

CHAPTER IV

ELASTIC CONSTANTS OF SOME PURE COMPOUNDS AND MIXTURES EXHIBITING THE RE-ENTRANT NEMATIC PHASE

4.1 Introduction

It is a well established fact that near the AN transition point, smectic-like short range order builds up in the nematic phase and this gives rise to pretransitional increases in k_{22} and k_{33} (de Gennes 1971). In compounds and mixtures exhibiting re-entrant nematic phase, one can expect such pretransitional increases not only close to the AN transition point in the normal nematic phase, but also close to the AN_r transition point in the re-entrant nematic phase. In fact, Gladis (1975) has measured k_{33} in the normal and re-entrant nematic phases of mixtures and has observed such pretransitional increases.

One of the well-established methods of measuring elastic constants of a nematic liquid crystal is the Freedericksz transition technique (Freedericksz and Repiewa 1927). In this technique k_{33} is determined using a homeotropically oriented sample and k_{11} and k_{22} are determined using homogeneously oriented samples. We have seen earlier that it is fairly easy to align the liquid crystals exhibiting the re-entrant nematic phase homeotropically whereas it is quite difficult to align them homogeneously. Hence we have determined only k_{33} using this technique. The pretransitional increase in k_{22} was studied using the light

scattering technique (Orsay Liquid Crystal Group 1969) wherein homeotropically aligned samples could be used.

We have also measured the splay and bend elastic constants of some other liquid crystal samples using Fredericksz transition technique. The results of these measurements are given in subsequent chapters. In the following, we describe the principle of the technique and the experimental set up used in measuring k_{11} and k_{33} .

4.2 Fredericksz transition technique of measuring k_{11} and k_{33}

Nematogenic compounds are diamagnetic in nature. All the compounds for which we have measured the elastic constants have at least two phenyl rings in their molecules. Such compounds possess fairly large positive diamagnetic anisotropy $\Delta\chi$, where $\Delta\chi = \chi_{||} - \chi_{\perp}$, $\chi_{||}$ being the susceptibility along the long axis of the molecule and $\chi_{\perp}$ being the susceptibility in a perpendicular direction. Because of this anisotropy, under the influence of a magnetic field, the molecules tend to align parallel to the direction of the field. The magnetic torque acting on the molecules is

$$\tau_m = \Delta\chi (\vec{n} \cdot \vec{H}) \vec{n} \times \vec{H} \quad (4.1)$$

The magnetic energy density is

$$u_m = - \frac{1}{2} \Delta\chi (\vec{n} \cdot \vec{H})^2 \quad (4.2)$$

where $\Delta\chi$ is defined as the diamagnetic anisotropy per unit

volume ($\Delta \chi \approx 10^{-7}$ C.G.S. units). Obviously, $\chi_{\parallel}$ has the least value when $\vec{n}$ is parallel to $\vec{H}$.

In measuring elastic constants by the Freederickss transition technique, the glass plates used in the sample cell are subjected to prior treatment such that the liquid crystal aligns either homogeneously or homeotropically in the cell, as the case may be and the anchoring of the molecules at the glass surfaces is usually quite strong. A magnetic field is applied in a direction exactly perpendicular to the director. As we shall see later, there will be no distortion in the sample below a threshold field H_0 . Beyond H_0 , the director orientation is distorted. This is called Freederickss transition (Freederickss and Replewa 1927).

4.3 Expressions for the threshold fields

Corresponding to the three curvature elastic constants, there are three different geometries in which the Freederickss transition can take place (Freederickss and Replewa 1927, Saupe 1960, Gruler et al 1972). In all the cases, the director must be strongly anchored to the surfaces binding the sample.

Geometry I (Splay). Let us consider a homogeneously aligned sample held between two glass plates as shown in figure 4.1b. The undistorted director is along the z -axis and the applied magnetic field is along the x -axis. Let $\theta(x)$ be the angle between the local director $\vec{n}(x)$ and the z -axis. In

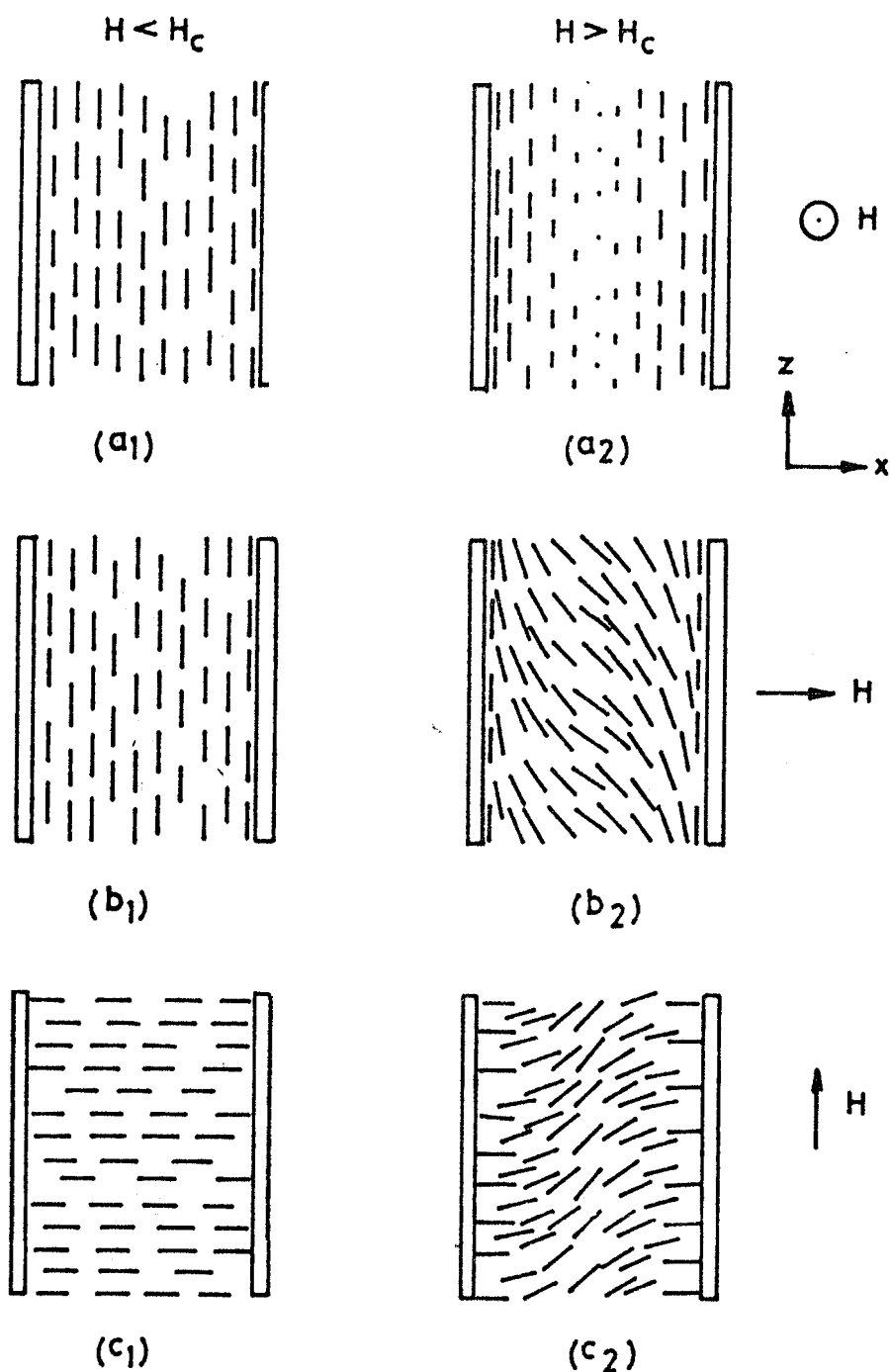


FIGURE 4.1

The geometries for studying the Freedericksz transitions related to (a) twist (b) splay and (c) bend elastic constants. Molecular alignment (1) below H_c and (2) above H_c are shown schematically.

chapter I, we have seen that the elastic energy density is given by the expression

$$W_e = \frac{1}{2} k_{11} (\Delta \cdot \vec{n})^2 + \frac{1}{2} k_{22} (\vec{n} \cdot \Delta \times \vec{n})^2 + \frac{1}{2} k_{33} [\vec{n} \times (\Delta \times \vec{n})]^2 \quad (4.3)$$

In the geometry under consideration

$$\vec{n} = (\sin \phi, 0, \cos \phi) \text{ and } \vec{H} = (H, 0, 0)$$

and the distortion is a combination of splay and bend. Since d varies only along x , $\nabla = (d/dx, 0, 0)$.

