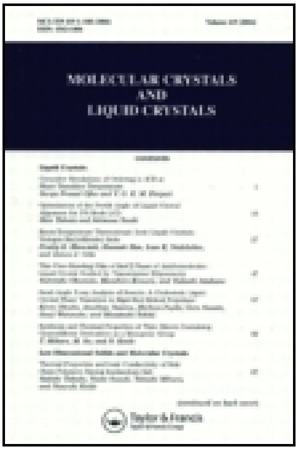

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The Bend and Splay Elastic Constants on Approaching an Injected Smectic Phase[†]

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Measurements have been made of the splay and bend elastic constants (k_{11} and k_{33}) of a series of hybrid mixtures exhibiting an injected smectic phase. We have observed large pre-transitional increases in k_{11}, k_{33} and k_{33}/k_{11} close to the smectic phase. Outside this pre-transitional region k_{11} increases and k_{33} decreases on approaching the injected smectic phase by changing composition or temperature. The results have been attributed to an enhancement in the smectic-like local ordering in accord with a recent theory.

INTRODUCTION

Multiplexed twisted nematic display devices require nematogens with sharp electro-optic characteristics.[1] These can be achieved using hybrid mixtures containing both terminally cyano-substituted nematogens and nematogens with non-polar end groups. These mixtures show the required low ratio of the bend to splay elastic constants (k_{33}/k_{11}). The addition of just 30 m% of a *p*-dialkyl substituted nematogen to a terminally cyano-substituted nematogen produces a large reduction in k_{33}/k_{11}.[2] The use of homologues with longer alkyl chains can offer further reductions in k_{33}/k_{11}; for example the BDH hybrid mixtures[3] E130 and E140 owe their excellent multiplexing properties to the use of long alkyl chain components. However, this approach can create problems, since the use of long alkyl chains sometimes results in the introduction of an injected smectic phase.[3,4]

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 6–10, 1982.

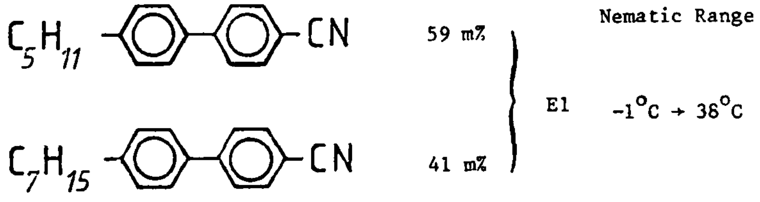
We have measured the elastic constants of a series of hybrid mixtures to study the effects of the injected smectic phase. The results are rationalized by considering the pre-transitional smectic region separately from the rest of the phase diagram where we suggest, following the work of Leadbetter and Mehta[5] and Van der Meer *et al.*,[6] that the smectic-like local ordering is important.

EXPERIMENTAL METHOD

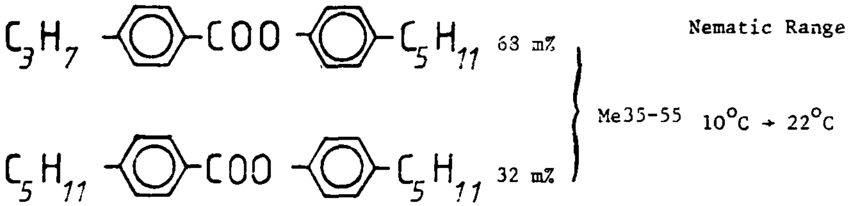
The splay and bend elastic constants (k_{11} and k_{33}) were determined from the capacitance–voltage characteristics of a homogeneously aligned (zero twist and tilt) nematic layer, distorted by an electric field applied normal to the layer.[2] An automatic system was used to measure the change in capacitance to within 0.01%, and the voltage to 10^{-4} V at various temperatures stabilized to 0.1°C over a range of 0°C to 100°C. The capacitance–voltage data and the permittivity components are fitted to the continuum theory by a three parameter, non-linear, least squares fitting program to give k_{11} and k_{33} to within 2% and 5%, respectively. Generally, the deviations between the fitted curve and the experimental data points were less than 10^{-4} V, which represents the resolution of the voltage measurements. However, within a few degrees centigrade of the injected smectic phase, the deviations increased and the accuracy of these results is somewhat less.

