Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Dielectric studies of nematic-smectic A-reentrant nematic transition in the 8OCB/6OCB mixtures

J. Jadżyn[a]; G. Czechowski[a]
[a] Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland

To cite this Article Jadżyn, J. and Czechowski, G.(1989) 'Dielectric studies of nematic-smectic A-reentrant nematic transition in the 8OCB/6OCB mixtures', Liquid Crystals, 4: 2, 157 — 163
To link to this Article: DOI: 10.1080/02678298908029068
URL: http://dx.doi.org/10.1080/02678298908029068

LIQUID CRYSTALS, 1989, VOL. 4, NO. 2, 157–163

Dielectric studies of nematic–smectic A–reentrant nematic transition in the 8OCB/6OCB mixtures

by J. JADŻYN and G. CZECHOWSKI
Institute of Molecular Physics, Polish Academy of Sciences,
Smoluchowskiego 17/19, 60-179 Poznań, Poland

(*Received 13 April 1988; accepted 29 July 1988*)

The results of measurement of the anisotropies of the electric permittivity and conductivity for pure 8OCB and 6OCB together with their mixtures are presented. It was found that (i) the dielectric properties of mesophases composed of molecules with a strong tendency to antiparallel association in the nematic phase (8OCB) and molecules which do not exhibit such a tendency (6OCB) undergo a drastic change in mixtures with a relatively low concentration of 6OCB, (ii) the effect of smectic density modulation in the N–S_A–N_R sequence is very subtle, and (iii) for concentrations higher than a critical value the nematic phase exhibits a smectic-like ordering which vanishes with increasing concentration of 6OCB.

