

CHAPTER III

ORIENTATIONAL ORDER PARAMETERS OF COMPOUNDS AND MIXTURES
EXHIBITING RE-ENTRANT NEMATIC PHASE3.1 Introduction

As already described in chapter I liquid crystals are characterised by long-range orientational ordering of the rod-shaped molecules. The orientational order parameter is defined as (Zwetkoff 1942)

$$s = \frac{1}{2} (\overline{3 \cos^2 \theta} - 1) \quad (3.1)$$

where θ is the angle made by the long axis of the molecule with the director $\vec{n}$ and the bar denotes a statistical average.

Most of the characteristic properties of nematic liquid crystals are directly related to the orientational order parameter. Hence the determination of the order parameter is of considerable importance. It can be measured using a number of techniques such as optical birefringence (Chatelain 1955), infrared dichroism (Maier and Englert 1960) and ultraviolet dichroism (Maier and Saupe 1956), nuclear magnetic resonance (Spence et al 1953, Doane et al 1972), diamagnetic anisotropy (Saupe and Maier 1961, Gasparoux et al 1973), etc. We have measured the order parameters of a few compounds and mixtures exhibiting the re-entrant nematic phase by two techniques, viz., infrared dichroism and optical birefringence.

As described in chapter II all the compounds and mixtures which show the re-entrant nematic phase studied by us consist of molecules with cyano end-groups. It is very difficult to get good homogeneously aligned samples in the smectic phase of such compounds. This is also true in the nematic phase at temperatures close to the smectic-nematic transition point. Hence we could not measure the order parameters using techniques which require homogeneously aligned samples. We have therefore used methods which involve measurements with homeotropically aligned samples.

3.2a Infrared dichroism method

To determine s from IR studies one can use vibrational transition of any bond in the molecule with a moment which makes a known angle θ with the long axis. One can determine s by IR dichroism method either using a homogeneously aligned sample (Maier and Englert 1960, Saupe and Maier 1961) or using a homeotropically aligned sample (Kelker et al 1973, Fernandes and Venugopalan 1976). The former method needs polarised IR radiation. But in the latter case one can use unpolarised radiation as in this case it propagates along the optic axis and hence the choice of a specific direction of electric vector has no significance. For reasons mentioned in the introduction, we have used only homeotropically aligned samples in determining s .

For a given sample, the dichroic ratio R is defined as

the ratio of the integrated absorption in the mesophase to that in the isotropic phase. It can be shown (see for example, Fernandes and Venugopalan 1976) that

$$R = 1 - s(1 - \frac{3}{2}\sin^2 \theta)$$

or $s = \frac{1 - R}{1 - \frac{3}{2}\sin^2 \theta} \quad (3.2)$

While evaluating R from the experimental data, it is necessary to find the integrated absorption of the band and not just the peak absorption coefficient. Also the experimental absorption profile has to be corrected for the effects of finite spectral slit width. We have represented the true absorption profile by a Lorentzian function following Ramsay's procedure (Ramsay 1952). The corrected integrated absorption strength is then calculated using the experimentally observed values of the peak absorption coefficient, the width of the absorption profile at an appropriate height (as will be described later) and the spectral slit width of the instrument. It is known that for suitably isolated bands, the Lorentzian function modified for the effects of finite spectral slit width gives a reasonably satisfactory experimental profile (Fernandes and Venugopalan 1976). The experimental value of R would be, in general, different from the true value because the refractive indices of the mesophase are different from those of the isotropic liquid. Further, the local field in the mesophase is anisotropic in nature. However, it has been

estimated that the error involved due to these factors is about 2 per cent (Fernandes and Venugopalan 1978). As this error is less than the uncertainty involved in the experimental observations (which is estimated to be about 5 per cent), we have ignored this error.

3.2b Birefringence method

We could not use the conventional prism method (Chatelain 1955, Madhusudana et al 1971) to find the birefringence of our samples for reasons mentioned earlier. Hence we have measured the birefringence using homeotropically aligned samples by a new method.

