A study of the induced helical pitch in a reentrant nematic mixture

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The temperature dependence of the induced helical pitch is reported for cholesteric and reentrant cholesteric phases of liquid crystal systems comprising 4-*n*-hexyloxy and 4-*n*-octyloxy-4′-cyanobiphenyl with a non-mesogenic optically active dopant. It was found that on adding small quantities of the dopant that the temperature range of the S_A phase is narrowed and subsequently disappears, while short range smectic fluctuations persist, influencing the helical twisting features. Critical index values were determined from the temperature dependence of the pitch.

Formation of a reentrant nematic phase (N_R) for mesogenic molecules with terminal polar groups is due to the temperature dependent dimerization of the polar molecules and can be described at the microscopic level in terms of the corresponding packing entropy gains in the system of interacting aromatic cores and aliphatic chains as compared with the conventional smectic A structure [1]. In general this picture is confirmed by the gradual increase of the nematic order parameter, S, for the phase sequence N–S_A–N_R [2]. A peculiar feature of both S_A–N and S_A–N_R transitions is the presence of smectic fluctuations. Addition of an optically active dopant to the reentrant nematic system gives rise to an induced helical structure in the N and N_R phases with the helical pitch, P, critically increasing in both cases on approaching the S_A phase [3]. There are few studies of the temperature dependence of the helical pitch in such systems and they provide only a qualitative description [3–5]. However, in a previous paper [6] the possibility of a numerical treatment of the temperature dependence of the pitch was shown for the cholesteric phase of 4-*n*-butyloxybenzylidene-4′-*n*-butylaniline (BBBA) induced by adding a non-mesogenic optically active dopant, and the values of intrinsic pitch P_0 and critical index $v_\perp$ were obtained. The character of the $P(T)$ dependence has been explained by the influence of the correlation length of smectic fluctuations on the critical growth of the helical pitch.

It would be interesting to analyse helical twisting features in systems possessing a N_R phase, to describe the temperature and concentration dependence of the helical pitch over the whole temperature range and to determine corresponding critical index values. To carry out these studies we have chosen liquid crystal mixtures of 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) and 4-*n*-octyloxy-4′-cyanobiphenyl (8OCB) which possess a N_R phase in the molar concentration range $y = x_{6OCB}/x_{8OCB} \approx 0\cdot31$–$0\cdot45$. Using a polarizing microscope, the limiting concentration value y_0 of $0\cdot437$ was obtained, differing somewhat from $0\cdot427$ [7]; this was probably due to different
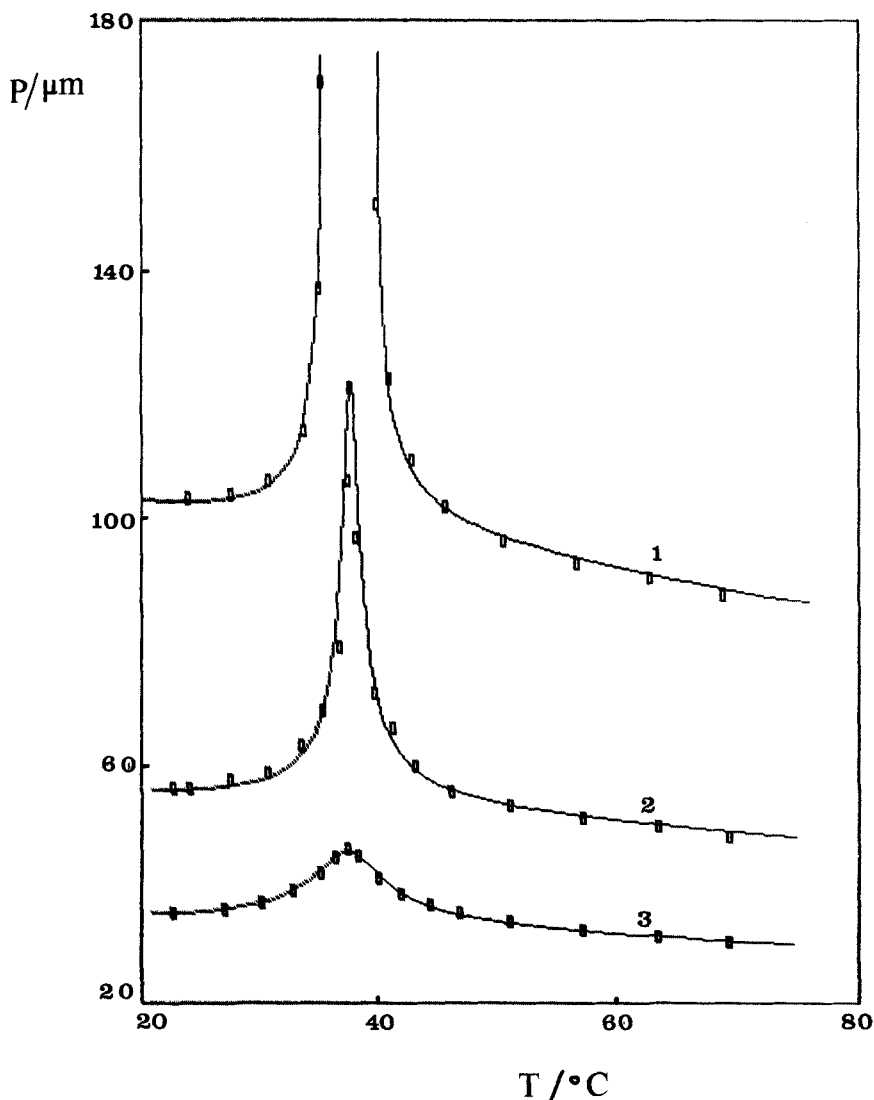
Figure 1.   The temperature dependence of the pitch for system II (see the table) optically active
dopant concentrations: (1) x_{OAD} = 0·04 mol %; (2) 0·07 mol %; (3) 0·11 mol %. The solid
lines correspond to numerical calculations.