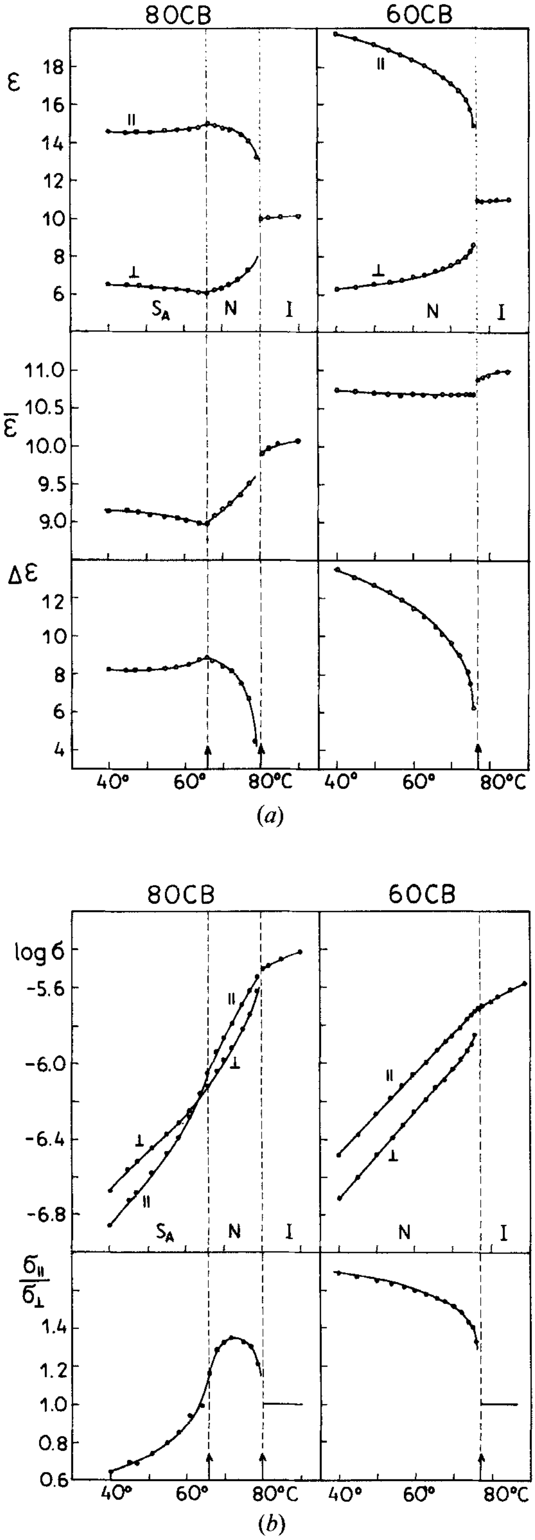
1. Introduction

The phase transition between a one dimensional solid-like smectic A and the three dimensional liquid-like nematic is one of the most important transitions in the physics of liquid crystals. The interest in this transition is enhanced by a variety of smectic A phases for which the parameters describing a structure of layers can be correlated with the molecular structure and the molecular interactions. A relatively small modification of the molecular properties may lead to a considerable change in the stability of the mesophase, and in some cases it may even cause a reversal of the natural phase sequence, for example the nematic phase can appear at a temperature lower than that of the stable smectic phase. Numerous experimental and theoretical papers were devoted to studies of this reentrant nematic phase, which was discovered by Cladis in 1975 [1]. This phase has been observed in mixtures [1, 2] as well as in single compounds at high [3] and atmospheric [4] pressure. At present many compounds and mixtures are known in which a reentrant nematic phase is observed [5, 6].

The mixture of 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) and 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) is a classic system in which the stable nematic reentrant phase is observed. Much precise and reliable data concerning this system have been reported in literature. Here, we present the results of electric permittivity and conductivity measurements carried out for pure 8OCB and 6OCB and seven of their mixtures: four from the concentration range in which the smectic phase exists, and three from that in which there is only the nematic phase.

2. Experimental

8OCB and 6OCB were synthesized by R. Dąbrowski and his coworkers. The transition temperatures of the pure compounds and their mixtures were in agreement with the literature values [7, 8]. The equipment and measuring method are described in a previous paper [9].



(a)

(b)

Figure 1. Electric permittivity (*a*) and conductivity (*b*) for pure 8OCB and 6OCB. ($\bar{\varepsilon} = \frac{1}{3}(\varepsilon_\parallel + 2\varepsilon_\perp)$, $\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp$).

3. Results and discussion

(*a*) *Pure 8OCB and 6OCB*

Figure 1 shows the results of electric permittivity and conductivity measurements for the pure mesogens.

In the *isotropic phase* both compounds exhibit quite similar properties. Their permittivity decreases slightly while approaching the isotropic–nematic transition, which indicates that the extent of their antiparallel association increases. Such behaviour is typical for nematogens with a terminal cyanide group. The difference in the value of permittivity in the isotropic phase of 8OCB and 6OCB reflects the difference in their molar volume (about 10 per cent). The activation energy for ionic movement determined from the electrical conductivity measurements in the isotropic phase is the same for both compounds and amounts to 0·28 ± 0·01 eV.

In the *nematic phase* the essential differences in dielectric properties of both compounds are observed. In 8OCB a strong antiparallel molecular association causing a considerable decrease in $\bar{\varepsilon}$ appears. This process lasts until the transition to the smectic A phase at about 67° C. The behaviour of 6OCB is quite different. The constant value of $\bar{\varepsilon}$ over the whole nematic range indicates that the extent of self-association achieved in the isotropic phase remains constant (excluding a jump at the nematic–isotropic transition). As a consequence of the strong reduction in the value of $\varepsilon_{\parallel}$ for 8OCB, 6OCB reveals a considerably larger dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$. These results agree with those obtained by Buka and Bata [10].

The electrical conductivity measurements also revealed quite different behaviour for these compounds. In nematic 8OCB we obtain significantly higher values of the conductivity activation energy ($E_{A\parallel} = 0{\cdot}83\,\mathrm{eV}$, $E_{A\perp} = 0{\cdot}80\,\mathrm{eV}$) in relation to those for 6OCB ($E_{A\parallel} = 0{\cdot}46\,\mathrm{eV}$, $E_{A\perp} = 0{\cdot}49\,\mathrm{eV}$). In the vicinity of the nematic–smectic A transition a considerable decrease in the value of $\sigma_{\parallel}$ for 8OCB changes the sign of the anisotropy. This effect is always accompanied with the formation of smectic layers which create an energy barrier for ions moving along the direction perpendicular to the layers (parallel to the director) [11–13].