From equation (4.3) we get the elastic energy density as

$$\begin{aligned} W_e &= \frac{1}{2} k_{11} (\nabla \cdot \vec{n})^2 + \frac{1}{2} k_{33} [\vec{n} \times (\nabla \times \vec{n})]^2 \\ &= \frac{1}{2} (k_{11} \cos^2 \phi + k_{33} \sin^2 \phi) (d\phi/dx)^2. \end{aligned}$$

The magnetic energy density is $W_m = -\frac{1}{2} \Delta \chi H^2 \sin^2 \phi$. Therefore, the total energy per unit volume is

$$W = \frac{1}{2} (k_{11} \cos^2 \phi + k_{33} \sin^2 \phi) (d\phi/dx)^2 - \frac{1}{2} \Delta \chi H^2 \sin^2 \phi \quad (4.4)$$

For equilibrium, this energy should be a minimum. Using the Euler-Lagrange equation,

$$\frac{d}{dx} \left[\frac{\partial W}{\partial (d\phi/dx)} \right] - \frac{\partial W}{\partial \phi} = 0 \quad (4.5)$$

and simplifying, we get

$$\frac{d^2\phi}{dx^2}(k_{11} \cos^2 \phi + k_{33} \sin^2 \phi) + (d\phi/dx)^2(k_{33}-k_{11})\sin \phi \cos \phi + \Delta\chi H^2 \cos \phi \sin \phi = 0$$

Multiplying by $2(d\phi/dx)$ and rearranging, we get,

$$\frac{d}{dx}[(d\phi/dx)^2(k_{11}\cos^2\phi + k_{33}\sin^2\phi) + \Delta\chi H^2\sin^2\phi] = 0.$$

Integrating,

$$(d\phi/dx)^2(k_{11}\cos^2\phi + k_{33}\sin^2\phi) + \Delta\chi H^2\sin^2\phi = C, \text{ a constant.}$$

The distortion always starts at the mid-plane of the sample and it has the maximum value in this plane. Therefore, at $x = \frac{x_0}{2}$, $\phi = \phi_m$ and $\frac{d\phi}{dx} = 0$ where x_0 is the thickness of the sample and ϕ_m is the maximum deformation. Substituting these in the above equation, we get, $C = \Delta\chi H^2 \sin^2 \phi_m$. Therefore

$$(d\phi/dx)^2(k_{11} \cos^2 \phi + k_{33} \sin^2 \phi) = \Delta\chi H^2 (\sin^2 \phi_m - \sin^2 \phi)$$

$$\int_0^{\phi_m} \left[\frac{k_{11} \cos^2 \phi + k_{33} \sin^2 \phi}{\sin^2 \phi_m - \sin^2 \phi} \right]^{\frac{1}{2}} d\phi = (\Delta\chi)^{\frac{1}{2}} \int_0^{x_0/2} H dx$$

Substituting $\sin \phi = \sin \phi_m \sin \psi$ and simplify*, we get

$$\int_0^{\pi/2} \left[\frac{1 - \left(\frac{k_{11}-k_{33}}{k_{11}} \right) \sin^2 \phi_m \sin^2 \psi}{1 - \sin^2 \phi_m \sin^2 \psi} \right]^{\frac{1}{2}} d\psi = (\Delta\chi/k_{11})^{\frac{1}{2}} H \frac{x_0}{2}.$$

In the limit $\phi_m \rightarrow 0$, $H = H_0$. Therefore,

$$\int_0^{\pi/2} d\psi = (\Delta\chi/k_{11})^{1/2} H_0 \frac{x_0}{2}$$

i.e.,

$$\frac{\pi}{2} = (\Delta\chi/k_{11})^{1/2} \frac{H_0 x_0}{2} \quad \text{or} \quad k_{11} = \Delta\chi \frac{H_0^2 x_0^2}{\pi^2} \quad (4.6)$$

where H_0 is the threshold field for the Fredericks transition.

Geometry II (Bend). Let us consider a homeotropically aligned sample held between two glass plates as shown in figure 4.1c. The undistorted director is along the x-axis and the applied magnetic field is along the z-axis. If $\phi(x)$ is the angle made by the local director with the x-axis,

$$\vec{n} = (\cos \phi, 0, \sin \phi) \quad \text{and} \quad \vec{H} = (0, 0, H).$$

Since $\vec{n}$ varies only along x, $\nabla = (d/dx, 0, 0)$.

In this case, the distortion is again a combination of bend and splay. The elastic energy density is given by

$$\begin{aligned} w_e &= \frac{1}{2} k_{11} (\nabla \cdot \vec{n})^2 + \frac{1}{2} k_{33} [\vec{n} \times (\nabla \times \vec{n})]^2 \\ &= \frac{1}{2} (k_{11} \sin^2 \phi + k_{33} \cos^2 \phi) (d\phi/dx)^2. \end{aligned}$$

The magnetic energy density is, $w_m = -\frac{1}{2} \Delta\chi H^2 \sin^2 \phi$.

Therefore, the total energy per unit volume is

$$w = \frac{1}{2} (k_{11} \sin^2 \phi + k_{33} \cos^2 \phi) (d\phi/dx)^2 - \frac{1}{2} \Delta\chi H^2 \sin^2 \phi.$$

At equilibrium, this should be a minimum. Using Euler-Lagrange

equation and simplifying as in the previous case, we get,

$$\int_0^{\pi/2} \left[\frac{1 - \left(\frac{k_{33} - k_{11}}{k_{33}} \right) \sin^2 \theta_m \sin^2 \psi}{1 - \sin^2 \theta_m \sin^2 \psi} \right]^{1/2} d\psi = \left(\Delta\chi / k_{33} \right)^{1/2} \frac{H x_0}{2}$$

At $H = H_0$, $\theta_m \rightarrow 0$

$$\int_0^{\pi/2} d\psi = \left(\Delta\chi / k_{33} \right)^{1/2} \frac{H_0 x_0}{2}$$

i.e.,

$$\frac{\pi}{2} = \left(\Delta\chi / k_{33} \right)^{1/2} \frac{H_0 x_0}{2} \quad \text{or} \quad k_{33} = \Delta\chi \frac{H_0^2 x_0^2}{\pi^2} \quad (4.7)$$

4.3 Experimental set up

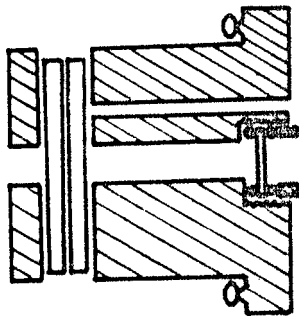
a. The oven. Since the experiments are to be performed with the sample in a magnetic field, the oven and the sample holder were constructed using only non-magnetic materials. Nichrome tape is used for the heating coil in the oven. It is wound over a suitably insulated hollow copper cylinder and was heated by passing direct current. Since the oven is to be placed in a magnetic field it is preferable to use DC rather than AC for heating as in the latter case the current-carrying wires are set into vibrations in the magnetic field.

The lengths of the ovens used were deliberately made large to minimise temperature gradients in the sample. In measuring k_{33} , an oven of length ~ 14 cms was used. However,

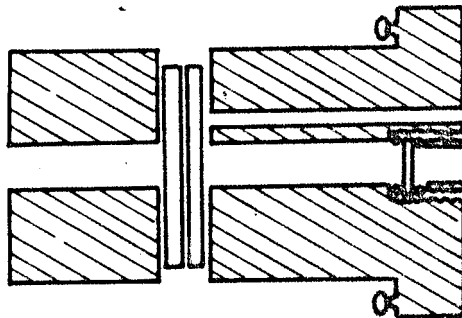
in the measurement of k_{11} , a much shorter oven (length ~ 5 cms) had to be used as in this case the magnetic field acts along the axis of the cylindrical oven.

b. Sample holder. The sample holder consists of a cylindrical block of copper with a rectangular slot cut into one of its faces (figure 4.2). The liquid crystal cell is placed in this slot and is held tightly by means of another similar cylindrical block fixed with the help of brass screws to the first one. The screws can be tightened carefully to get a cell of uniform thickness. The sample holder used in the measurement of k_{11} (figure 4.2a) is shorter compared to that used in the measurement of k_{33} (figure 4.2b). Through holes (~ 8 mm in diameter) present along the axis of the cylinder enables optical observations. This hole is covered at the ends by glass windows. After placing the sample holder inside the oven, the oven can be evacuated and can be filled with an inert gas like nitrogen.

c. Temperature measurement. The temperature of the sample was measured using a calibrated chromel-constantan thermocouple. One junction of the thermocouple is fixed to the sample holder so that it is in contact with one of the glass plates of the cell. The other junction is in contact with a massive copper block placed in melting ice. The thermo e.m.f. was measured using a nanovoltmeter (Keithley Model 148). A nanovolt source (Keithley Model 260) connected in series with



(a)



(b)

Figure 4.2

Schematic diagram of the sample holders used in the study of (a) splay elastic constant, and (b) bend elastic constant.

the thermocouple was used to offset a part of the e.m.f. The accuracy of temperature measurement was $\sim 0.01^\circ\text{C}$. After setting the current in the heating coil to a given value, a sufficient time (~ 30 minutes) was allowed before taking measurements to ensure that the temperature is steady and uniform.

d. Optical set-up. The optical set up used in the measurement of k_{11} is shown in figure 4.3. A horizontal beam of light from a sodium lamp (or a laser) is linearly polarised and is incident on mirror M_1 . The light reflected from M_1 is made to fall on the sample normally and its polarisation is adjusted to be at an azimuth of 45° with respect to the undistorted director. The light beam transmitted through the sample is reflected from mirror M_2 . After passing through the analyser it was received either by a low power microscope^D or by a photodetector (UDT Model 450). The whole set up was mounted on a base provided with side screws S_1 and S_2 and levelling screws L_1 , L_2 and L_3 .

