

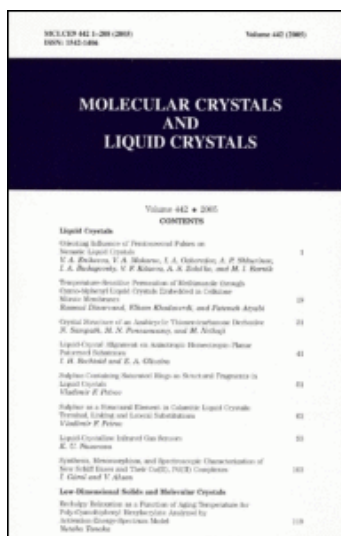
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Ratio of the Bend to Splay Constants of Some Binary Mixtures Exhibiting the Induced Smectic-A Phase

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We report the ratios of bend to splay (k_{33}/k_{11}) elastic constants of 4'-*n*-heptyl-4-cyanobiphenyl (7CB), (2-hydroxy)-*p*-ethoxybenzylidene-*p*'-butylaniline (OH-EBBA) and two of their mixtures which exhibit the induced smectic A phase. k_{33}/k_{11} goes down to ~ 0.6 for the composition which is rich in OH-EBBA.

INTRODUCTION

It is now well established that when two nematogenic compounds, only one of which has the strongly polar cyano end-group, are mixed together, the mixtures exhibit an "induced smectic-A" phase (denoted hereafter by the symbol A_I) over a certain range of compositions.¹⁻⁴ The A_I -nematic transition temperature exhibits a maximum for a definite composition. Mutual interactions between the strongly polar and weakly polar (or nonpolar) molecules appear to be responsible for the formation of the A_I phase. Supporting evidence for this conclusion comes from the X-ray studies of Engelen *et al.*⁵ on some systems exhibiting this phase. Neighboring molecules in the strongly polar cyano-compounds have antiparallel correlations,⁶ with the result that in a pure one-component system composed of a cyano-compound there is a bilayer structure⁷ with a layer spacing ~ 1.4 times the length of the molecules. In mixtures exhibiting the A_I phase, the spacing is "monolayer" (corresponding to an appropriate average of the molecular

lengths of the two constituents) for compositions relatively rich in the weakly polar component. As the composition of the cyano-component is increased and the maximum in the A_I - N transition point is crossed, the layer spacing increases and finally reaches the value corresponding to the bilayer structure of the pure cyano compound.

Recently we⁸ have studied the phase diagram of binary mixtures of 7CB and OH-EBBA which exhibit the A_I phase. In this paper, we report the measurements of the splay and bend elastic constants of some compositions of the 7CB-OHEBBA mixtures,⁹ and discuss the results in terms of a physical model.

EXPERIMENTAL

7CB and OH-EBBA were synthesized in our chemistry laboratory. The phase transition temperatures were determined using a polarization microscope equipped with a Mettler hot stage (Model FP-52). In some cases the phase transitions were also studied using a differential scanning calorimeter (Perkin Elmer model DSC-2). The splay and bend elastic constants were determined by the Freedericksz transition technique. The experimental details are given in some of our earlier publications^{10,11} and will not be repeated here.

RESULTS AND DISCUSSION

(a) Phase diagrams.

The phase diagram of the mixtures of 7CB and OH-EBBA is shown in Figure 1. The two pure compounds show only the N phase but the mixtures having between about 15–65 mole per cent of 7CB exhibit an A_I phase in addition to the N phase. The peak in the A_I - N transition curve occurs at ~35 mole per cent of 7CB. The NI transition is also influenced by this peak, as can be seen from the figure. For higher percentages of 7CB, the A_I - N transition takes place over fairly wide ranges of temperature, i.e., A_I and N phases coexist over relatively broad temperature ranges. For these compositions, when the mixture is cooled from the N phase, batonnets begin to appear in the field of view of the microscope at a certain temperature indicating that the NA_I transition has just started. The transition is complete only after cooling the sample by a few degrees when the batonnets cover the entire area giving rise to a focal conic texture. For percentages of 7CB lower than that corresponding to the

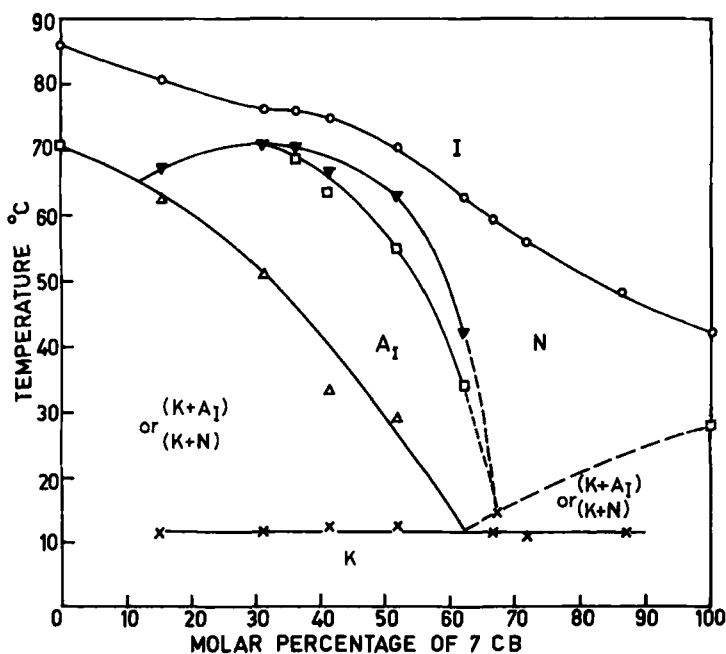


FIGURE 1 Phase diagram for the mixtures of 7CB and OH-EBBA.