(*b*) *Mixtures of 8OCB and 6OCB*

Figure 2 shows the phase diagram for the 8OCB/6OCB mixtures, obtained by Kortan and coworkers [8]. The transition temperatures obtained from our dielectric

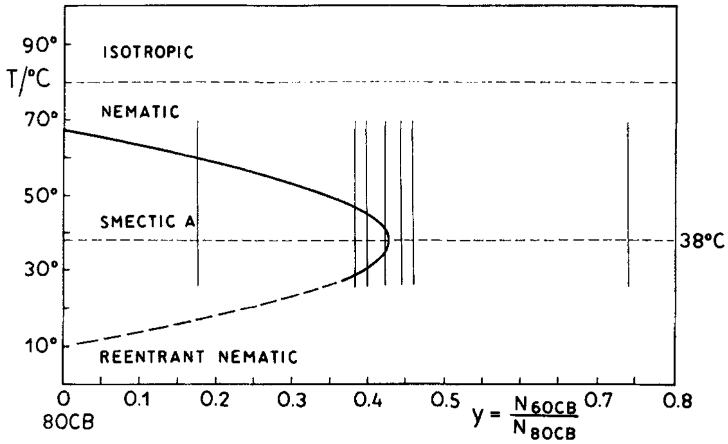
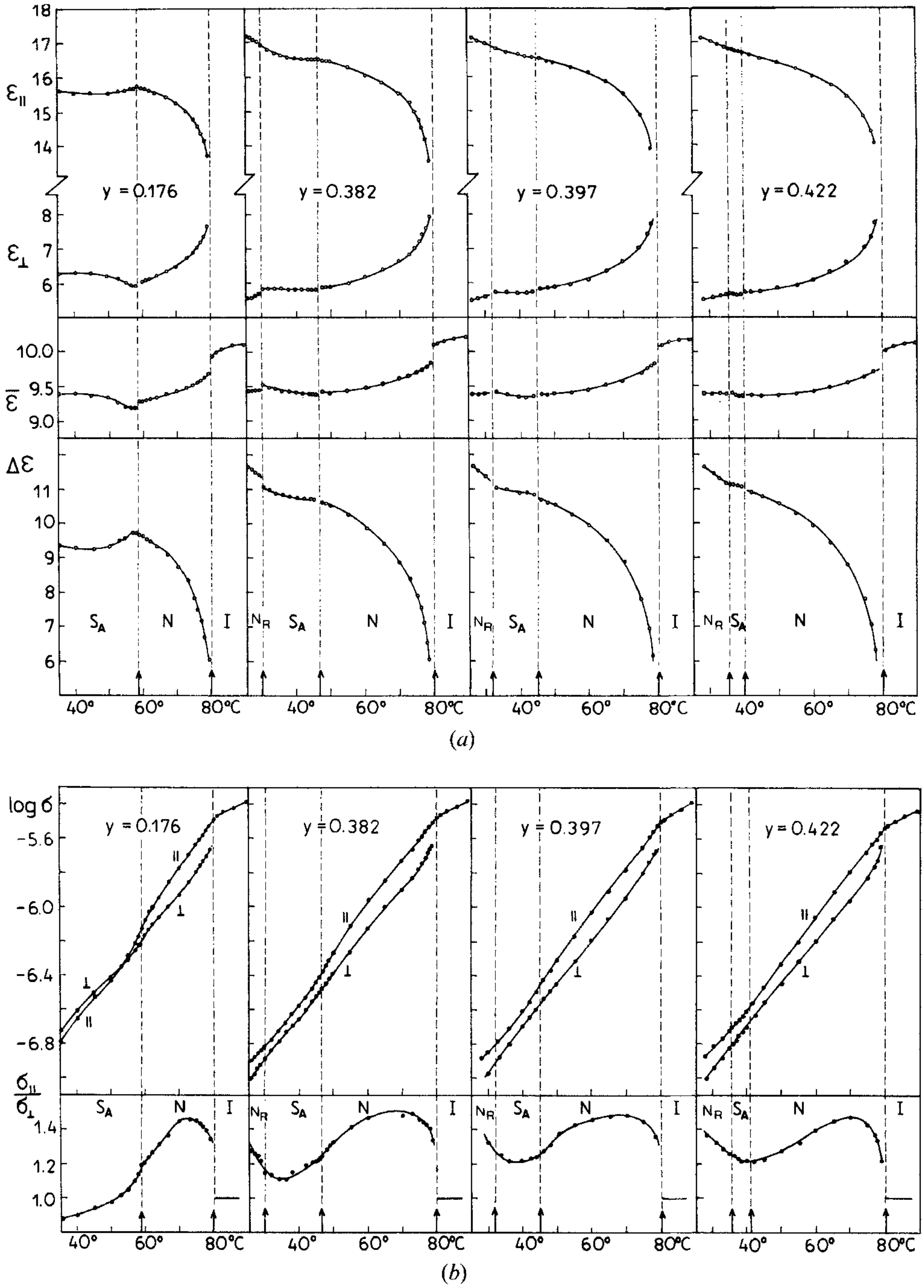


Figure 2. Phase diagram for the 8OCB/6OCB mixture [8]. The vertical lines denote the concentrations at which the dielectric measurements were made.

measurements, which were carried out for concentrations denoted by the vertical lines in figure 2, agree very well with this diagram.