In the measurement of k_{33} , the light incident normally on the sample is adjusted to have its vibrations at an angle of 45° to the direction of the magnetic field. After transmission through the sample and an analyser, the light is received by a low power microscope or a photodetector. In this case also, the assembly is mounted on the same base as that used in the measurement of k_{11} .

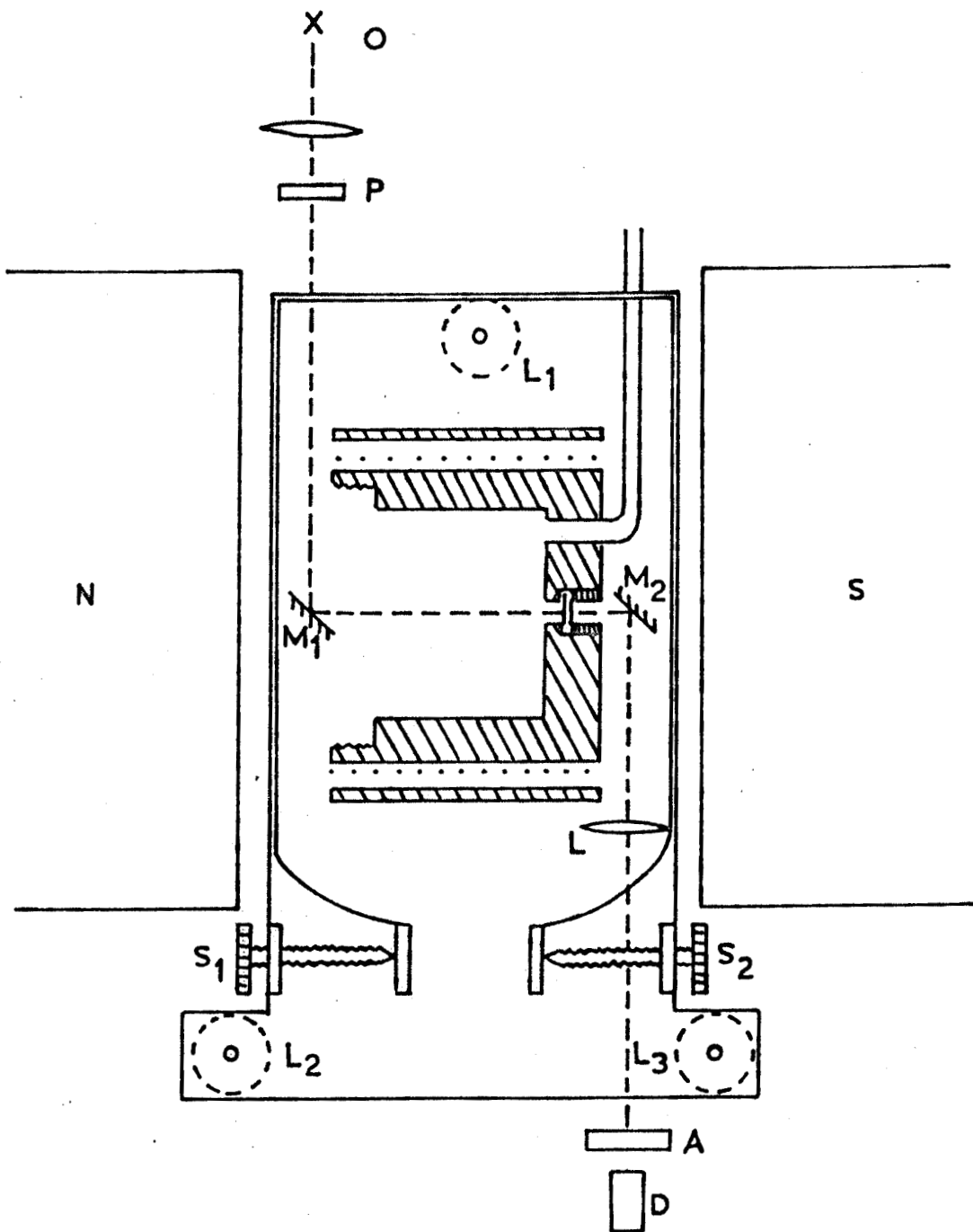


FIGURE 4.3

Schematic diagram showing the set up used in the measurement of k_{11} . Heater with the base is placed between the pole-pieces N and S of an electromagnet. The direction of propagation of the light beam (starting from the source O) is shown by the dashed line.

The initial adjustments were made by observing the sample through the microscope and using sodium lamp as the source of light. While taking the actual readings a helium-neon laser was used as the source of light and the microscope was replaced by a photodetector. The signal from the &OW-detector was fed @ a microvoltmeter (Keithley Model 155) whose output was connected to the y channel of an x-y recorder (Riken Denshi Model F-43P).

The magnetic field was measured using a gaussmeter (RFL Model 750D) with a Hall probe. The measurement was accurate to ± 25 gauss. The output of the gaussmeter was connected to the x-channel of the x-y recorder.

e. Alignment of the director with respect to the magnetic field. From equation 4.1 it is quite evident that magnetic torque is zero only when $\phi = 0$ or $\phi = \pi/2$. Consequently, a threshold field exists only if the undistorted director is exactly normal to $\vec{H}$. If $\vec{n}$ is slightly off-normal, the director pattern is distorted even for small values of $\vec{H}$ and a tail is formed near the critical field (Rapini and Papoular 1969).

In the experiment $\vec{n}$ is adjusted to be exactly normal to $\vec{H}$ as follows. The levelling screws L_1 , L_2 and L_3 are adjusted to have the nematic film in the vertical plane. Then by using screws S_1 and S_2 , $\vec{n}$ could be made exactly normal to $\vec{H}$. Under the action of a magnetic field stronger than H_0 , the director

will get tilted (in the plane containing $\vec{n}$ and $\vec{H}$) with respect to the initial orientation. When $\vec{n}$ is exactly normal to $\vec{H}$, the two possible directions of tilt are equally probable. Under such circumstances, regions of opposite deformation separated by inversion walls are formed in the sample. Thus to have $\vec{n}$ exactly perpendicular to $\vec{H}$, the screws S_1 and S_2 are to be adjusted to get the maximum number of inversion walls in the sample.

f. Measurement of critical field. With the sample in the isotropic phase, the analyser was rotated to get an extinction with the laser as the source of light. The sample was then cooled to the nematic phase. When the temperature was steady, the magnetic field was slowly increased. At the threshold field a sharp change in the intensity of light transmitted through the sample is observed.

4.4 Light Scattering Studies

The intensity of light scattered from a nematic liquid crystal gives useful information about the spontaneous fluctuations of the director in the medium. The Orsay liquid crystal group (1969), Delaye et al (1973), Chu and McMillan (1975) and others have used light scattering technique to study the orientational fluctuations in different samples.

In our experiment, a light beam polarised to have its electric vibrations normal to the plane of scattering (horizontal

plane) is incident along the director of a homeotropically aligned sample. In this scattering geometry, only the bend and twist fluctuations in the sample give rise to the scattering of light. However, when the angle of scattering is small, the wave vector of the fluctuation contributing to the scattering will be nearly normal to the director. Then the intensity of the depolarised component of the scattered light will arise mainly due to the twist fluctuations and it will be more or less independent of k_{33} . In such a case the scattered intensity $I \propto [(\Delta n)^2/k_{22}]$ where Δn is the birefringence of the sample (see Chu and McMillan 1975, Orsay Liquid Crystal Group 1969).

