} and S_{A_1} types; (*b*) X-ray scattering on the fluctuation density waves of S_{C_d} and S_{A_1} types, θ is the tilt angle in smectic C layers, $\theta \approx 18$–$20°$; (*c*) the densitometer trace of the S_{C_d}-like fluctuation scattering regions along the $q_\perp$ direction.

magnitude, see figure 7. The S_{A_1} fluctuation correlation length $\xi_{\parallel}$ increases slightly when the temperature is lowered thus displaying the proximity of the reentrant nematic phase to the $N_{Re} \leftrightarrow S_{A_1}$ transition line; however, this line is inaccessible because OOBOSCA crystallizes. It follows from our experiment that the monomeric lamellar structure of the N_{Re} phase dominates at low temperatures, see figures 2 and 7.
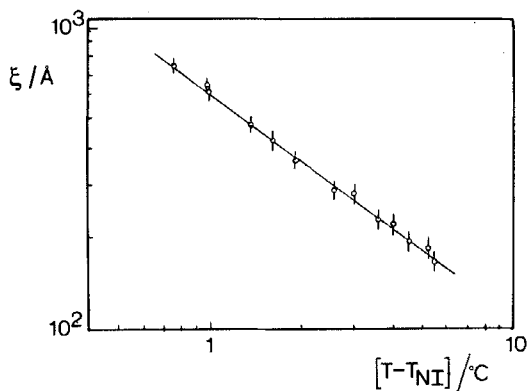
Figure 6.   The longitudinal correlation length $\xi_\parallel$ versus temperature in the nematic phase for OOBOSCA using a double logarithmic scale.
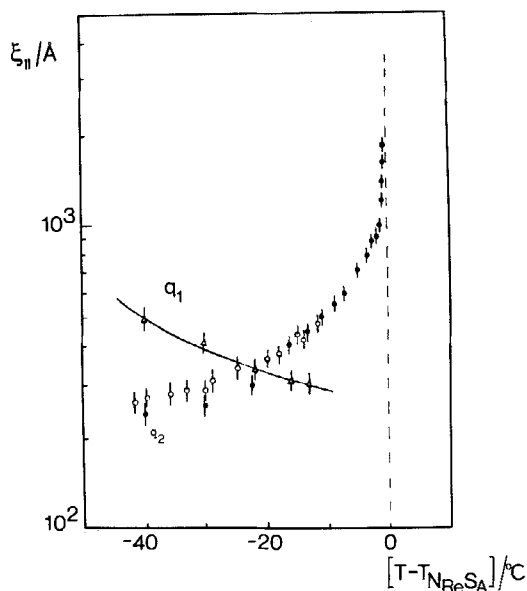

Figure 7.   The longitudinal correlation length of the monolayer (q_1) and partial bilayer (q_2) versus temperature in the reentrant nematic phase for OOBOSCA (○, ● denote different series of measurements).

Such examples were known earlier for lower homologues ($n \lesssim 7$–9) of some three ring compounds with a similar molecular structure, e.g. for alkoxybenzoyloxy-cyanostilbenes, the smectic A_1 phase is indeed, observed at low temperatures [2, 25–28].

    The data on longitudinal correlation lengths show that the reentrant nematic phase differs considerably from the conventional nematic phase and this difference is caused not only by the existence of fluctuating smectic domains of the S_{A_1} type. It follows from the data in figure 7, that even at $T \ll T_{S_A N}$ the magnitude of $\xi_{\parallel 2}$ is rather high, $\xi_{\parallel 2} \approx 300$–400 Å while in the ordinary nematic phase this value does not exceed 100 Å at $T - T_{S_A N} \approx 10°C$, see figure 7 (cf. also [17]). In addition, the temperature

dependence $\xi_{\|2}(T - T_c)$ does not follow a simple power law over the full nematic range as for ordinary nematic phases, see figure 6. Such behaviour may be connected with the effects of curvature of the smectic A–nematic phase boundary. The non-linearity of the phase boundary leads to an increase of the bare correlation length and a decrease of the range of the simple power law behaviour of the observed divergence with an approach to particular points on the phase diagram, for example, the reentrant point [24], or multicritical $NS_{A_1}S_{A_d}$ and $NS_A S_C$ points [29]. The exist- ence of the smectic A_1 fluctuations and the change of fluctuation regime from S_{A_d} to S_{C_d} type in the reentrant nematic phase of OOBOSCA makes this assumption highly probable.