Consider a monochromatic light beam incident obliquely on a homeotropically aligned liquid crystal sample as shown in figure 3.1. On entering the sample the light beam splits into two - one beam having its electric vibrations perpendicular to the plane of the figure and the other having its electric vibrations in the plane of the figure. Let $a_{\perp}$ ($= n_o$) and $a_{\parallel}$ be the refractive indices for these two beams respectively. The two beams emerge from the sample in directions which are parallel to the direction of the incident beam.

Let θ_i be the angle at which the light is incident on the sample and let $\theta_{\perp}$ and $\theta_{\parallel}$ be the angles of refraction for the two beams. Let n_o and n_e be the ordinary and extraordinary refractive indices of the medium. Then using the standard

equation for the index ellipsoid, we can write

$$\frac{n_{||}^2 \sin^2 \theta_{||}}{n_e^2} + \frac{n_{||}^2 \cos^2 \theta_{||}}{n_o^2} = 1 \quad (3.3)$$

The two glass plates which confine the liquid crystal sample do not make any contribution to the path difference between the two beams.

The optical path difference between the two beams of light emerging from the sample is (see figure 3.1)

$$\Delta = \frac{n_{||} l}{\cos \theta_{||}} + GE \sin \theta_1 - \frac{n_o l}{\cos \theta_{\perp}} \quad (3.4)$$

where l is the thickness of the sample.

Now using the relation, $n_{||} = \frac{\sin \theta_1}{\sin \theta_{||}}$ and equation (3.3) we get,

$$n_{||}^2 = n_o^2 \left[1 + \sin^2 \theta_1 \left(\frac{1}{n_o^2} - \frac{1}{n_e^2} \right) \right]$$

and

$$\frac{n_{||} l}{\cos \theta_{||}} = \frac{l [n_o^2 n_e^2 + (n_e^2 - n_o^2) \sin^2 \theta_1]}{n_o n_e (n_e^2 - \sin^2 \theta_1)^{1/2}}$$

It can be easily shown that

$$\begin{aligned} GE \sin \theta_1 &= l (\tan \theta_{\perp} - \tan \theta_{||}) \sin \theta_1 \\ &= l \frac{\sin^2 \theta_1}{n_o} \left[\frac{n_o}{(n_o^2 - \sin^2 \theta_1)^{1/2}} - \frac{n_e}{(n_e^2 - \sin^2 \theta_1)^{1/2}} \right] \end{aligned}$$

Also

$$\frac{n_0^2}{\cos^2 \theta_1} = \frac{n_0^2}{(n_0^2 - \sin^2 \theta_1)^{1/2}}$$

Substituting these values in equation (3.4) we get,

$$\Delta = l \left[\frac{n_0^2}{n_e^2} (n_0^2 - \sin^2 \theta_1)^{1/2} - (n_0^2 - \sin^2 \theta_1)^{1/2} \right]. \quad (3.5)$$

This path difference can be measured using a quarter wave plate and a pair of polaroids. Then using equation (3.5) one of the refractive indices can be calculated if the other is known. Between n_e and n_0 , it is easier to measure n_0 by an independent method.

We have measured n_0 using the prism method. A small angled (angle $\sim 2-3^\circ$) hollow glass prism was taken and the sample was filled at the edge of the prism. The liquid crystal was aligned in such a way that the molecules were perpendicular to the glass plates. Using a spectrometer the angle A of the prism and the angle of deviation D for a beam incident normally on the prism were measured. Then n_0 was calculated using the expression

$$n_0 = \frac{\sin(A + D)}{\sin A} \quad (3.6)$$

The liquid crystal sample inside the prism is slightly deformed. But when the incident light is polarised in such a way that the electric vibrations are parallel to the edge of

the prism, this deformation does not affect the measurements. In fact, the image produced by the refracted beam was quite sharp.

3.3 Experimental

a Infrared (IR) dichroism studies

Oven and sample holder. The oven was constructed by winding a nichrome wire uniformly over a mica sheet wrapped around a rectangular copper frame (Part A in figure 3.2). This frame is mounted inside a similar frame, the intervening space being filled with plaster of Paris to reduce heat losses. Copper plates with rectangular windows are inserted into the oven through the open sides. One plate B is fixed permanently to the frame. A groove C cut into its side facilitates the mounting of the assembly on an insulating stand inside the sample chamber of the spectrometer. The sample contained between two sodium chloride windows is placed inside the oven and is held in position by the copper plate D which can be fixed to A using removable screws.