4.5 Sat up for light scattering experiment

a. Oven and sample holder. To have a good temperature control and stability, a massive oven with two heating coils was used. A nichrome tape is wound evenly on a mica sheet wrapped around a long, hollow copper cylinder (~ 18 cm in length and ~ 5 cm in diameter). This is kept inside a coaxial copper tube and a second nichrome tape is wound over the tube as in the previous case. The entire assembly is then kept inside a thick, hollow copper cylinder. The space between the heating coils and the copper cylinders is filled with asbestos powder. Precautions were taken to see that the heating coils are insulated very well from the copper cylinders. The oven was heated by passing the same direct current through the two heater coils.

The sample holder consists of a cylindrical block of copper with a rectangular slot on one of the flat faces. The cell consisting of two optically flat glass plates B (figure 4.4) (10 x 28 mm) separated by mylar spacers was placed in this slot. The cell was held in position by a copper disc fixed to the block by means of screws. The whole assembly was then screwed into a long (~ 8 cm) copper cylinder C. A through hole D present in the sample holder makes optical observations possible. The sample-holder is placed inside the oven described above.

The glass plates constituting the cell were subjected to prior treatment with CTAB to get a homeotropic alignment of liquid crystal. The sample was filled into the cell in the nematic phase by capillary action. The thickness of the sample film was ~ 50 μ .

The temperature of the sample was measured using a chromel-alumel thermocouple and a nanovoltmeter.

b. Optical set up. A horizontal beam of light from a helium-neon laser A was reduced in intensity using a pair of polaroids B (figure 4.5). B polarises the emergent light beam such that the electric vibrations of the beam are in the vertical plane (i.e., perpendicular to the plane of the figure). After passing through a chopper C (PAR Model 192) and a pin-hole D of diameter ~ 1 mm, the beam was incident normally on the

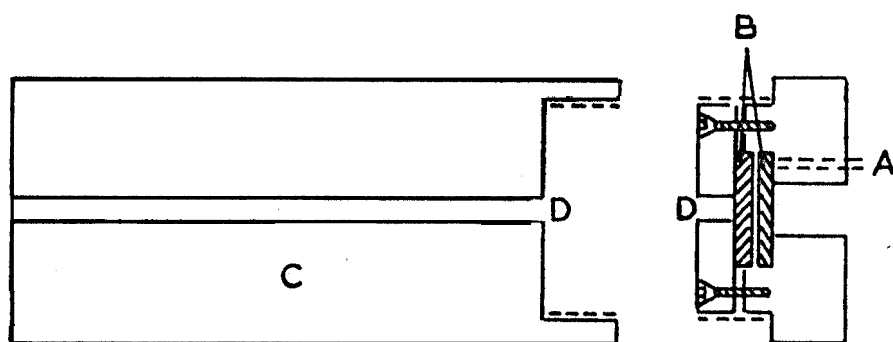


FIGURE 4.4

Schematic diagram of the sample holder used in the light scattering experiment.

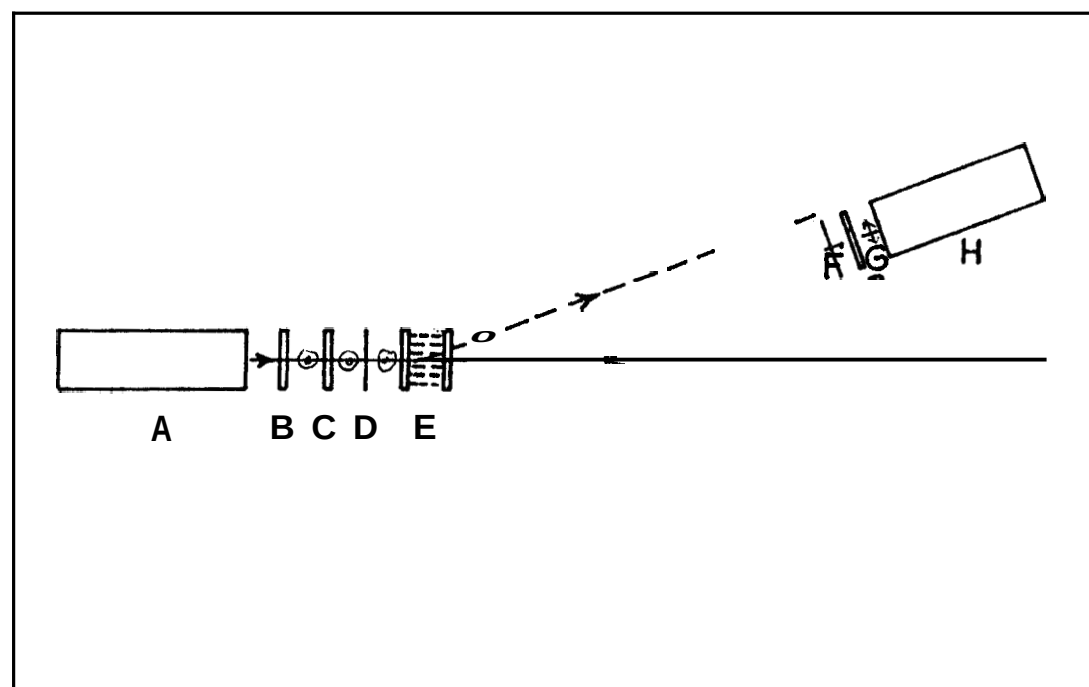


FIGURE 4.5

Schematic diagram of the optical set up used in the light scattering experiment.

sample B. The light scattered from the sample at an angle $\sim 7^\circ$ was made to pass through a pin-hole F and a polaroid G which is in a crossed position with respect to B. The depolarized component of the scattered light was then received by a photomultiplier H (Hamamatsu Type R585). The photomultiplier was mounted on one arm of a spectrometer to facilitate the adjustment of the angle of scattering to a suitable value.

The signal from the photomultiplier was fed to a lock-in-amplifier (PAR Model 186) for which the reference signal was provided by the chopper. The amplified signal from the lock-in-amplifier was connected to the y channel of a x-y recorder. The output of the nanovoltmeter which measures the thermo e.m.f. was connected to the x channel. Thus the recorder plots intensity of light against the thermo e.m.f.

The sample was cooled slowly ($\sim 0.1^\circ$ per minute) from the nematic phase down to the re-entrant nematic phase and the intensity of light scattered was recorded in the entire temperature range.

4.6 Results and discussion

a Bend elastic constant. We have measured the bend elastic constants of two pure compounds, viz., 11 CPMBB and 12 CPMBB and a mixture of 8 OCB and 10 OMCP (in the molar ratio 45:55). All the three samples exhibit the re-entrant nematic phase as described in Chapter II. The measurements were taken

in both the normal and the re-entrant nematic phases.

From equation 4.7, we have,

$$k_{33} = \Delta\chi \frac{x_o^2 H_o^2}{\pi^2}$$

where $\Delta\chi$ is the anisotropy of volume diamagnetic susceptibility of the sample. We can write $\Delta\chi = \Delta\chi_m \cdot \rho$ where ρ is the density and $\Delta\chi_m$ is the anisotropy in the mass susceptibility of the perfectly oriented medium. $\Delta\chi_m = \Delta K/M$ where ΔK is the anisotropy of molar susceptibility and M is the molecular weight of the compound. Thus

$$k_{33} = \frac{x_o^2 H_o^2}{\pi^2} \frac{\Delta K}{M} \cdot \rho \quad (4.8)$$

The values of order parameter and density were determined from the birefringence data (see chapter III).

Calculation of ΔK . The anisotropy of molar susceptibility ΔK can be determined by measuring the principal susceptibilities of a single crystal of the compound if the crystal structure is known. Since these data are not available for the systems under study, we have calculated ΔK using a procedure given by Flygare (1974). Flygare extended Pascal's (1949) method of calculating bulk susceptibilities so calculate the principal susceptibilities of anisotropic aromatic molecules. He himself has stated that this method will be very useful to calculate ΔK of liquid crystals. Sherrell and Crallin (1979), Leenhouts et al (1979)

and others have calculated ΔK of a number of mesogens by this method. Flygare (1974) has, in fact, tabulated the local atom and bond susceptibilities which can be used in such calculations. Some of these values used in our calculations are given in table 4.1. However, the susceptibilities of phenyl rings calculated following the procedure will be different from the actual values due to the fact that the effect of delocalisation of electrons has not been taken into account in the calculations. The correction that has to be applied to the calculated value of out-of the plane susceptibility of a phenyl ring is -35.2×10^{-6} C.G.S. units (Flygare 1974). We have tabulated these values for the phenyl and biphenyl ring systems also in table 4.1. These corrections have to be taken into account explicitly while evaluating ΔK . The calculations were done using the formulae.

$$\begin{aligned}
 K_x &= \sum_{\text{all bonds}} \chi_{\xi} \cos^2(\xi, x) + \chi_{\eta} \cos^2(\eta, x) + \chi_{\zeta} \cos^2(\zeta, x) \\
 K_y &= \sum_{\text{all bonds}} \chi_{\xi} \cos^2(\xi, y) + \chi_{\eta} \cos^2(\eta, y) + \chi_{\zeta} \cos^2(\zeta, y) \\
 K_z &= \sum_{\text{all bonds}} \chi_{\xi} \cos^2(\xi, z) + \chi_{\eta} \cos^2(\eta, z) + \chi_{\zeta} \cos^2(\zeta, z) \\
 &\dots (4.9)
 \end{aligned}$$

where χ_{ξ} , χ_{η} and χ_{ζ} are the values of principal susceptibilities of a given bond in the molecule, x, y, z are three arbitrary orthogonal axes in the molecule, (ξ, x) is the angle between ξ -axis of the bond and the x -axis of the molecule, etc.