We now consider the reentrant behaviour of OOBOSCA; various models have been proposed to understand reentrant polymorphism. The well-known approach is based on a combination of the McMillan theory for the S_A-N phase transition with a consideration of the association effects for polar molecules [4, 5, 30]. In this approach the phase transition are thought to be of the percolation type and occur at a certain concentration of dimers in a liquid crystal. The direct reason for the reentrant behaviour is an unfavourable increase of the packing entropy for molecules in smectic layers with increasing quantity of dimers at low temperature. Any other mechanism resulting in the unfavourable packing of molecules or their flexible moieties in smectic layers causes the same effect. For example, it has been shown [7], that the temperature dependent conformation of terminal alkyl chains affects the reentrant behaviour of liquid crystals. In microscopic theory [6, 31] the reentrant phase sequences are explained in terms of the stability of different dipolar configurations of the molecules. It is shown in the theory that a triplet of nearest-neighbour molecular dipoles may or may not be frustrated depending on the molecular close-packing conditions and the positional fluctuations ocurring along the direction parallel to the average molecular axis. Because of the corrigated architec- ture of the rigid parts and the alkyl chains the nearest neighbour molecules have a discrete set ($n = 4$–5) of energetically preferred positions of mutual permeation. Such a set of molecular permeations determines the effective molecular length of the neighbouring molecules. Phenomenological theory [8] discusses reentrant behaviour in terms of the competition between two virtually possible density waves of S_{A_1} and S_{A_d} types.

In order to understand the features of the reentrant behaviour of OOBOSCA we consider the temperature dependence of the interlayer distances d_1 and d_2, see figure 3. The distance d_2 changes continuously near the $S_{A_d} \leftrightarrow N$ and $N_{Re} \leftrightarrow S_{A_d}$ phase tran- sitions. Hence, the changes in d_2 are due to some processes of a general type involving the whole liquid-crystalline range. In addition, the period of the dimeric density wave in the smectic A_d phase of OOBOSCA does not change monotonically displaying a minimum in the middle of its range. As far as we know, such behaviour of d_2 has not been observed previously in liquid crystals exhibiting reentrant polymorphism, though d_2 could increase [25], decrease [32] or be constant [33, 34] with decreasing temperature. The temperature change in d_2 may be accounted for by a change in either the dimer size or the ratio of monomers and dimers. The change in d_2 may also be a result of competition between density waves of S_{A_1} and S_{A_d} types [8], or may be connected with some process of dipolar frustration [6, 31]. When the reentrant behaviour is due to a change in the ratio of the monomer and dimer quantities [4, 5] the sign of $\partial d_2/\partial T$ is predetermined unambiguously by the temperature behaviour of the ratio, $N/(N + M)$, where N and M are the quantities of the dimers and the

monomers, respectively. It is a result of a simple relationship between the interlayer
distance and the molecular lengths in the ordinary (L_M) and dimerized (L_D) states