Temperature control and measurement. The oven was heated by passing a direct current through the nichrome wire. It was found that after setting the current to a given value a period of about 90 minutes was needed for the temperature to settle down to a steady value. The large cross-sectional area of the sodium chloride windows together with the fact that

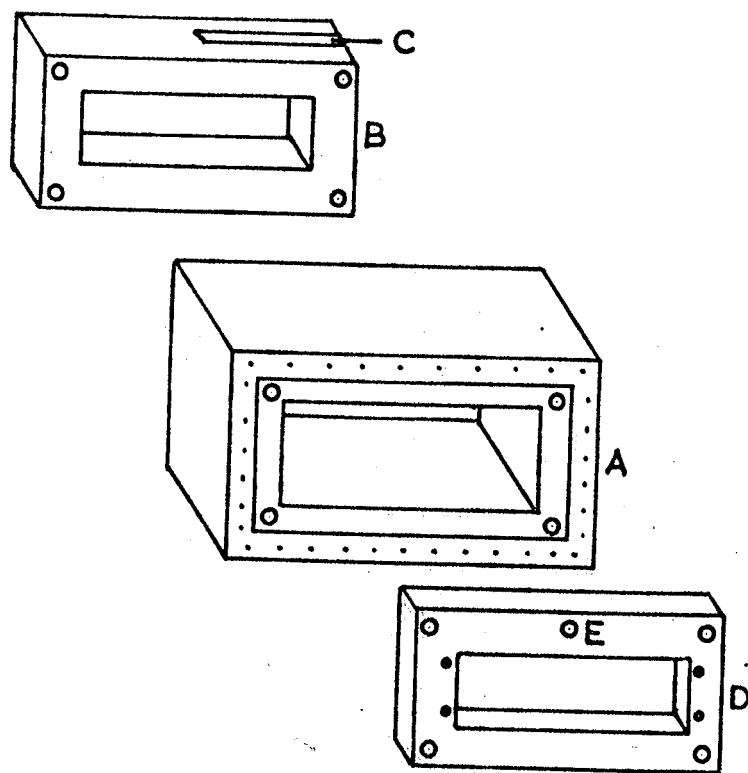


FIGURE 3.2

Schematic diagram of the oven (A) and sample holder assembly used for studying the IR absorption in a liquid crystal sample.

only the edges of the windows are in contact with the oven, gives rise to a temperature gradient in the sample. At the highest temperature of measurement this gradient was found to be about 1°C between the centre and the edge of the sample. The temperature was measured using a calibrated chromel-alumel thermocouple and a multimeter (APLAB model 1005). The error in the measured value of temperature was estimated to be about $\pm 0.5^{\circ}\text{C}$.

Preparation of sample. Samples were prepared in the sandwich configuration between two sodium chloride windows ($53 \times 28 \times 5$ mm) separated by mylar spacers. The windows were first polished and the polished surfaces were then rubbed in a random manner on chamois leather. This facilitates homeotropic alignment of the sample. The liquid crystal was filled in the sandwich cell by allowing it to flow between the windows by capillary action. To avoid the possibility of decomposition of the samples at high temperatures, they were filled in the nematic phase.

The oven containing the sample cell was placed in the sample chamber of a double beam IR spectrometer (Leitz Model 081) and the IR spectra were recorded at different steady temperatures in the isotropic, nematic, smectic A and the re-entrant nematic phases.

b Birefringence measurements

Oven and the sample holder. The oven consists of a rectangular copper frame over which a heating coil is evenly wound, with a thin insulating sheet of mica in between. This assembly is kept inside a similar hollow frame made of asbestos sheets and the intervening space is filled with asbestos powder. The oven was heated by passing a direct current through the heating coil.