To calculate the principal susceptibilities of a molecule, its structure should be known. In our calculations, we have assumed that all the phenyl rings of a molecule lie in the same plane. We have chosen the z-axis to be along the long axis of the molecule which is assumed to be the line joining the extreme phenyl rings of the molecule, the x-axis perpendicular to this and lying in the planes of the benzene rings and the y-axis perpendicular to this plane. The angles between the various bonds and these axes were estimated by constructing a model of the molecule using Dreiding models. The susceptibilities along and perpendicular to the long axis are given by K_z and $\frac{K_x + K_y}{2}$ respectively. The anisotropy in the molar susceptibility is then given by $\Delta K = K_z - \frac{K_x + K_y}{2}$.

The values of ΔK for the mixtures were calculated using an additive law. If ΔK_1 is the diamagnetic anisotropy of the component having mole fraction p_1 and ΔK_2 that of the component having mole fraction p_2 , $\Delta K = p_1 \Delta K_1 + p_2 \Delta K_2$. The calculated values of ΔK are given in table 4.2.

The bend elastic constants of 11 CPMBB, 12 CPMBB and the mixture of 8 OCB and 10 OMCPD are plotted against relative temperatures in figures 4.6, 4.7 and 4.8 respectively. The values are also listed in tables 4.3, 4.4 and 4.5. As the sample is cooled down from the NI transition point, the value of k_{33} increases in a smooth manner. When the temperature approaches the AN transition point, k_{33} increases steeply. This

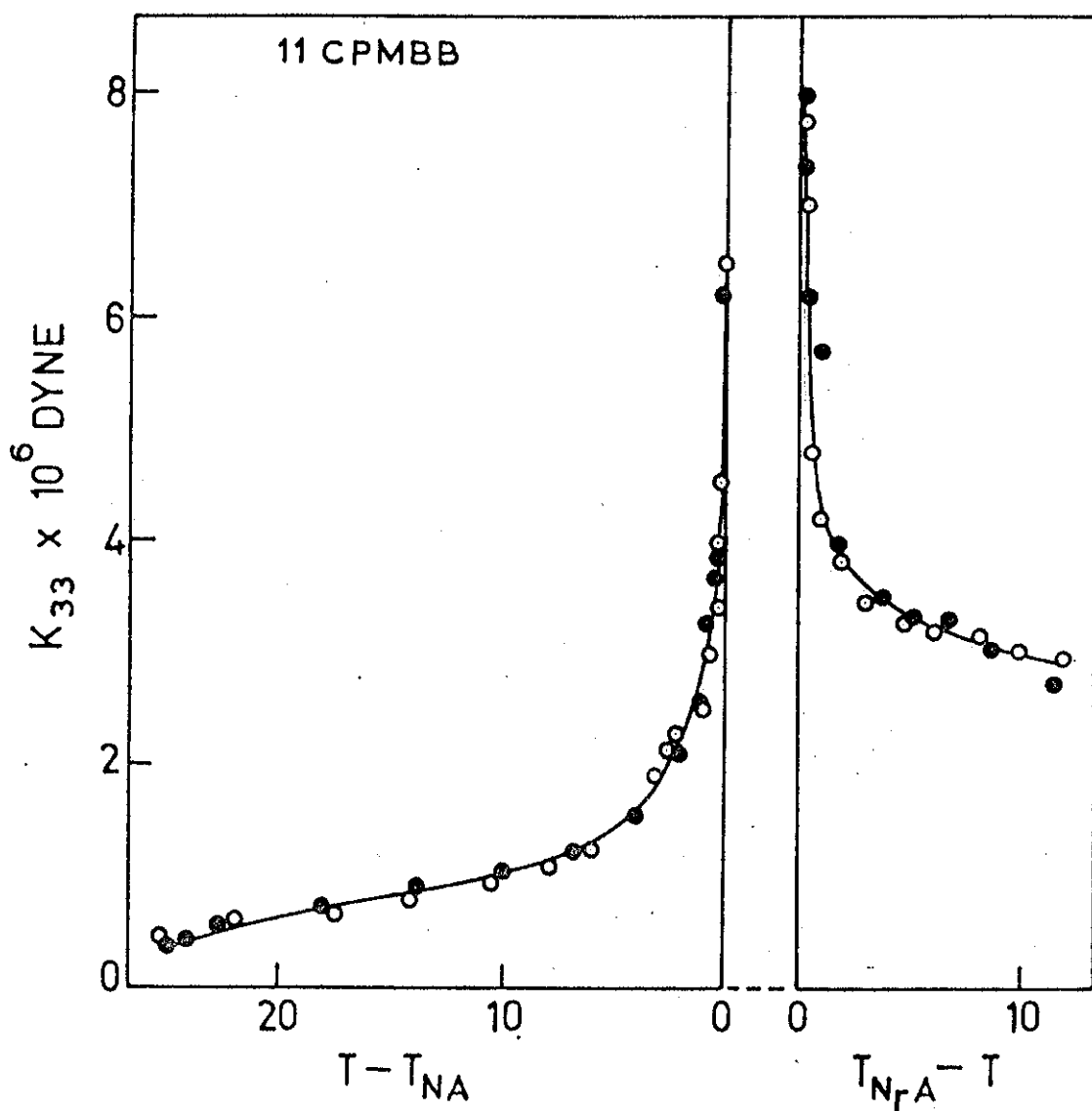


FIGURE 4.6

The bend elastic constant of 11 CPMBB plotted as function of relative temperature. The open and filled circles represent the values obtained with two independent samples. (The temperature range of smectic A phase is represented by a dashed line which is not drawn to scale.)