$$d_2 = X_D L_D + (1 - X_D) L_M,$$

where X_D is the dimer concentration. This expression agrees well with experimental
data on d_2 for two ring compounds [4] and nematic mixtures of strongly and weakly
polar compounds [35–37]. So, it may be assumed that a decrease of d_2 in the high
temperature nematic phase and the neighbouring smectic A phase is caused by a
decrease of dimer concentration in OOBOSCA. This general tendency correlates
with a more pronounced monomeric lamellar structure of OOBOSCA at low tem-
peratures, see figure 2 and 3. With decreasing temperature in the partial bilayer state
as the free energies of monomeric and dimeric states become comparable the system
will begin to exhibit local fluctuations into the monolayer phase, these destroy the
partial bilayer order. Calculations which illustrate this effect have been given by Prost
and Barois in their phenomenological approach [8] and by Indekeu and Berker in
terms of dipolar frustrations [6, 31]. However, the non-monotonous character of the
$d_2(T)$ curve requires some additional mechanism to be considered. In our opinion, it
is the coupling of conformational degrees of freedom of the alkyl chains with
parameters which characterize the density and local polarization states of partial
bilayer smectics. At a microscopic level this may be discussed qualitatively as follows.
The partial bilayer smectics being loose enough in the alkyl chain regions as compared
to nematics, are very sensitive to any effect caused by changes in the packing entropy.
This is clearly seen for OOBOSCA. OOBOSCA has a rigid core consisting of a cyano
group attached to three phenyl rings linked by CH = N and COO groups and a
flexible *n*-octyloxy chain, see figures 1 and 8. The two benzene rings closest to the
polar head are not coplanar since the torsion angle between the aniline phenyl ring
and the plane of the CH = N fragment is about 30–60°. Furthermore, the plane of
the carboxyl group is rotated by about $\pi/2$ with respect to the salicilidene moiety. Thus,
the presence of the branched bridge fragments in OOBOSCA leads to the loss of
planarity for the aromatic rings. As a result the transverse dimensions of a rigid core
in the associated state increase as compared to the transverse sections of the alkyl
chains in the all-trans configuration, see figure 8. This leads to an unfavourable
increase of the packing entropy, which decreases the stability of the smectic A_d phase.
The response of the system on increasing the free volume in the S_{A_d} phase may be an
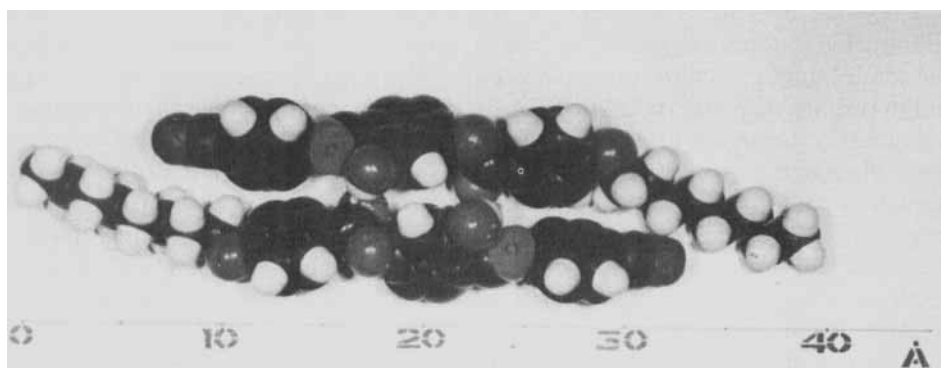

Figure 8.   A molecular model for a dimer of OOBOSCA.

orientational melting of the terminal alkyl chains [38], or an appearance of n-alkyl (alkyloxy) chain conformers since it costs easily achievable energy to make a trans-gauche rotation about any carbon–carbon bond. These conformers may be energetically favoured depending on temperature, the structure of the rigid core and the degree of overlapping of associated molecules. The conformers can give a dense packing in the S_{A_d} phase even at a large concentration of dimers at sufficiently high temperatures where their conformational disorder is high. At low enough temperatures, when the molecules are mainly in the all-trans conformation the unfavourable packing of alkyl chains can cause the transition to either the nematic or monolayer smectic A_1 phases. It is likely that the conformational order of the alkyl chains can affect the degree of overlapping of molecules in the S_{A_d} phase, which leads to a change in the dimer layer spacing. Thus, alkyl chain flexibility can affect the stability of nematic and smectic phases in liquid crystals of molecules with strongly dipolar heads via effects of packing. The numerical results obtained by Dowell [7] illustrate these effects well.

It can also be seen from the results in figure 8 that the OH group of one molecule in a dimer is in close proximity of the COO group of a neighbouring molecule. Thus, the formation of intermolecular hydrogen bonds is possible through the oxygen atoms of the carbonyl groups. Hence two types of associates can occur in OOBOSCA, one for antiparallel correlation of the electric dipoles and the other for hydrogen bonds. At high temperatures the intermolecular hydrogen bonds are destroyed, and the ordinary type of association is realized. At relatively low temperatures the intermolecular hydrogen bonds can stabilise the dimers more appreciably.

5. The change of the fluctuation regime of the reentrant nematic from the S_A to S_C type

At low temperatures the splitting of the small angle reflections with period d_2 was observed, see figure 5. The densitometer trace of the two dimensional diffraction pattern along the $q_\perp$ coordinate in reciprocal space is shown in figure 5. Two intensity maxima are easily seen in the figure. This result points to the appearance of fluctuating domains of the smectic C type in the N_{Re} phase. The change in the structure is confirmed by the break in the $d_2(T)$ curve, see figure 3. The tilt angle of molecules in the smectic layer is shown to be of the order of 15–18° (see figure 5). Thus, with decreasing temperature a change of the fluctuation regime of the nematic is observed from the S_A to S_C type, that is, the phase transition of the $S_{C_d} \leftrightarrow S_{A_d}$ type occurs within correlated domains with smectic order in the reentrant nematic phase.

As a rule a change of the fluctuation regime from the S_A to the S_C type is explained by the existence of a NS_AS_C multicritical point [39]. In this case a crossover line appears from one fluctuation regime to the other. Since the phase diagram for the nOBOSCA series is unknown and crystallization occurs before the formation of the S_A or S_C phases, we have no possibility to discuss our experimental data in terms of the existence of the NS_AS_C point.