The sample holder (figure 3.3) consists of a U-shaped copper block E. The cell in which the sample is to be filled is kept in the central part of the copper block and is held in position by a rectangular copper frame C fixed from above to E. This assembly is covered by another copper block D which is fixed to E again with the help of removable screws. A through hole B (~ 2 mm in diameter) present in the sample holder allows a light beam to be incident on the sample at an angle of 60° . The dimensions of the sample holder are selected in such a way that it fits exactly into the rectangular frame of the oven.

Temperature measurement. The sample holder contains a hole A through which one junction of a chromel-almel thermocouple can be inserted close to the centre of the sample. The other junction of the thermocouple was kept in contact with melting ice. The thermo e.m.f. of this calibrated thermocouple was measured using a multimeter (APLAB Model 1005). A sufficient time (about 30 minutes) was allowed before taking any measurement

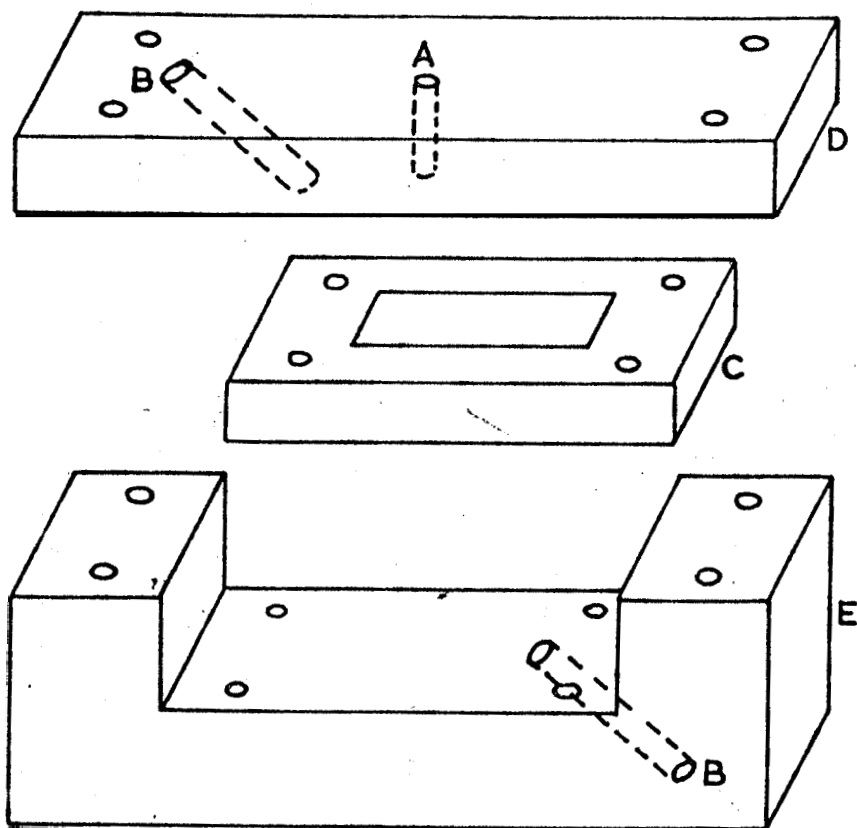


FIG. 3
FIGURE 3.3

Exploded view of the sample holder used for measuring the birefringence of liquid crystals by the oblique incidence method.

so that the temperature was well stabilised. The temperature could be measured to an accuracy of about $\pm 0.25^{\circ}\text{C}$.

Sample preparation. Glass plates of the proper size (18 x 18 x 1.4 mm) were thoroughly cleaned. They were cleaned first with soap solution and were then kept in strong chromic acid for about 20 minutes. Finally, they were rinsed thoroughly with distilled water and dried. The surface quality was tested by ensuring that a thin film of water sticks to the glass surfaces uniformly. To get a good alignment of the liquid crystal, cleanliness of glass surfaces is absolutely essential.

To get a homeotropically aligned liquid crystal sample, the glass plates were treated with suitable surfactants. The cleaned glass plates were dipped in a dilute solution of cetyl trimethyl ammonium bromide (CTAB) in chloroform (~ 10 mg in 2 ml) and were dried. The glass plates were then rubbed circularly using filter paper so that a thin uniform layer of CTAB is formed on the plates.