peak in the A_I/N transition curve, the A_I/N transition takes place over a relatively short temperature range which has not been explicitly shown in the diagram. For low concentrations of either of the components, the mixtures show only the nematic mesophase. For some 7CB-rich compositions, the A_I/N , solid-nematic ($K-N$) and solid- A_I transition temperatures could not be determined accurately. These have been represented by dashed lines in the diagram.

We may now try to understand the physical mechanism of the formation of the A_I phase. At low concentrations of 7CB, individual molecules of 7CB may be expected to be surrounded by OH-EBBA molecules. The strongly polar 7CB molecules polarize the neighboring OH-EBBA molecules. This interaction would conceivably be very strong if the OH-EBBA molecules collect around a 7CB molecule such that a layered arrangement is formed. Another interaction which can be considered is a charge transfer interaction, OH-EBBA acting as an electron donor and 7CB as an acceptor. Sharma *et al.*¹² have demonstrated the formation of charge-transfer complexes between alkyl amino biphenyls and various acceptor mesogens by the observation of

an additional absorption band with negative dichroism in mixtures of such compounds. This interaction also favors the formation of layers. Beyond a certain concentration of 7CB, the layered arrangement takes on long range characteristics giving rise to the A_I phase. As the concentration of 7CB is increased, some of the neighbors of a given 7CB molecule will be 7CB molecules themselves, and above $\sim 35\%$ concentration, a part of 7CB will retain the bilayer structure. As a consequence the average layer spacing starts to increase. Further, since pure 7CB shows only the nematic phase, the build up of the bilayer structure at the cost of the monolayer structure reduces the $A_I N$ transition point. Thus, in the A_I phase and in the N phase close to $T_{A_I N}$, the medium with compositions having more than 35% of 7CB consists of a mixture of bilayer and monolayer species. The presence of both of these species also explains the relatively wide regions of coexistence of the A_I and N phases in the phase transition region.

(b) Elastic constants.

The splay and bend elastic constants can be determined by using the formula¹⁰

$$k_{ii} = \frac{x_0^2 H_c^2}{\pi^2} \frac{\Delta K}{M} s \rho \quad (1)$$

where x_0 is the thickness of the sample, H_c the Freedericksz threshold field, ΔK the anisotropy of the molar mass susceptibility of a perfectly oriented medium with $s = 1$, ρ the density, and M the molecular weight. In order to get the absolute values of elastic constants, we should know the absolute values of ΔK , s and ρ for all the systems studied. These measurements will be reported later. We can however get the ratios of k_{33}/k_{11} directly from the present measurements, since only x_0 and H_c corresponding to the bend and splay constant experiments are needed for this purpose.

We have made the measurements for 7CB, OH-EBBA, mixture I of these compounds in the molar ratio 16 : 84 and mixture II in the molar ratio 62 : 38. The transition temperatures for these systems are given in Table I. In Figure 2 we have plotted the ratio (k_{33}/k_{11}) as a function of relative temperature for all the cases considered. $k_{33}/k_{11} \approx 0.8$ for OH-EBBA and decreases slightly with decrease of temperature. This result can be compared with the k_{33}/k_{11} ratio of OH-MBBA,¹³ which is slightly greater than 1 at lower temperatures and becomes less than 1 as the temperature approaches T_{NI} . In 7CB, $k_{33}/k_{11} \approx 1$ at temperatures close to T_{NI} and gradually increases as the temperature is decreased. In

TABLE I
Transition temperatures of the systems under study

	Smectic-nematic	Nematic-isotropic
OH-EBBA	—	85.8°C
Mixture I ^a (84% of OH-EBBA)	65°C	80.5°C
Mixture II ^a (38% of OH-EBBA)	42°C	62.5°C
7CB	—	42.2°C

^a Corresponds to the highest point in coexistence region.

mixture II, at higher temperatures k_{33}/k_{11} is intermediate between those of the pure components. Close to T_{NI} , it is slightly less than 1 and increases as the temperature is decreased, and shows the usual pretransitional increase close to the $A_I N$ transition temperature. Mixture I has the lowest values of k_{33}/k_{11} and it decreases as the temperature is