Figure 3 shows the results of the permittivity and conductivity measurements obtained for the mixtures of 8OCB and 6OCB in which the smectic A phase exists.



(*a*)

(*b*)

Figure 3. Electric permittivity (*a*) and conductivity (*b*) for the 8OCB/6OCB mixtures measured in the nematic, smectic A and reentrant nematic phases.

In three mixtures of concentration $y = 0{\cdot}383$, $0{\cdot}397$ and $0{\cdot}422$ the reentrant nematic phase (N_R) was observed. These results lead to the following conclusions.

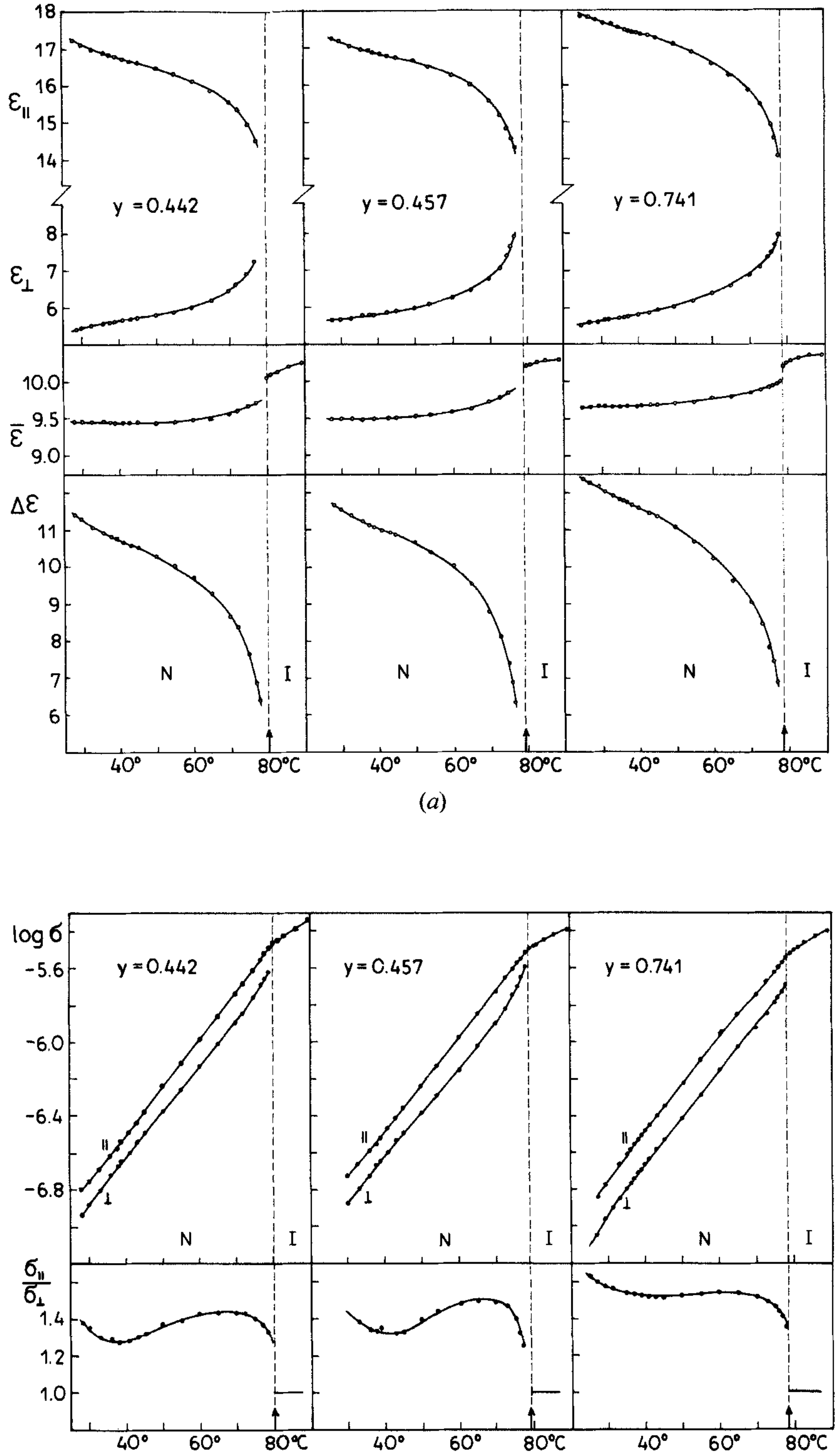
Increasing the concentration of 6OCB causes an increase in $\varepsilon_{\parallel}$ (in both nematic and smectic phases), which for the more or less constant value of $\varepsilon_{\perp}$ leads to an increase in the mean value of the electrical permittivity $\bar{\varepsilon}$ and dielectric anisotropy $\Delta\varepsilon$. Since the mixtures studied are composed of molecules in which the direction of the dipole moment (the cyano group) is the same as the direction of the molecular long axes an increase in $\varepsilon_{\parallel}$ means that in successive mixtures, shown in figure 3, the amount of dimers with antiparallel correlation, i.e. with a compensated dipole moment, is reduced. Especially drastic changes in the dielectric properties (and the electrical conductivity) are observed in mixtures with a relatively low concentration of 6OCB. Similar results were obtained by Buka and Bata [10], who interpreted the results of their electrical permittivity measurements in terms of a correlation factor.