The glass plates were placed one over the other in the groove cut in the sample holder with two strips of mylar spacers in between. They were held tightly by the copper frame C (Figure 3.3) which was fixed by means of four screws to E. The uniformity of the thickness of the air film between the glass plates was ascertained by observing interference fringes in a light beam reflected from the cell. The screws were tightened

in such a way that straight fringes as few in number as possible were seen in the field of view.

Thickness measurement. The thickness of the air film between the two glass plates was measured using channelled spectrum. (Figure 3.4). White light from a source O is rendered parallel by a lens L_1 and is allowed to fall normally on the air film between the glass plates. The light reflected from the air film is allowed to converge on the slit S_1 of a constant deviation spectroscopy (Adam and Hilger Ltd.). In the field of view of the spectroscopy alternate bright and dark fringes are seen due to interference of light reflected from the two surfaces forming the air film. The thickness of the air film was calculated using the expression

$$x_0 = \frac{n \lambda_{m+n} - \lambda_m}{2(\lambda_{m+n} - \lambda_m)} \quad (3.7)$$

where λ_m is the wavelength corresponding to any dark fringe (say, m^{th}) and λ_{m+n} that corresponding to the $(m+n)^{\text{th}}$ fringe.

The sample was filled in the cell in the nematic phase by capillary action. The sample holder was placed inside the oven in such a way that the longer edges of the glass plates are horizontal and the shorter edges are vertical.

Optical set up. A horizontal beam of light from a helium-neon laser ($\lambda = 6328 \text{ \AA}$) is passed through a polariser B (see figure 3.5) and is then incident on the sample C at an

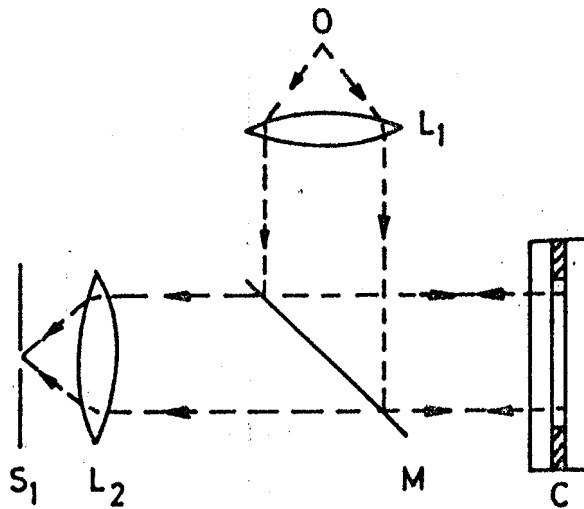


FIGURE 3.4

Arrangement to measure the thickness of the sample by forming the channelled spectrum.