HYBRID MIXTURES

The terminally cyano-substituted nematogen studied was the BDH eutectic mixture El[7] which contains:



For the non-polar end group nematogen the following *p*-dialkyl nematic mixture was used:



The phase diagram for the series of hybrid mixtures is shown in Figure 1. El and Me35-55 were chosen to ensure a nematic range of at least 20°C over most of the phase diagram; the melting point was a problem only at very high Me35-55 compositions. An injected smectic A phase (S_A) is centered about the 55 m% Me35-55 composition. The nematic to smectic transition temperatures (T_{SN}) are sufficiently low to ensure little effect on the nematic to isotropic temperatures (T_{NI}), which, to a good approximation, vary linearly with composition across the phase diagram.

ELASTIC CONSTANT RESULTS

Measurements of k_{11} and k_{33} were made at fixed reduced temperatures for various compositions of the hybrid mixture. The results for k_{33} are shown in Figure 2. At a fixed reduced temperature, k_{33} is found to reduce rapidly as the concentration of Me35-55 increases for mixtures containing less than

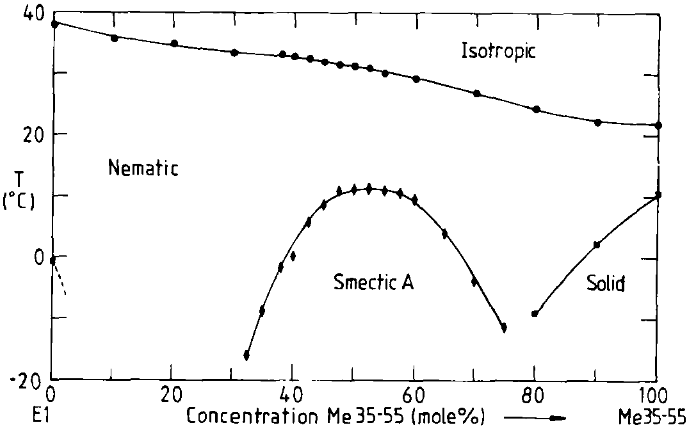


FIGURE 1 Phase diagram of the hybrid mixtures.

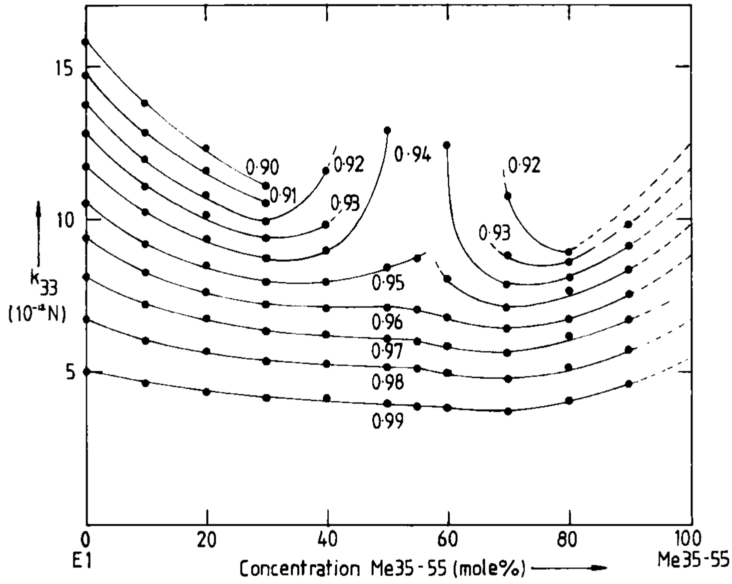


FIGURE 2 Bend elastic constants (k_{33}) at equal reduced temperatures (T/T_{NI} = 0.90 to 0.99).

40 m% Me35-55. We have observed a similar trend for a large number of terminally cyano-substituted nematogens when these are mixed with *p*-dialkyl substituted nematogens, where this reduction in k_{33} at least partially accounts for the sharp decrease in k_{33}/k_{11} reported for these mixtures.[2] For hybrid mixtures exhibiting the injected smectic phase, k_{33} is found to increase with decreasing temperature as T_{SN} is approached and to diverge rapidly a few degrees from the transition.

The k_{11} results illustrated in Figures 3 and 4 show a general increase for all compositions as the injected smectic phase is approached, and within a few degrees of T_{SN} the increase is more rapid. This trend has also been observed by Scheuble *et al.*,[8] for hybrid mixtures containing 8 CB with up to 15m% *p*-dialkyl substituted nematogen.