Reentrant polymorphism involving the smectic C phase is a well-known phenomenon for liquid crystals whose molecules have both a longitudinal dipole at one end and properly located transverse dipoles [3, 12, 27, 33, 40, 41]. However, there are only a few examples when the smectic C lamellar organization appears in the fluctuation form in the nematic or smectic A phases in the absence of $S_C \leftrightarrow N$ or $S_C \leftrightarrow S_A$ phase transitions [26, 28, 42–45]. It should be noted that the smectic C

fluctuations coupled with the density wave are unstable in the neighbourhood of the smectic A phase. For example, in the mesogen studied in [44] the S_C-type fluctuation appears for the monomeric density wave in the smectic A_d phase. In studies [26–28] fluctuations of the S_{C_d}-type were observed against the background of the monomeric smectic A_1 structure. A question arises as to why the transition into the smectic C phase at the fluctuation level in OOBOSCA is coupled with the density wave not of the S_{A_1} type but of the S_{A_d} type.

It is well-known that the smectic C phase is more stable for liquid crystals consisting of molecules with large transverse dipole moments far removed from a molecular centre of gravity [46, 47]. In a dimer of OOBOSCA, in contrast to a monomer, there are two oppositely directed, transverse dipoles due to the oxygen atoms in the alkyoxy groups. The intermolecular hydrogen bonds, through the oxygen atoms of the carbonyl groups can also stabilize the smectic C phase (see figure 8). As a result, the transition into the smectic C phase at the fluctuation level is coupled with the dimeric density wave, see figure 5.

References

[1] CLADIS, P. E., 1975, *Phys. Rev. Lett.*, **35**, 48.

[2] HARDOUIN, F, LEVELUT, A. M., ACHARD, M. F., and SIGAUD, G., 1983, *J. Chim. phys.*, **80**, 53.

[3] NGUYEN HUU TINH, 1983, *J. Chim. phys.*, **80**, 83.

[4] CLADIS, P. E., BOGARDUS, R. K., and AADSEN, D., 1978, *Phys. Rev.* A,**18**, 2292.

[5] LONGA, L., and DE JEU, W. H., 1982, *Phys. Rev.* A, **26**, 1632.

[6] INDEKEU, J. O., and BERKER, A. N., 1986, *Physica* A, **140**, 368.

[7] DOWELL, F., 1987, *Phys. Rev.* A, **36**, 5046.

[8] PROST, J., and BAROIS, P., 1983, *J. Chim. phys.*, **80**, 65.

[9] HARDOUIN, F., 1986, *Physica* A, **140**, 359.

[10] SHASHIDHAR, R., SOMASEKHAR, S., and RATNA, B. R., 1986, *Molec. Crystals liq. Crystals*, **133**, 19.

[11] SHASHIDHAR, R., RATNA, B. R., KRISHNA PRASAD, S., SOMASEKHAR, S., and HEPPKE, G., 1987, *Phys. Rev. Lett.*, **59**, 1209.

[12] WEISSFLOG, W., PELZL, G., WIEGELEBEN, A., and DEMUS, D., 1980, *Molec. Crystals liq. Crystals Lett.*, **56**, 295.

[13] BOLOTIN, B. M., PILEIVA, D. S., ETINGEN, N. B., and NARKEVICH, YU. S., 1985, *Zh. Org. Khim.*, **21**, 362.

[14] BLINOV, L. M., 1983, *Electro-optical and Magneto-optical Properties of Liquid Crystals* (Wiley).

[15] PELZL, G., KOLBE, P., PREUKSCHAS, U., DIELE, S., and DEMUS, D., 1979, *Molec. Crystals liq. Crystals*, **53**, 167.

[16] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett., Paris*, **36**, 69.

[17] L'VOV, YU. M., OSTROVSKII, B. I., and FEIGIN, L. A., 1987, *Kristallografiya*, **32**, 972 (1987, *Sov. Phys. Crystallogr.*, **32**, 571).

[18] OSTROVSKII, B. I., PAVLUCHENKO, A. I., PETROV, V. F., and SAIDACHMETOV, M. A., 1989, *Liq. Crystals*, **5**, 513.

[19] CHISTYAKOV, I. G., and CHAIKOVSKY, W. M., 1969, *Molec. Crystals liq. Crystals*, **7**, 269.

[20] DE VRIES, A., 1970, *Molec. Crystals liq. Crystals*, **10**, 219.