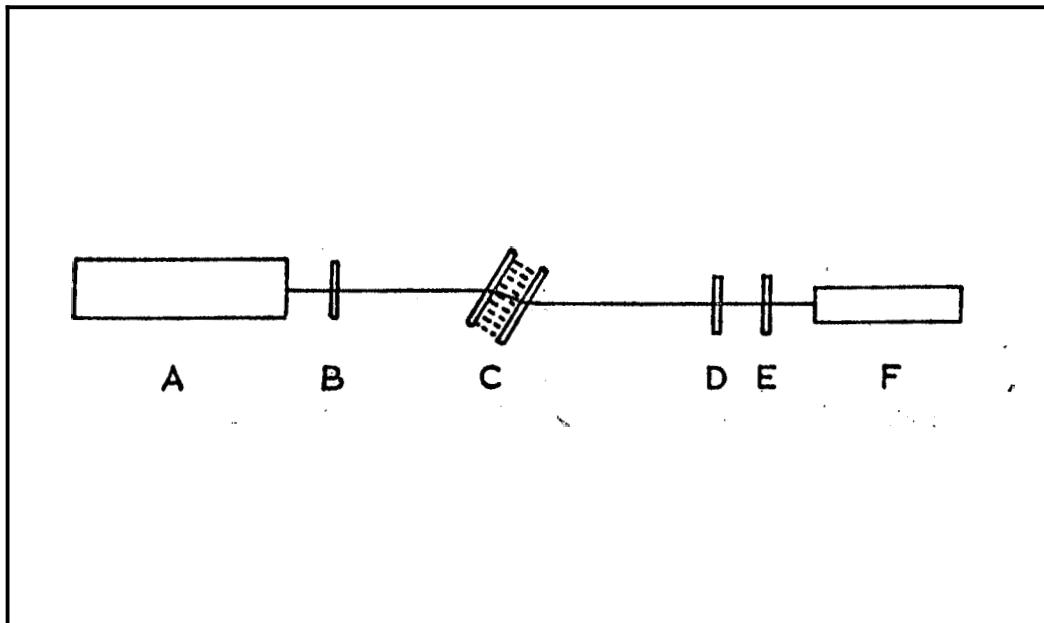


FIG. 3.5

FIGURE 3.5

Schematic diagram of the optical set up used In measuring the birefringence by the oblique incidence method.

oblique angle through the hole present in the sample holder. It then passes through a quarter wave plate D and an analyser E and is finally received by a photodetector F (UDF Model 450). The signal in the photodetector was measured using a micro-voltmeter (Keithley Model 155).

Initially, D is taken out of the path of the light beam and with the sample in the nematic phase the polariser and the analyser were rotated to get minimum intensity. Then the axis of the polariser will be parallel to one of the effective principal axes of the sample. The quarter wave plate D was introduced between the sample and the analyser and was rotated to restore the minimum intensity. Then the principal axes of the quarter wave plate would also be in the vertical and horizontal directions. The polariser and the $\lambda/4$ plate were rotated by 45° each in the same direction. This ensures that the electric vector of the light entering the cell is at an angle of 45° to the effective principal axes of the sample and the principal axes of the quarter wave plate are at 45° to those of the sample.

When light passes through 1 cm of the birefringent liquid crystal whose principal axes are at 45° to the electric vector of the light beam, the emergent beam consists of two components of equal amplitudes, one component being phase shifted by $\frac{2\pi}{\lambda} \Delta$ (see equation 3.5) with respect to the other. When these two orthogonal components pass through a quarter

wave plate arranged as described earlier, they are converted into two circularly polarised beams of opposite sense. Superposition of these yields a linearly polarised light beam with its vibration rotated by $\frac{\pi}{\lambda} \Delta$ with respect to the direction of vibration of the light beam incident on the liquid crystal.

In the present set up, however, light is incident on the sample at a fairly large oblique angle. The reflection coefficients of glass for parallel and perpendicularly polarised light are unequal. Therefore, the amplitudes of the two components of the light beam incident on the sample would not be exactly equal. Hence, in each trial, it was necessary to readjust the orientation of the polariser to get the best crossing.

After making these initial adjustments the sample was taken to the isotropic phase and the analyser was adjusted to get the minimum intensity. Then the sample was cooled to the nematic phase and when the temperature attained a steady value, the analyser was again rotated to get minimum intensity. If θ is the angle of rotation of the analyser in radians

$$\frac{\pi}{\lambda} \Delta = \theta$$

i.e.,

$$\frac{\pi}{\lambda} \left[\frac{n_0}{n_e} (n_e^2 - \sin^2 \theta_1)^{1/2} - (n_0^2 - \sin^2 \theta_1)^{1/2} \right] = \theta \quad (3.8)$$

The observations were taken at different temperatures in the

nematic, smectic A and the re-entrant nematic phases.

Determination of n_0 . As already mentioned, n_0 was measured by the prism method. A hollow glass prism was constructed using two glass plates treated with CTAB. The liquid crystal was mounted at the edge of the prism. The refractive index n_0 was determined by the normal incidence method using a precision goniometer spectrometer. The details of the experimental set up and the procedure adopted will be given in chapter V.