Thus, the dielectric studies show that the reentrant nematic phase appears in the 8OCB/6OCB mixtures when the concentration of antiparallel dimers in the smectic A phase is greatly reduced in relation to pure 8OCB. This fact seems to be in contrast with the model of reentrant phase formation, according to which an increase in concentration of the antiparallel dimers in the already densely packed smectic A_d layers would lead to the S_A–N_R transition [14–16]. This difference has been discussed and convincingly illustrated by Chandrasekhar [17]. The discovery of the S_A–N_R phase transition made by Peltz and coworkers [18] in binary mixture of two terminal non-polar compounds, in which the smectic layers are monomolecular (A_1) means that the antiparallel correlations are not the only mechanism creating the reentrant nematic phase.

Another important conclusion can be drawn from the results of electrical conductivity measurements. A typical nematic–smectic A transition is always accompanied by a considerable decrease in the conductivity measured along the direction in which the long molecular axes are oriented ($\sigma_{\parallel}$), i.e. perpendicular to the smectic layers. Since the perpendicular component of the conductivity ($\sigma_{\perp}$) is usually insensitive to the nematic–smectic A transition, a decrease in $\sigma_{\parallel}$ leads to a change in the conductivity anisotropy in the smectic phase. This effect is also observed in pure 8OCB (cf. figure 1).

In the 8OCB/6OCB mixtures it looks quite different. So significant a decrease in $\sigma_{\parallel}$ to cause a detectable change in the conductivity anisotropy at the nematic–smectic A transition is observed only for the lowest concentration of 6OCB ($y = 0{\cdot}176$) studied. For higher concentrations of 6OCB at both the nematic–smectic A and smectic A–reentrant nematic transitions only subtle changes in conductivity are observed. However, these changes are quite distinctly visible in the temperature dependence of the $\sigma_{\parallel}/\sigma_{\perp}$ ratio; approximately in the middle of the temperature range in which the smectic phase exists (at about 38°C) $\sigma_{\parallel}/\sigma_{\perp}$ achieves its minimum value. Similar behaviour of the conductivity has been observed for other systems with a reentrant nematic phase [19–21].

Thus, the electrical conductivity measurements, especially $\sigma_{\parallel}$, show that the effect of density modulation in the smectic phase of the 8OCB/6OCB mixture is very subtle. This conclusion is in agreement with the results of N.M.R. measurements which showed that the N–S_A–N_R transitions in the 8OCB/6OCB mixture [22] are accompanied by a subtle change in the orientational order parameters. Analogous results have been obtained for 4-(4″-*n*-octyloxybenzoyloxy)benzilidene-4′-cyanoaniline (OBBC), which as a pure compound exhibits a reentrant nematic phase [23].



(a)

(b)

Figure 4. Electric permittivity (a) and conductivity (b) of the purely nematic 8OCB/6OCB mixtures. ($y > y_0$).

The drastic change in the permittivity and conductivity observed already for low concentration of 6OCB corresponds to the results of calorimetric studies carried out by Lushington *et al.* [24].