impurity concentrations in the initial substances. The dopant used was 2-(4′-
phenylbenzylidene)-p-menthane-3-one, the concentration of which varied from 0·04
to 0·36 mol %. Variation of the optically active dopant concentration allowed us to
study the $P(T)$ critical behaviour at different distances from the reentrant point. The
direct measurement of the helical pitch was carried out by the Grandjean–Cano
method using a polarizing microscope. The glass surfaces were rubbed with diamond
paste (dimension of the grain ≈ 1 μm) to obtain the preferred planar orientation. The
wedge angle was changed from 0·6° to 1·8° depending on the measured pitch value. The
temperature was monitored with an accuracy of 0·05°C. The temperature dependence
of the pitch was measured with slow cooling in the N* phase and slow heating in the
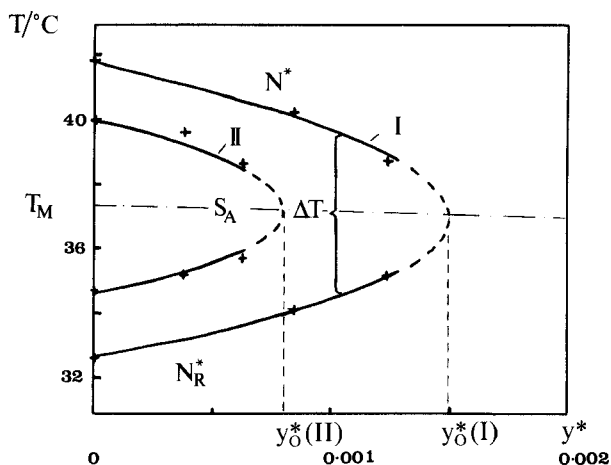
Figure 2. Parts of the phase diagrams for the mixtures studied: (I) $y = 0.425$; (II) $y = 0.433$. The dashed lines represent extrapolated data.

N_R^* phase. The transition to the smectic A phase was identified by the appearance of the characteristic needle texture [4], with the needles oriented normal to the free boundary with air in the thick part of the wedge and directed deep into the sample. Such a texture could have been caused by a difference in the surface tension values on the orientating surfaces with different boundary conditions.

The temperature dependence of the induced helical pitch for different dopant concentrations is shown in figure 1 and parts of the phase diagram for different compositions ($y_1 = 0.425$ and $y_2 = 0.433$) are given in figure 2. Increasing the dopant concentration results in the pitch decreasing and the S_A phase range narrowing. The $P(T)$ dependence measured is characterized by an asymmetrical pitch growth on approaching the N^*–S_A and N_R^*–S_A transitions. The S_A phase disappears at a certain dopant concentration, and the $P(T)$ plot is transformed into a continuous curve with a sharp peak P_M, decreasing with further addition of the optically active dopant. Comparison of the $P(T)$ dependence for different matrix compositions indicates that the broader the initial smectic range the greater is the dopant concentration needed to destroy the S_A phase. Disappearance of the S_A phase for $y \approx 0.31$ corresponding to the maximum smectic range occurs below a dopant concentration of ≈ 2.2 mol %. A detailed study of the complete phase diagram for the ternary mixture 6OCB + 8OCB + OAD is important to understand molecular interaction effects and it will be reported elsewhere. We note that the character of the ternary mixture phase diagram depends upon the mesogeneity of the dopant, i.e. the similarity of shape and molecular structure of the dopant and the liquid crystal molecules. In our case the non-mesogenic 2-(4′-phenylbenzylidene)-*p*-menthane-3-one causes a slight depression of the nematic–isotropic transition temperature T_{NI} and T_M, where T_M is the temperature for P_M corresponding to the midpoint of the smectic range (see the table). It follows from our experiments that T_M coincides with the midpoint of the smectic range ΔT (see figure 2).