Measurement of density. Using the refractive index data one can calculate the density of a sample from the relation

$$\rho = \frac{3}{4\pi} \cdot \frac{M}{N} \cdot \frac{1}{\bar{\alpha}} \frac{\bar{n}^2 - 1}{\bar{n}^2 + 2} \quad (\text{see equation 1.9}) \quad (3.9)$$

To find the value of $\bar{\alpha}$, it is necessary to measure the density of the sample at a known temperature. The density of 11 GPMBB and 12 GPMBB were measured by the capillary tube method. A small length (~ 2 cms) of the sample was drawn into the middle of the capillary in a tube of length ~ 10 cms. This was kept inside an oven.

The oven consists of a thick walled copper tube having a rectangular slot of about 2 mm width cut along the length of the tube. A nichrome tape wound suitably on this tube serves as the heating coil. The tube is surrounded by an aluminium

3.4 Results and discussion

Infrared diaphragm studies. We have determined the absolute order parameters of two pure compounds, viz., 11 OPMBB and 12 CPMBB and a mixture of 11 OPMBB and 10 OMOPB (in the molar ratio 45 : 55) using the IR technique. The measurements were taken in the isotropic, nematic, smectic A and re-entrant nematic phases. The transition temperatures for these systems are given in table 3.1. (Hereafter all the tables will be given at the end of the chapter.)

The IR absorption band used in our studies was the localized -C≡N stretching mode (at 2247 cm^{-1}). This is a strong and distinct vibrational band which is almost free from any overlap from neighbouring bands.

The angle θ between the long axis of the molecule and the -CN end-group was evaluated by constructing a geometrical

model of the molecule. (The angle was $\sim 12^\circ$ for 11 OPMBB and 12 OPMBB and was $\sim 18^\circ$ for 10 OMOPC.) In 11 OPMBB, 12 OPMBB as well as 10 OMOPC, the long axis of the molecule was assumed to be the line joining the centres of the two extreme phenyl rings of the molecule. An effective value of θ for the mixture was calculated using the formula $\theta = p_1\theta_1 + p_2\theta_2$ where p_1 and p_2 are the mole fractions of the components 1 and 2 of the mixture and θ_1 and θ_2 are the corresponding angles.

Using homeotropically aligned samples and unpolarised radiation the absorption strength of the -CN band was studied as a function of temperature. A typical set of absorption peaks obtained in the isotropic, nematic, smectic A and re-entrant nematic phases are shown in figure 3.6. At each temperature three runs of the spectrum were taken and the average value of the dichroic ratio was calculated. If I is the intensity value corresponding to the absorption peak and I_0 , that corresponding to the base line, the width of the absorption band corresponding to the intensity $(II_0)^{1/2}$ was taken as Δy_2 . This was measured using a travelling microscope. A correction K for the finite spectral slit width was applied following Ramsay's procedure (Ramsay 1952). Then the integrated absorption of the band is equal to $K \cdot \ln(I_0/I) \Delta y_2$.

The dichroic ratio R is the ratio of the integrated absorption in the liquid crystalline phase to that in the