Figure 4 shows the results obtained for mixtures in which the concentration of 6OCB is higher than the critical value ($y_0 = 0{\cdot}427$), i.e. for mixtures with a nematic phase only. It is clearly visible that the dielectric properties (especially the conductivity) of this phase are essentially different from those of a typical nematic phase, e.g. in pure 6OCB. Analogous to other mixtures, in which the reentrant nematic phase exists [25], in nematics composed of the 8OCB/6OCB we also observe the smectic-like ordering which is gradually reduced on going away from the critical concentration. This effect manifests itself distinctly in the temperature dependence of $\sigma_{\|}/\sigma_{\perp}$, the minimum of which is located at a temperature similar to that observed in the smectic phase, i.e. about 38°C (cf. figure 3). Our dielectric studies agree with the observation made by Kortan *et al.* [8] who found on the basis of X-ray scattering studies the smectic-like fluctuations for concentrations of 6OCB greater than y_0.

The authors are greatly indebted to Professor R. Dąbrowski for the high purity samples of 6OCB and 8OCB. This work was supported by the Polish Academy of Sciences within the framework of Project CPBP 01.12.

References

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

[2] GUILLON, D., CLADIS, P. E. and STAMATOFF, J., 1978, *Phys. Rev. Lett.*, **41**, 1598.

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

[4] HARDOUIN, F., SIGAUD, G., ACHARD, M. F., and GASPAROUX, H., 1979, *Solid St. Commun.*, **30**, 265; 1979, *Physics Lett.* A, **71**, 347.

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

[6] TINH, N. H., 1983, *Molec. Crystals liq. Crystals*, **91**, 285.

[7] CHEN, N. R., HARK, S. K., and HO, J. T., 1981, *Phys. Rev.* A, **24**, 2843.

[8] KORTAN, A. R., VON KÄNEL, H., BIRGENEAU, R. J., and LITSTER, J. D., 1981, *Phys. Rev. Lett.*, **47**, 1206; 1984, *J. Phys., Paris*, **45**, 529.

[9] JADŻYN, J., and KĘDZIORA P., 1987, *Molec. Crystals liq. Crystals*, **145**, 17.

[10] BUKA, A., and BATA, L., 1986, *Molec. Crystals liq. Crystals*, **135**, 49.

[11] MIRCEA-ROUSSEL, A., and RONDELEZ, F., 1975, *J. chem. Phys.*, **63**, 2311.

[12] MIRCEA-ROUSSEL, A., LEGER, L., RONDELEZ, F., and DE JEU, W. H., 1975, *J. Phys., Paris*, **C1, 36**, 93.

[13] HEPPKE, G., and SCHNEIDER, F., 1974, *Ber. Bunsenges. phys. Chem.*, **78**, 910.

[14] CLADIS, P. E., 1981, *Molec. Crystals liq. Crystals*, **67**, 177.

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

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

[17] CHANDRASEKHAR, S., 1985, *Molec. Crystals liq. Crystals*, **124**, 1.

[18] PELZL, G., DIELE, S., LATIF, I., WEISSFLOG, W., and DEMUS, D., 1982, *Crystal. Res. Technol.*, **17**, K78.

[19] BOCK, M., and HEPPKE, G., 1980, *Advances in Liquid Crystal Research and Applications*, edited by L. Bata (Pergamon Press), p. 131.

[20] BOCK, M., GÖBL-WUNSCH, A., HEPPKE, G., RATNA, B. R., and SHASHIDHAR, R., 1982, *Molec. Crystals liq. Crystals*, **72**, 77.

[21] DĄBROWSKI, R., JADŻYN, J., PRZEDMOJSKI, J., and BARAN, J., 1987, *Crystal Res. Technol.*, **22**, 861.

[22] EMSLEY, J. W., LUCKHURST, G. R., PARSONS, P. J., and TIMIMI, B. A., 1985, *Molec. Phys.*, **56**, 767.

[23] MIYAJIMA, S., AKABA, K., and CHIBA, T., 1984, *Solid St. Comm.*, **49**, 675.

[24] LUSHINGTON, K. J., KASTING, G. B., and GARLAND, C. W., 1980, *Phys. Rev.* B, **22**, 2569.

[25] RATNA, B. R., SHASHIDHAR, R., BOCK, M., GÖBL-WUNSCH, A., and HEPPKE, G., 1983, *Molec. Crystals liq. Crystals*, **99**, 285.