The ratio k_{33}/k_{11}, shown in Figure 5 for reduced temperatures of 0.96 and 0.94, is decreased on approaching the injected smectic phase, except in the region close to the smectic phase (within 15°C of T_{SN}) where k_{33}/k_{11} is found to increase rapidly with decreasing temperature. This occurs because k_{33} diverges more rapidly than k_{11} in this pre-transitional region.

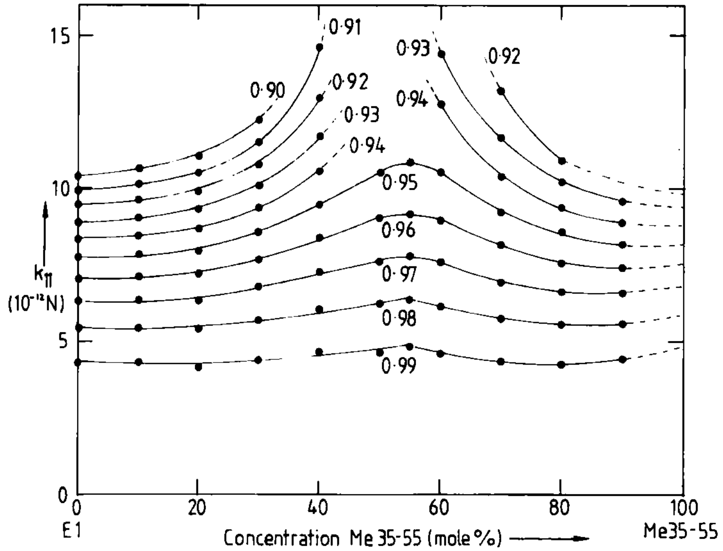


FIGURE 3 Splay elastic constants (k_{11}) at equal reduced temperatures (T/T_{NI} = 0.90 to 0.99).

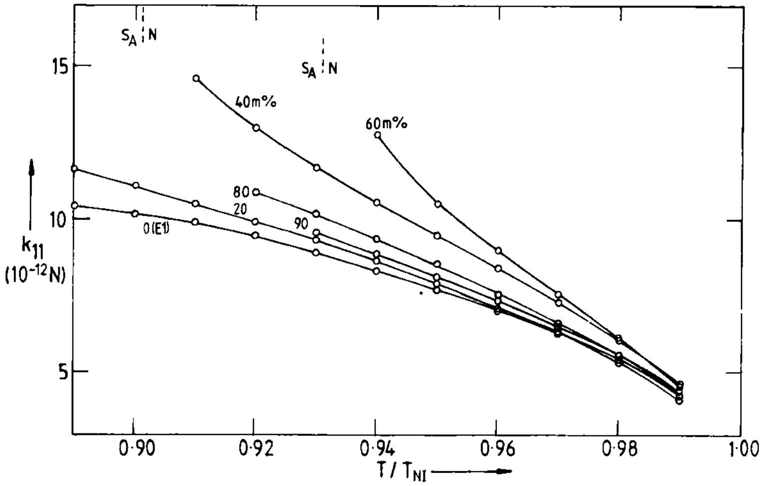


FIGURE 4 Splay elastic constants (k_{11}) at various concentrations of Me35-55 up to 90 m%.

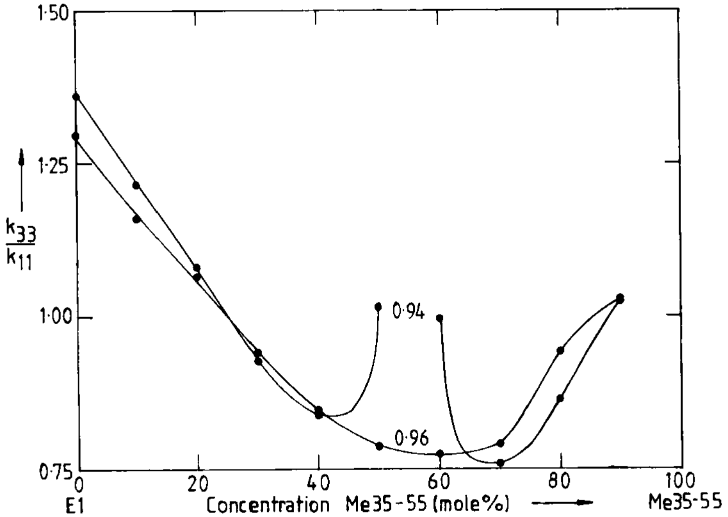


FIGURE 5 Ratio of bend to splay elastic constants (k_{33}/k_{11}) at equal reduced temperatures (T/T_{NI} = 0.94 and 0.96).