21] McMILLAN, W. L., 1973, *Phys. Rev.* A, **8**, 328.

22] BAROIS, P., PROST, J., and LUBENSKY, T. C., 1985, *J. Phys., Paris*, **46**, 391.

23] LITSTER, J. D., ALS-NIELSEN, J., BIRGENEAU, R. J., DANA, S. S., DAVIDOV, D., GARSIA-GOLDING, F., KAPLAN, M., SAFINYA, C. R., and SCHAETZING, R., 1979, *J. Phys., Paris, Coll. C3*, **40**, 339.

24] KORTAN, A. R., VON KANEL, H., BIRGENEAU, R. J., and LITSTER, J. D., 1984, *J. Phys., Paris*, **45**, 529.

25] HARDOUIN, F., and LEVELUT, A. M., 1980, *J. Phys., Paris*, **41**, 41.

26] BROWNSEY, G. I., and LEADBETTER, A. J., 1980, *Phys. Rev. Lett.*, **44**, 1608.

27] FONTES, E., HEINEY, P. A., HASELTINE, J. L., and SMITH, A. B., 1986, *J. Phys., Paris*, **47**, 1533.

28] EVANS-LUTTERODT, K. W., CHUNG, J. W., OCKO, B. M., BIRGENEAU, R. J., CHIANG, C., GARLAND, C. W., CHIN, E., GOODBY, J., and NGUYEN HUU TINH, 1987, *Phys. Rev.* A, **36**, 1387.

29] SOLOMON, L., and LITSTER, J. D., 1986, *Phys. Rev. Lett.*, **56**, 2268.

30] DE JEU, W. H., 1983, *Phil. Trans. R. Soc.* A, **309**, 217.

31] INDEKEU, O., and BERKER, A. N., 1986, *Phys. Rev.* A, **33**, 1158.

32] VAZ, N. A. P., YANIV, Z., and DOANE J. W., 1983, *Molec. Crystals liq. Crystals*, **101**, 47.

33] SHASHIDHAR, R., RATNA, B. R., SURENDRANATH, V., RAJA, V. N., KRISHNA PRASAD, S., and NAGASHUSHAN, C., 1985, *J. Phys., Lett, Paris*, **46**, 445.

34] DIELE, S., JAECKEL, D., DEMUS, D., and SACKMANN, H., 1982, *Crystal Res. Technol.*, **17**, 1591.

35] CLADIS, P. E., GUILLON, D., BOUCHET, F. R., and FINN, P. L., 1981, *Phys. Rev.* A, **23**, 2594.

36] ZEINALOV, R. A., BLINOV, L. M., GREBYONKIN, M. F., OSTROVSKII, B. I., and SAIDACHMETOV, M. A., 1988, *Kristallografiya*, **33**, 185.

37] BLINOV, L. M., GREBYONKIN, M. F., ZEINALOV, R. A., OSTROVSKII, B. I., and PETROV, V. F., 1989, *Kristallografiya*, **34**, 398.

38] AVERYANOV, E. M., ADOMENAS, P. V., ZUIKOV, V. A., and ZYRIANOV, V. YA., 1986, *Zh. eksp. Teor. Fiz.*, **91**, 552.

39] MARTINEZ-MIRANDA, L. J., KORTAN, A. R., and BIRGENEAU, R. J., 1986, *Phys. Rev. Lett.*, **56**, 2264.

40] MADHUSUDANA, N. V., SHADASHIVA, B. K., and MOODITHAYA, P. L., 1979, *Curr. Sci.*, **48**, 613.

41] PELZL, G., DIELE, S., WIEGELEBEN, A., and DEMUS, D., 1981, *Molec. Crystals liq. Crystals Lett.*, **64**, 163.

42] DIELE, S., ROTH, K., and DEMUS, D., 1987, *Krist. Res. Technol.*, **21**, 97.

43] MADHUSUDANA, N. V., MOODITHAYA, P. L., and SURESH, K. A., 1983, *Molec. Crystals liq. Crystals*, **99**, 239.

44] LEVELUT, A. M., and DRUON, C., 1982, *J. Phys. Lett., Paris*, **43**, 193.

45] HARDOUIN, F., LEVELUT, A. M., NGUYEN HUU TINH, and SIGAUD, G., 1979, *Molec. Crystals liq. Crystals Lett.*, **56**, 35.

46] McMILLAN, W. L., 1973, *Phys. Rev.* A, **8**, 1921.

47] VAN DER MEER, B. W., and VERTOGEN, G., 1979, *J. Phys., Paris, Coll. C3*, **40**, 222.