Since a small amount of the dopant added to the 6OCB + 8OCB reentrant nematic mixture influences the phase diagram in the same way as the addition of extra 6OCB, the boundary of the S_A phase in the T–y^* coordinates should be a parabola (where $y^* = x_{OAD}$ mol %$/x_{6OCB+8OCB}$ mol %). Then, accounting for the doubling of

Characteristics of the 8OCB + 6OCB systems ((I) $y = 0.425$, (II) 0.433) doped with 2-(4'-phenylbenzylidene)-p-menthane-3-one.

System	x_{OAD}/mol %	T_{NI}/°C	$T_{S_A N*}$/°C	T_M/°C	$T_{N_R^* S_A}$/°C	$\nu_{N_R^*}$	ν_{N*}
	0.09	78.3	40.3	37.25†	34.2	0.49	0.48
I	0.14	78.15	–	37.0	–	0.41	0.39
	0.36	78.0	–	37.1	–	0.24	0.22
	0.04	78.35	39.7	37.5†	35.3	0.64	0.50
II	0.07	78.3	–	37.55	–	0.54	0.50
	0.11	78.2	–	37.3	–	0.48	0.46

$$\dagger\, T_M = (T_{N_R^* S_A} + T_{S_A N*})/2.$$

the critical index at the reentrant point [7], P can be expressed as

$$P = P_0(T) + A[(T - T_M)^2 - (\Delta T/2)^2]^{-\nu}, \qquad y^* < y_0^*,$$

$$P = P_0(T) + A[(T - T_M)^2 + B(y^* - y_0^*)]^{-\nu}, \quad y^* > y_0^*,$$

where $\Delta T = T_{S_A N*} - T_{N_R^* S_A}$, y_0^* is the value of the mole ratio y^* corresponding to the reentrant point on the T–y^* diagram. The values of the critical index ν, as well as the constants A and B were found numerically by minimizing standard deviations of the values according to the procedure in [6]. $P_0(T)$ was approximated as a linear function with the slope and initial value calculated at the experimental point, where fluctuations are minimal.

The numerical calculations performed separately for the high temperature branch ($T > T_M$) and the low temperature branch ($T < T_M$) lead to different values of ν. Considering the reentrant behaviour we cannot neglect the temperature dependence of the orientational order parameter S. So, S_A–N and S_A–N_R transitions take place against the background of different degrees of orientational order. Apart from this, with y values close to the initial mixture value y_0 and the lower non-mesogenic dopant concentrations the critical indices increase (see the table), apparently approaching the corresponding $\nu_\perp$ values of the initial mixture (0.62 [7]). This implies that the perpendicular correlation length $\xi_\perp = \xi_\perp^0 (T/T_c - 1)^{-\nu_\perp}$ (where T_c corresponds to $T_{S_A N*}$ or $T_{N_R^* S_A}$) plays a major role in determining the helical twisting in the pretransitional regions, in agreement with our earlier assumption [6].

The high sensitivity of the reentrant system to the impurity content indicates the presence of strong smectic fluctuations. The influence of the optically active dopant upon the smectic phase is similar to that of an increased 6OCB concentration, but the molecular mechanisms are different. In the latter case orientational order is preserved, while in the former case the non-mesogenic impurity causes a decrease of the smectic correlation length, modifying the system in a manner similar to the helium to mean field crossover. Finally, we note that the critical exponents obtained are dependent on the $T_{S_A N}/T_{NI}$ values. The complete description of the processes in such systems is a complex problem, requiring a proper estimate of the correlation length $\xi_\perp^0$ versus $T_{S_A N}/T_{NI}$.

References

[1] LONGA, L., and DE JEU, W. H., 1982, *Phys. Rev.* A, **26**, 1632.
[2] EMSLEY, J. W., LUCKHURST, G. R., PARSONS, P. J., and TIMIMI, B. A., 1985, *Molec. Phys.*, **56**, 767.

[3] CHILAYA, G. S., DESTRADE, C., ELASHVILI, Z. M., IVCHENKO, S. P., LISETSKY, L. N., NGUYEN HUU TINH., and VINOKUR, K. D., 1985, *J. Phys. Lett. Paris*, **46**, L-75.

[4] VAZ, N. A. P., YANIV, Z., and DOANE, J. W., 1983, *Molec. Crystals liq. Crystals Lett.*, **92**, 75.

[5] ISAERT, N., JOLY, G., DESTRADE, C., and NGUYEN HUU TINH, 1988, *Revue Phys. Appl.*, **23**, 273.

[6] TOLMACHEV, A. V., LISETSKY, L. N., and TISHCHENKO, V. G., 1988, *Kristallografia*, **33**, 788.

[7] KORTRAN, A. R., VON KANEL, H., BIRGENEAU, R. J., and LITSTER, J. D., 1981, *Phys. Rev. Lett.*, **47**, 1206.