DISCUSSION

In a "classical" nematic, the molecular centers have a random distribution, whereas a smectic A is characterized by imperfect layers formed by the alignment of the molecular centers in the plane normal to the director (**n**). This can be visualized as a periodic density wave parallel to **n**. X-ray measurements[9,10] show nematics to have weak, heavily damped density waves which are indicative of weak, short range smectic-like ordering. Typically, the ordering extends over a few molecules, so there can be no periodic layer structure, just a preference for the molecular centers to align in the plane normal to **n**. However, close to a smectic phase the correlation length of the smectic-like ordering increases dramatically, causing the formation of transient smectic regions identifiable with the pre-transitional region.[11,12] The elastic constant results for the hybrid mixtures can be rationalized by isolating the pre-transitional region from the "normal" nematic region where the smectic-like ordering is of much shorter range. Such a rationalization was first suggested by Gruler[13] who attributed the tempressure variation of the elastic constants, observed in the homologous series of 4,4′-di-n-alkoxyazoxybenzenes, to changes in the smectic-like ordering. He described four nematic regions, the additional two regions being pre-transitional isotropic ordering and "classical" nematic without any local ordering; we believe none of our measurements falls in these two regions.

Region I: Pre-transitional Ordering

Figure 2 clearly shows a pre-transitional increase in k_{33} for compositions exhibiting the injected smectic phase, within about 15°C of T_{SN}. This is expected because a bend deformation cannot be supported by a smectic structure as it would require a distortion of the layers.[13] In the pre-transitional region it is the transient, pseudo layers which oppose the bend deformation, causing an increase in k_{33} proportional to the correlation length of the ordering.[12]

A pre-transitional increase in k_{11} is also evident from Figures 3 and 4. Splay deformations are consistent with a smectic A structure and so this pre-transitional increase might appear anomalous. Similar pre-transitional increases in k_{11} have been observed in other systems exhibiting monolayer smectic A phases,[14–17] but they are not evident in systems with bilayer smectic A phases.[18–20] Recently, Madhusudana[21] has argued that the pre-transitional increase in k_{11} results from the re-normalization of k_{11}, predicted by the Grinstein and Pelcovits non-linear elastic theory of the smectic A phase.[22,23] This re-normalization is related to the smectic layer compression elastic constant which is believed to be significantly larger in monolayer smectics, causing the re-normalization effects to be more apparent.

Region II: Smectic-Like Local Ordering

The remainder of the phase diagram falls within the region characterized by damped density waves indicative of smectic-like local ordering. The elastic constants are illustrated in Figures 2, 3 and 5 and, disregarding the results in the pre-transitional region, they show that k_{11} increases and k_{33} decreases on approaching the injected smectic phase, leading to a sharp drop in k_{33}/k_{11} towards the center of the phase diagram.

The order parameters, obtained from refractive index measurements, normalized using a mean field extrapolation method,[24] vary approximately linearly across the phase diagram with a slight decrease of a few per cent over the S_A phase. Therefore, the large changes observed in k_{11} and k_{33} across the phase diagram cannot be attributed to changes in the order parameter.

A recent theoretical model by Van der Meer *et al.*,[6] enables us to rationalize our elastic constant results in terms of changes in the smectic-like local ordering. Their theory models the elastic constants of a nematic with perfect orientational order by assuming distributed harmonic forces between the molecules. Two pair distribution functions are considered, enabling both a "classical" nematic and a nematic with smectic-like local ordering to be simulated. The latter is modeled by assuming a Gaussian distribution for the function describing the positions of the molecular centers in a direction parallel to the director. Although their theory is for perfect ordering, we feel justified in applying it to our results, since at equal reduced temperature, the order parameter is found to be constant to within a few per cent.