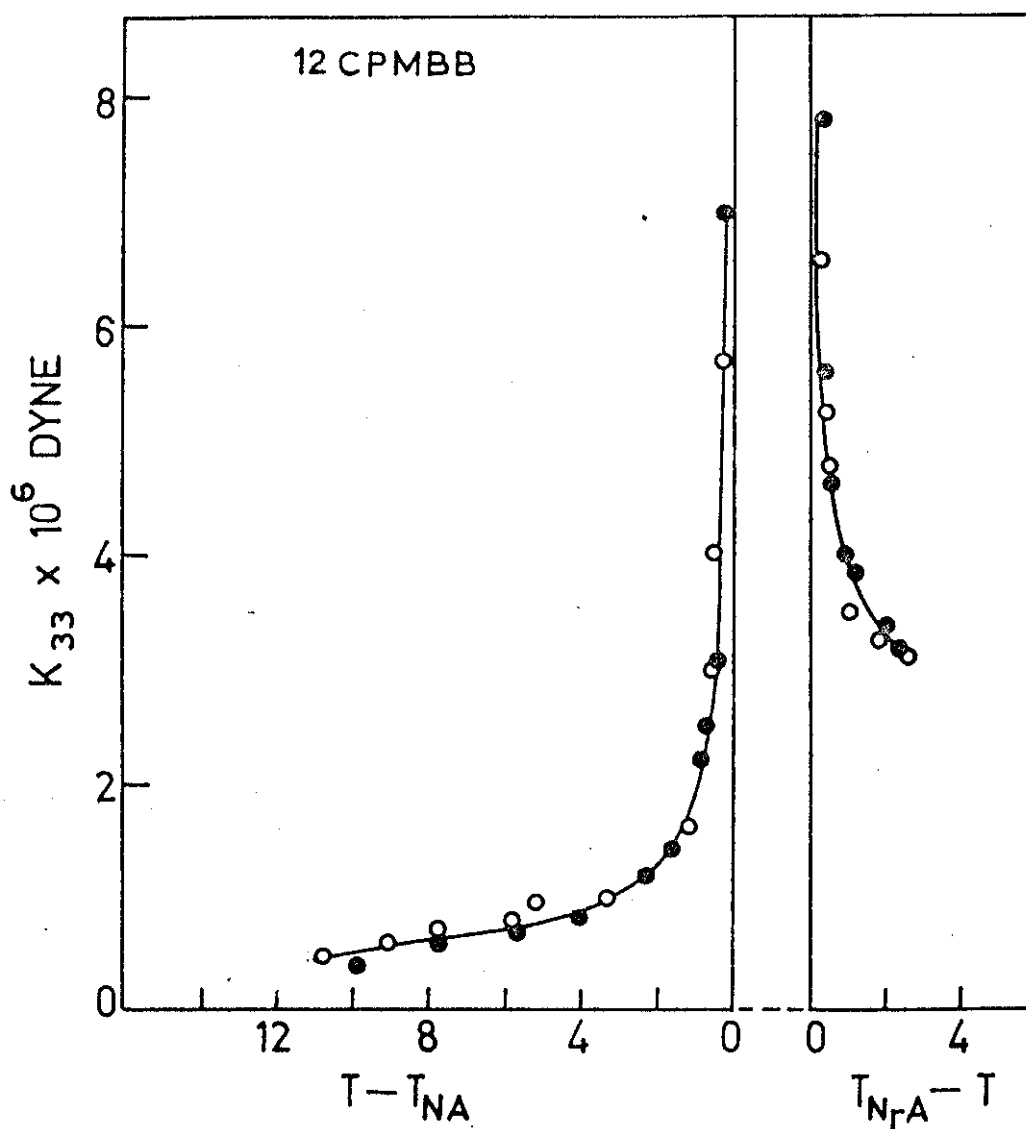


FIGURE 4.7

The bend elastic constant of 12 CPMBB plotted as function of relative temperature. The open and filled circles represent the values obtained with two independent samples. (The temperature range of smectic A phase is represented by a dashed line. It is not drawn to scale.)

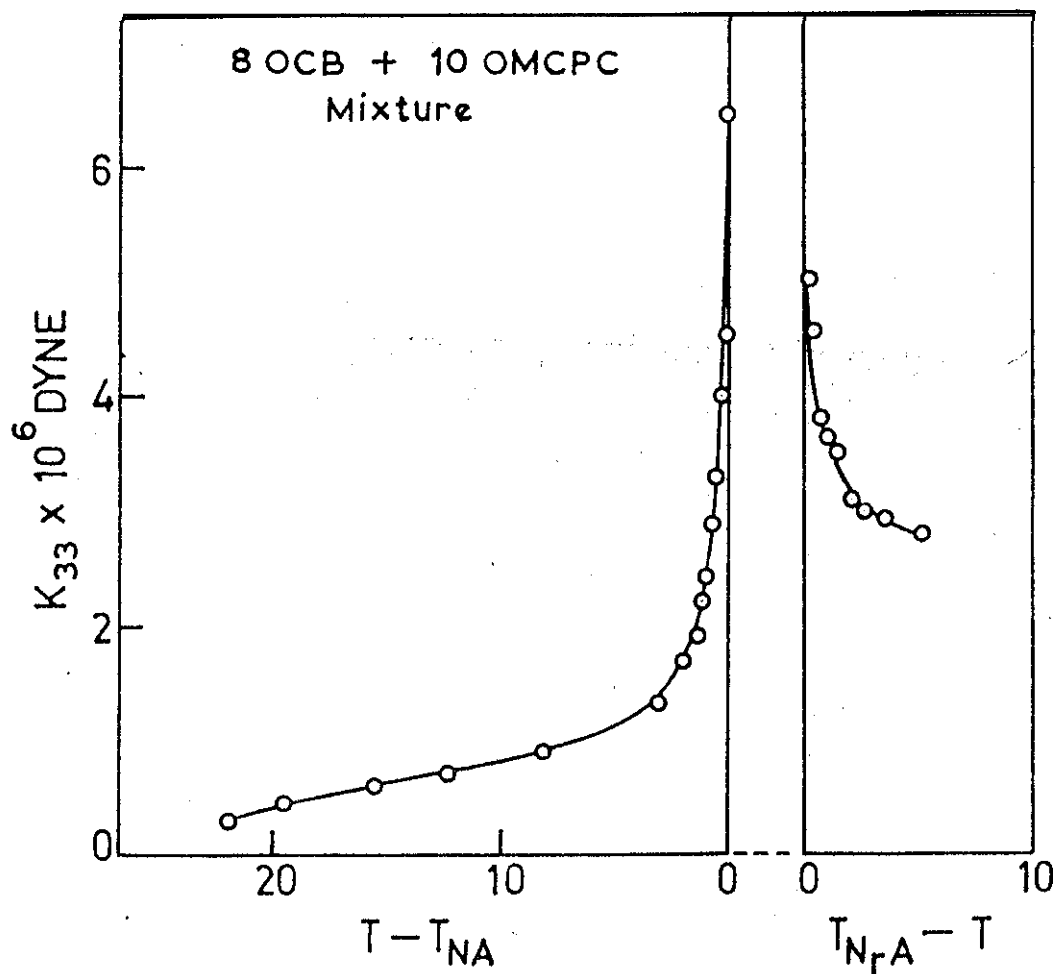


FIGURE 4.8

The bend elastic constant of the mixture of 8 OCB and 10 OMCPC plotted as function of relative temperature. (The temperature range of smectic A phase is represented by a dashed line which is not drawn to scale.)

is the pretransitional increase which arises due to the building up of smectic-like short range order in the nematic phase.

A similar pretransitional increase in k_{33} is observed in the re-entrant nematic phase as one approaches the AN_r *p-a-tion point. The temperature variation of k_{33} is almost parabolic about the smectic phase. However, the value of k_{33} in the re-entrant nematic phase is considerably higher than that in the nematic phase. The higher orientational order parameter of the re-entrant phase compared to that of the normal nematic phase (see figure 3.11) explains a good part of the higher value of k_{33} in the re-entrant nematic phase. Further contributions may come from the different short range order and molecular associations in the two phases.

Gladis (1975) has measured the threshold field for bead deformation in the normal and the re-entrant nematic phases of a few mixtures and has observed pretransitional increases in k_{33} in the normal nematic and re-entrant nematic phases. Our observations are similar to these observations and confirm the fact that the phase which exists below the temperature of smectic A phase in the compounds and mixtures under study is a nematic phase.

b. Light scattering studies. In the experimental geometry under consideration, the intensity of the depolarised component of the light scattered is proportional to $[(\Delta n)^2/k_{22}]$. We

have not calculated the absolute values of k_{22} as our main interest was to know how it varies with temperature close to the AN and AN_T transition points.

The experiments were conducted on 11 CPMBB, 12 CPMBB and a mixture of 8 OOB and 10 OMCPD (in the molar ratio 45 : 55). The variation of the intensity of light scattered with temperature for these samples are shown in figures 4.9, 4.10 and 4.11.

In all the cases, the observations were taken as the sample was being cooled from the isotropic phase.

According to the mean field theory (Saupe 1960), in simple nematics $k_{22} \propto s^2$. In such cases, the intensity of scattered light will be almost temperature independent since the intensity $\propto [(\Delta n)^2/k_{22}]$ and $\Delta n \propto s$. In nematics which show a smectic phase at a lower temperature, there is a pretransitional increase in k_{22} and k_{22} is not proportional to s^2 . Consequently, the scattered intensity shows a decreasing trend as the AN transition point is approached. At the AN transition point, the intensity drops to zero. Throughout the smectic A phase, the scattered intensity will be zero due to the quenching of the twist fluctuations. But in the actual experiment, some intensity is observed in the smectic A phase. (Probably, this is produced by the defects on the surfaces of the glass plates forming the cell).

An analogous temperature variation of the intensity of scattered light is observed in the re-entrant nematic phase.