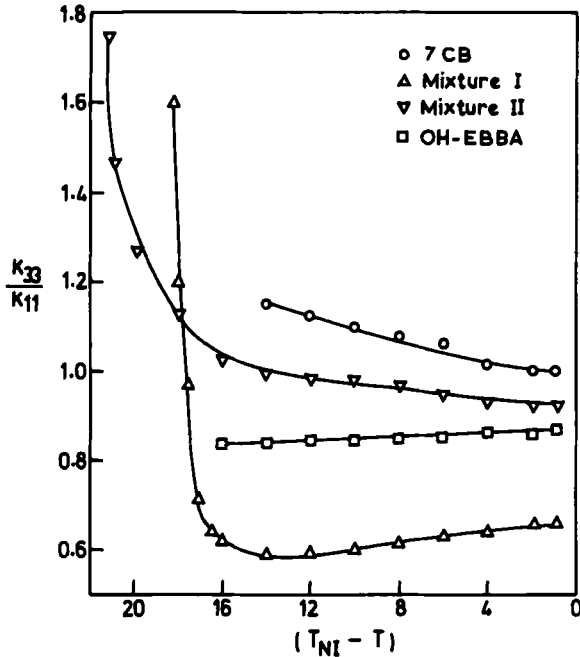


FIGURE 2 The ratio of (bend/splay) elastic constants of OH-EBBA, mixture I, mixture II and 7CB plotted against relative temperatures.

lowered from T_{NI} attaining a value <0.6 before it sharply increases as the $A_I N$ transition point is approached.

We can qualitatively understand some of these results in terms of Priest's theory¹⁴ of elasticity of nematic liquid crystals, which is a detailed analysis based on the mean field theory. The results of the theory can be expressed as

$$\left. \begin{aligned} k_{11}/\bar{k} &= 1 + \Delta - 3\Delta'(\bar{P}_4/\bar{P}_2) + \dots \\ k_{22}/\bar{k} &= 1 - 2\Delta - \Delta'(\bar{P}_4/\bar{P}_2) + \dots \\ k_{33}/\bar{k} &= 1 + \Delta + 4\Delta'(\bar{P}_4/\bar{P}_2) + \dots \end{aligned} \right\} \quad (2)$$

where $\bar{k} = (k_{11} + k_{22} + k_{33})/3$ and Δ and Δ' are molecular parameters depending on the nature of the compound and $\bar{P}_2 (=s)$ the average second order Legendre polynomial and \bar{P}_4 the average fourth order Legendre polynomial. If Δ and Δ' are positive, Eqs. (2) lead to result that if $k_{33}/k_{11} < 1$, (\bar{P}_4/\bar{P}_2) is negative. This means that \bar{P}_4 is negative since \bar{P}_2 is always positive for the systems under investigation. Negative \bar{P}_4 values have been observed experimentally in Raman scattering studies^{15,16} of some other compounds.

Further, Δ and Δ' are related to the length to breadth ratio (R) of the molecules.¹⁴ The higher the value of R , the larger will be the value of (k_{33}/k_{11}) . Indeed, in a pure hard rod model,¹⁴ Δ and Δ' are only functions of R , and it turns out that as R goes below ~ 1.5 , k_{33}/k_{11} will be less than 1¹³ even when \bar{P}_4 is positive.

Referring to Figure 1, it is clear that mixture I lies on the left side of the peak in the $A_I N$ transition curve and hence the layer spacing corresponds to an appropriate average length of the single molecules, as we argued earlier. On the other hand, the composition of mixture II lies on the right side of the peak in the $A_I N$ transition curve and the sample will be a mixture of monomolecular and biomolecular species. At any given relative temperature, the value of k_{33}/k_{11} for mixture I is lower than that of mixture II. This could either mean that (\bar{P}_4/\bar{P}_2) is more negative in mixture I than in mixture II, or, if it has comparable values in the two cases, the value of R is lower in mixture I than in mixture II. The latter explanation is to be preferred in view of the X-ray results. Moreover, in these cases where short-range order effects are strong, R has to be interpreted as equal to $\xi_{\parallel}/\xi_{\perp}$ ^{10,11} where ξ_{\parallel} and ξ_{\perp} are the correlation lengths of the cybotactic groups along and perpendicular to the director respectively, rather than as the length to breadth ratios of individual molecules.^{17,18} Lastly the value of (k_{33}/k_{11}) for mixture II lies in between those of mixture I and 7CB. This is again a consequence of

the fact that mixture II is indeed a mixture of monomolecular and bimolecular species.

Park and Labes¹⁹ have studied the splay elastic constants of mixtures of MBBA and 5CB which exhibit an induced smectic phase. They found that at the same relative temperature, as the concentration of 5CB in the mixture is increased from 0, k_{11} increases up to a certain concentration and thereafter remains almost constant. More recently, Scheuble *et al.*²⁰ have measured the k_{33}/k_{11} ratios of some multicomponent systems which also exhibit the induced smectic A phase. They found that there was a considerable lowering of k_{33}/k_{11} in compositions with 7–20% of the polar compound. These results are in agreement with the trend observed by us and could be explained in a similar manner.

In conclusion, we may point out that we^{10,11} and subsequently others¹⁷ found that $k_{33}/k_{11} < 1$ in some pure compounds and related this result to low values of $\xi_{||}/\xi_{\perp}$. In the present investigation, we have found a lowering of k_{33}/k_{11} in mixtures because of specific intermolecular interactions which also lead to the formation of the induced smectic A phase.

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