Their theory predicts that:

$$\frac{k_{33}}{k_{11}} = \frac{L^2}{W^2}\frac{4}{3}\frac{\langle be(\alpha)\rangle}{\langle st(\alpha)\rangle} \tag{1}$$

where L and W are the molecular length and width respectively, and α is the normalized displacement between molecules in a direction parallel to the director. $\langle be(\alpha)\rangle$ and $\langle st(\alpha)\rangle$ are the averages of functions of α and are related to the degree of smectic-like local ordering. An increase in the local ordering is simulated by increasing the intensity of the Gaussian distribution, and this results in a decrease in $\langle be(\alpha)\rangle/\langle st(\alpha)\rangle$. Thus from Eq. (1), the theory predicts a reduction in k_{33}/k_{11} with increasing smectic-like local ordering.

The theory also predicts that $k_{33}/k_{11} \propto L^2/W^2$. The widths of the molecules studied are very similar (within a few percent); whereas the molecular length L varies from approximately 20.1 Å for E1 to 23.4 Å for Me35-55, (lengths measured using CPK models). This would lead to an increase in k_{33}/k_{11} as the Me35-55 concentration is increased. Figure 5 shows that such a trend is apparent only at high Me35-55 concentrations.

From Eq. (1), the reduction in k_{33}/k_{11} can be explained by assuming a decrease in $\langle be(\alpha)\rangle/\langle st(\alpha)\rangle$, which would result from increased smectic-like local ordering. This seems physically reasonable since one might expect increased smectic-like local order as a precursor to the pre-transitional ordering. Also our rationalization correlates with the trends observed by Leadbetter and Mehta.[5] Their X-ray measurements of terminally cyano-substituted nematics showed that k_{33}/k_{11} decreased as the extent and magnitude of the damped density wave increased (this is related to an increase in smectic-like ordering).

For the individual elastic constants, the theory of Van der Meet *et al.*[6] predicts:

$$\begin{aligned} k_{11} &= \frac{1}{24} f\sigma^2 L^3 W^2 \frac{3}{8}\langle st(\alpha)\rangle \\ k_{33} &= \frac{1}{24} f\sigma^2 L^5 \frac{1}{2}\langle be(\alpha)\rangle \end{aligned} \tag{2}$$

where σ is the number density, and f is a force constant related to the molecular interaction energy. We have already attributed the reduction in

k_{33}/k_{11}, on approaching S_A, to an increase in the smectic-like local ordering which was quantified as a reduction in $\langle be(\alpha)\rangle/\langle st(\alpha)\rangle$. As this ratio decreases, the theory of Van der Meer, *et al.*, predicts that $\langle st(\alpha)\rangle$ increases and $\langle be(\alpha)\rangle$ decreases. Thus, from Eq. (2), the trends in k_{11} and k_{33} can be qualitatively attributed to changes in the smectic-like local ordering. However, the theory predicts a much larger reduction in $\langle be(\alpha)\rangle$ compared with the increase in $\langle st(\alpha)\rangle$, contrary to our experimental results for k_{33} and k_{11}. Eqs. (2) indicate that this discrepancy can partially be attributed to the increase in L reducing the effects of $\langle be(\alpha)\rangle$ and adding to the effects of $\langle st(\alpha)\rangle$.

CONCLUSIONS

Measurements have been made of the splay and bend elastic constants of a series of hybrid mixtures exhibiting an injected smectic phase. The results have been rationalized by considering the region exhibiting pre-transitional smectic fluctuations separately from the nematic region which has smectic-like local ordering. Pre-transitional increases in k_{33} and k_{11} have been observed; the anomalous behavior of k_{11} is attributed, after Madhusudana,[21] to the re-normalization of k_{11} close to T_{SN}. Remote from the pre-transitional region, we have attributed the large decrease in k_{33}/k_{11} to an increase in the smectic-like local ordering, as predicted by the recent theory of Van der Meer, *et al.*[6] This predicted increase in smectic-like local ordering, although physically reasonable, requires quantitative confirmation. X-ray measurements are in progress to estimate the intensity of the inner diffraction peak which enables the smectic-like local ordering to be quantified; these results will be reported shortly. The theory of Van der Meer, *et al.*, has also been applied to the individual elastic constants, and a qualitative correlation has been found between the elastic constants and the smectic-like local ordering.

These results have important implications in the formulation of mixtures for use in multiplexed twisted nematic devices. To achieve a very low value for k_{33}/k_{11} a nematic mixture is required that does not have a pre-transitional smectic region, but is otherwise as close as possible to the injected smectic phase in order to maximize the smectic-like local ordering.

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