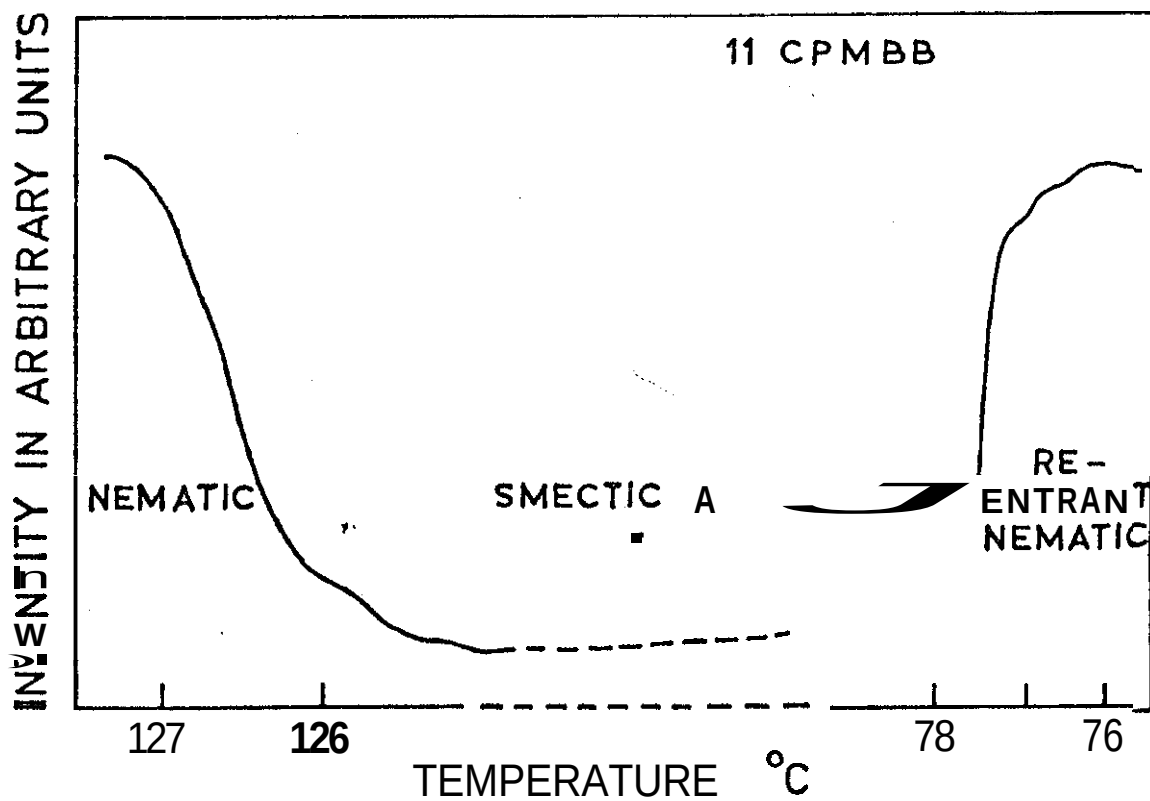


FIGURE 4.9

The intensity of light scattered from a homeotropically aligned sample of 11 CPMBB plotted against temperature. The dashed line indicates the smectic A phase.

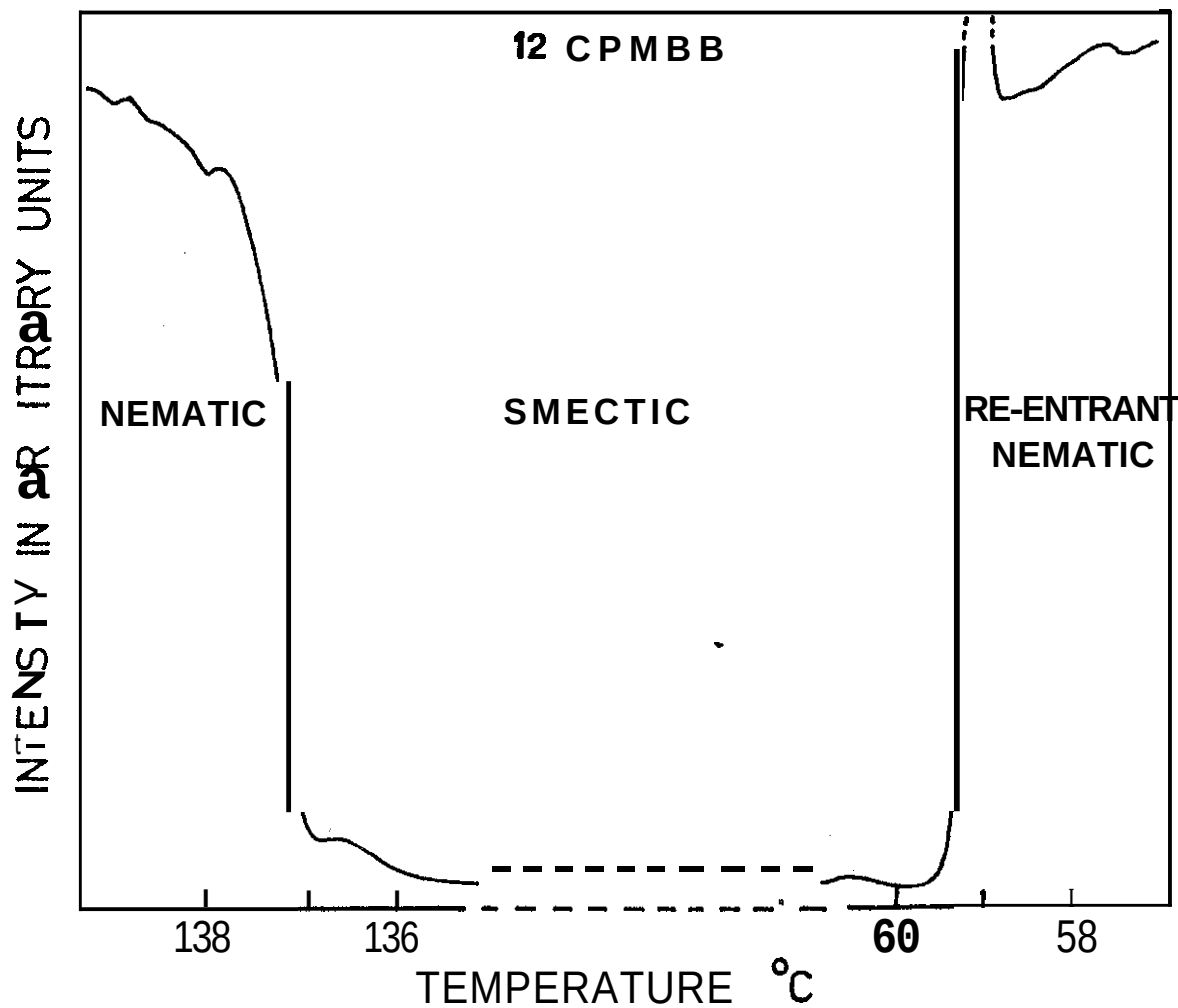


FIGURE 4.10

The intensity of light scattered from a homeotropically aligned sample of 12 CPMBB plotted against temperature. The dashed line indicates the smectic A phase.

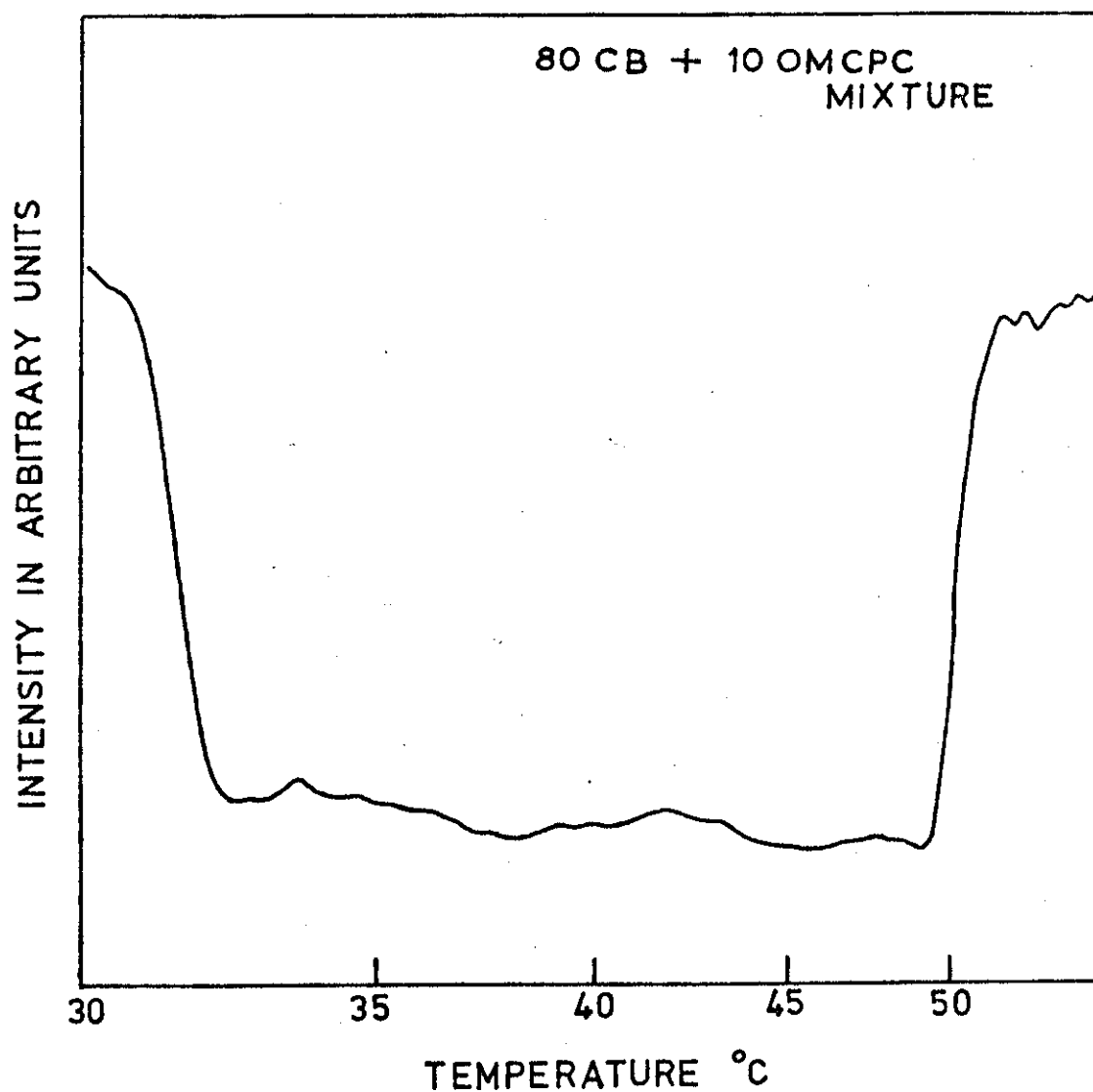


FIGURE 4.11

The intensity of light scattered from a homeotropically aligned sample of the mixture of 8 OCB and 10 OMCP plotted against temperature.

We have seen earlier (see table 2.2) that the AN and AN_x transitions of 12 CPMBB are weakly first order in nature. At the AN transition point, while going from the nematic to the smectic A phase the medium changes from a state having orientational order to a state in which an additional translational order comes into existence. The variation in the intensity of scattered light is fairly smooth during this transition. At the AN_x transition point the medium passes from a phase which ^{has} got a long-range translational order to a phase where this order is absent. The amplitude of thermal fluctuations increases sharply at this temperature due to a finite heat of transition. Further, in the present experiment the cooling is probably not slow enough to ensure the sample to be in perfect equilibrium. As a consequence of these factors, the intensity of light shoots up to a large value at the AN_x transition point (Figure 4.10). As the temperature is lowered further, the intensity falls back to the equilibrium value and then increases gradually with temperature. The enormous increase in the intensity at the AN_x transition point is observed only in 12 CPMBB. In the other two samples, the AN_x transition is almost ^a second order transition and hence this trend is not observed.

All these observations confirm that the phase obtained on cooling these samples from the smectic A phase is truly nematic in nature.

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TABLE 4.1

(a) Bond susceptibilities $\times 10^6$ C.G.S. units (Flygare et al 1974)

Bond	ξ	η	ζ
C-H	-5.6	-3.1	-3.1
C-C	-7.9	-0.2	-0.2
C=C	-0.8	+ 4.0	-13.8
C-O	-7.2	-6.7	-3.8
C=O	-1.3	+2.2	-13.0
O-H	-4.5	-7.5	-5.5
C=N	-13.7	-14.2	-14.2
C≡N	-16.5	-11.6	-11.6

(b) Comparison between experimental and calculated values (Flygare et al 1974)

Molecule	Average in-plane susceptibility		Average out-of-plane susceptibility		Correction for out-of-plane susceptibility
	Experi- mental	Calcu- lated	Experi- mental	Calcu- lated	
Benzene	-34.9 ± 2	-33.4	-94.6 ± 2.5	-59.4	-35.2
Biphenyl	-64.7	-62.3	-183.8	-113.0	-70.8

TABLE 4.2

Anisotropy of molar diamagnetic susceptibility

Sample	$\Delta K \times 10^6 \text{ cm}^3/\text{mole}$
11 CPMBB	81.0
12 CPMBB	81.0
(8OCB + 10 OMOPC)	43.7

TABLE 4.3

Bend elastic constants of 11 QPMBB

 $x_0 = 50.1 \mu$

(a) Normal nematic phase

(b) Re-entrant nematic phase

$T - T_{NA}$	H_a gauss	$k_{33} \times 10^6$ dynes
25.29	1550	0.457
21.80	1688	0.593
17.53	1750	0.684
14.12	1850	0.813
10.37	1950	0.955
7.98	2050	1.093
6.12	2150	1.224
4.09	2350	1.487
2.87	2625	1.872
2.51	2800	2.129
2.20	2950	2.302
0.93	3000	2.503
0.63	5250	2.940
0.50	3500	3.410
0.35	3775	3.967
0.18	4225	5.008
0.12	4800	6.464

$T_{NA} - T$	H_a gauss	$k_{33} \times 10^6$ dynes
0.10	4900	7.719
0.20	4650	6.951
0.73	3850	4.798
0.97	3600	4.195
1.82	3425	3.822
3.03	3250	3.443
4.87	3150	3.255
6.23	3100	3.174
8.28	3075	3.123
10.20	3012	3.016
12.10	2975	2.942

 $x_0 = 49.9 \mu$

(a) Normal nematic phase

(b) Re-entrant nematic phase

$T - T_{NA}$	H_a gauss	$k_{33} \times 10^6$ dynes
25.03	1475	0.330
24.29	1550	0.396
22.56	1688	0.537
18.09	1862	0.723
14.02	2000	0.917
9.81	2088	1.059
6.89	2212	1.232
3.89	2425	1.533
1.80	2825	2.114
1.26	3100	2.566
0.97	3350	2.997
0.85	3500	3.271
0.55	3700	3.656
0.35	3800	3.887
0.22	4300	4.978
0.10	4800	6.202

$T_{NA} - T$	H_a gauss	$k_{33} \times 10^6$ dynes
0.12	5000	7.973
0.23	4800	7.348
0.42	4400	6.174
0.53	4300	5.937
0.82	4125	5.464
1.78	3525	4.017
3.95	3275	3.467
5.38	3200	3.333
6.75	3200	3.340
8.78	3050	3.047
11.78	2875	2.726

TABLE 4.4

Bend elastic constants of 12 CPMBB

 $x_0 = 49.8 \mu$

(a) Normal nematic phase

$T - T_{NA}$	H_0 gauss	$k_{33} \times 10^6$ dyne
10.83	1650	0.507
9.06	1750	0.622
7.92	1800	0.692
5.81	1850	0.754
5.01	1950	0.854
3.69	2050	0.981
2.35	2250	1.215
1.05	2550	1.602
0.72	3100	2.390
0.67	3250	2.627
0.55	3500	2.075
0.40	3950	3.916
0.30	4750	5.663

(b) Re-entrant nematic phase

$T_{NA} - T$	H_0 gauss	$k_{33} \times 10^6$ dyne
0.30	4550	6.561
0.45	4050	5.199
0.55	~~3875~~	4.759
1.10	3325	3.504
1.95	3200	3.245
2.65	3125	3.095

 $x_0 = 49.9 \mu$

9.93	1500	0.354
7.65	1638	0.524
5.74	1750	0.638
4.07	1900	0.791
2.32	2250	1.164
1.60	2400	1.362
1.10	2800	1.674
0.80	3000	2.169
0.65	3175	2.430
0.45	3575	3.081
0.35	5000	6.026
0.30	5370	6.958

0.30	4950	7.818
0.40	4200	5.629
0.60	3800	4. w
0.95	3550	4.0at
1.25	3450	3.798
2.05	32.50	3.370
2.25	3150	3.166

TABLE 4.5

Bend elastic constants of (8 OJB + 10 OMCPD)
mixture

$$x_o = 50.3 \mu$$

(a) Normal nematic phase

(b) Re-entrant nematic phase

$T - T_{NA}$	H_o gauss	$k_{11} \times 10^6$ dynes	$T_{NR-A} - T$	H_o gauss	$k_{33} \times 10^6$ dynes
21.84	1575	0.255	0.20	4950	4.986
21.27	1625	0.289	0.40	4700	4.531
19.55	1775	0.400	0.70	4300	3.823
15.65	1900	0.526	1.00	4175	3.636
12.49	2050	0.663	1.30	4075	3.322
7.95	2750	1.328	2.20	3800	3.062
1.85	3100	1.703	2.70	3750	3.028
1.45	3262	1.886	3.50	3700	2.971
1.25	3500	2.191	4.00	3675	2.931
1.10	3675	2.415	5.60	3525	2.758
0.90	3775	2.548			
0.75	4012	2.881			
0.40	4275	3.271			
0.35	4500	3.658			
0.25	4762	4.096			
0.20	5012	4.537			