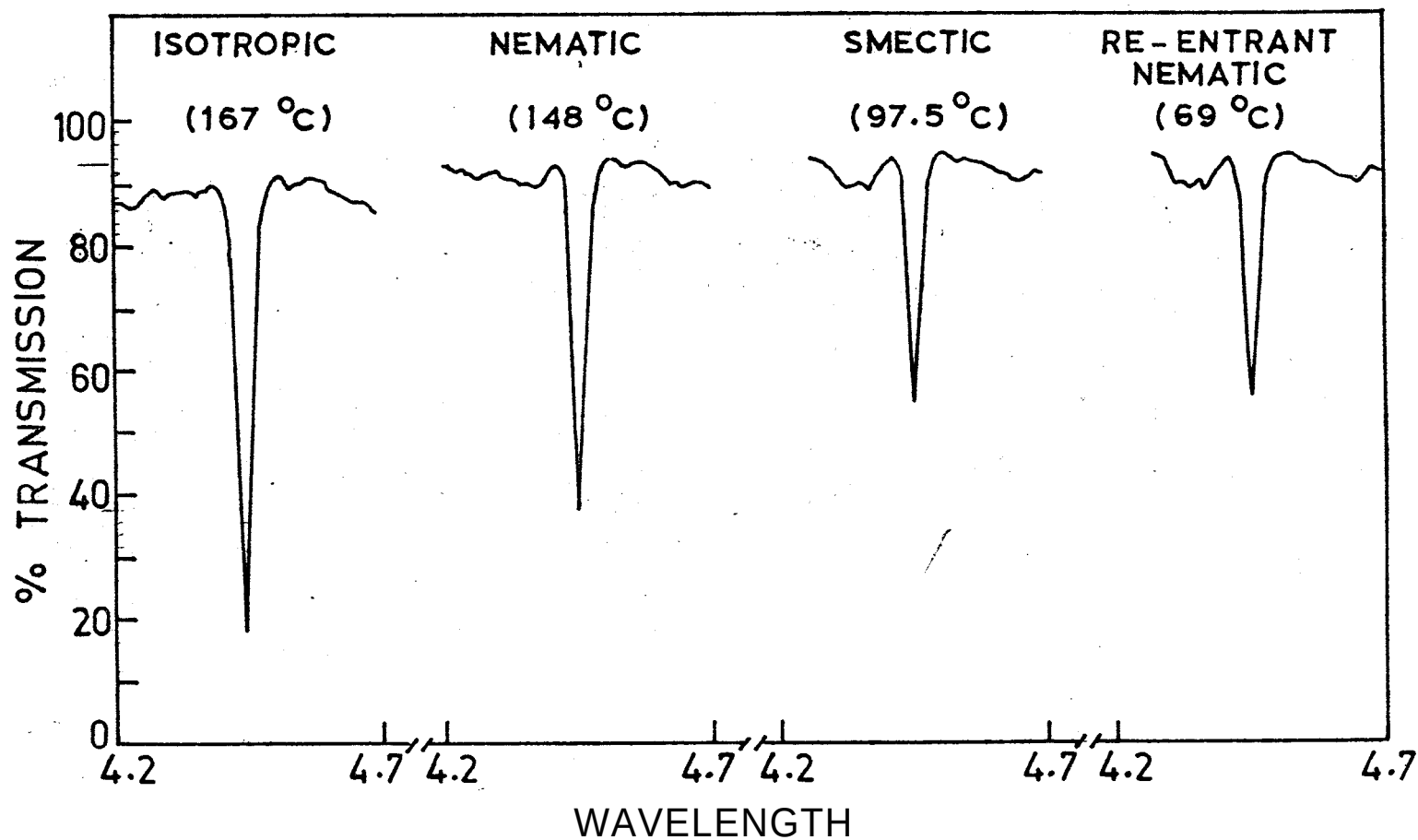


FIGURE 3.6

FIG.

Trace of the IR absorption peaks of the -CN stretching mode in 11 CPMBB in different phases. The wavelengths are given in microns.

isotropic phase. Knowing this the absolute value of s can be calculated using equation (3.2).

In the case of 12 CPMBB, the thermal range of appearance of the re-entrant phase is small and hence the compound had to be cooled at a comparatively fast rate. The alignment of the sample near the smectic - re-entrant nematic transition point in this case was not as good as that in the other two cases.

The values of s plotted against temperature are shown in figure 3.7. The estimated error in the value of s is about $\pm 5\%$.

As the sample is cooled from the isotropic phase the rate of increase of order parameter is fairly large close to the nematic-isotropic (NI) transition point. But with further lowering of temperature, the rate decreases. No abrupt or discontinuous change of s is noticed either at the smectic A - re-entrant nematic (AN_r) transition temperature or at the smectic A - re-entrant nematic (AN_r) transition temperature. Within the limits of accuracy of observations the changes appear to be smooth and continuous.

Birefringence measurement

We have determined the ordinary and extraordinary refractive indices of the two pure compounds 11 CPMBB and 12 CPMBB and a mixture of 8 OCB and 10 OMCPD (molar ratio 45 : 55). The measurements were taken in the nematic, smectic A and re-entrant

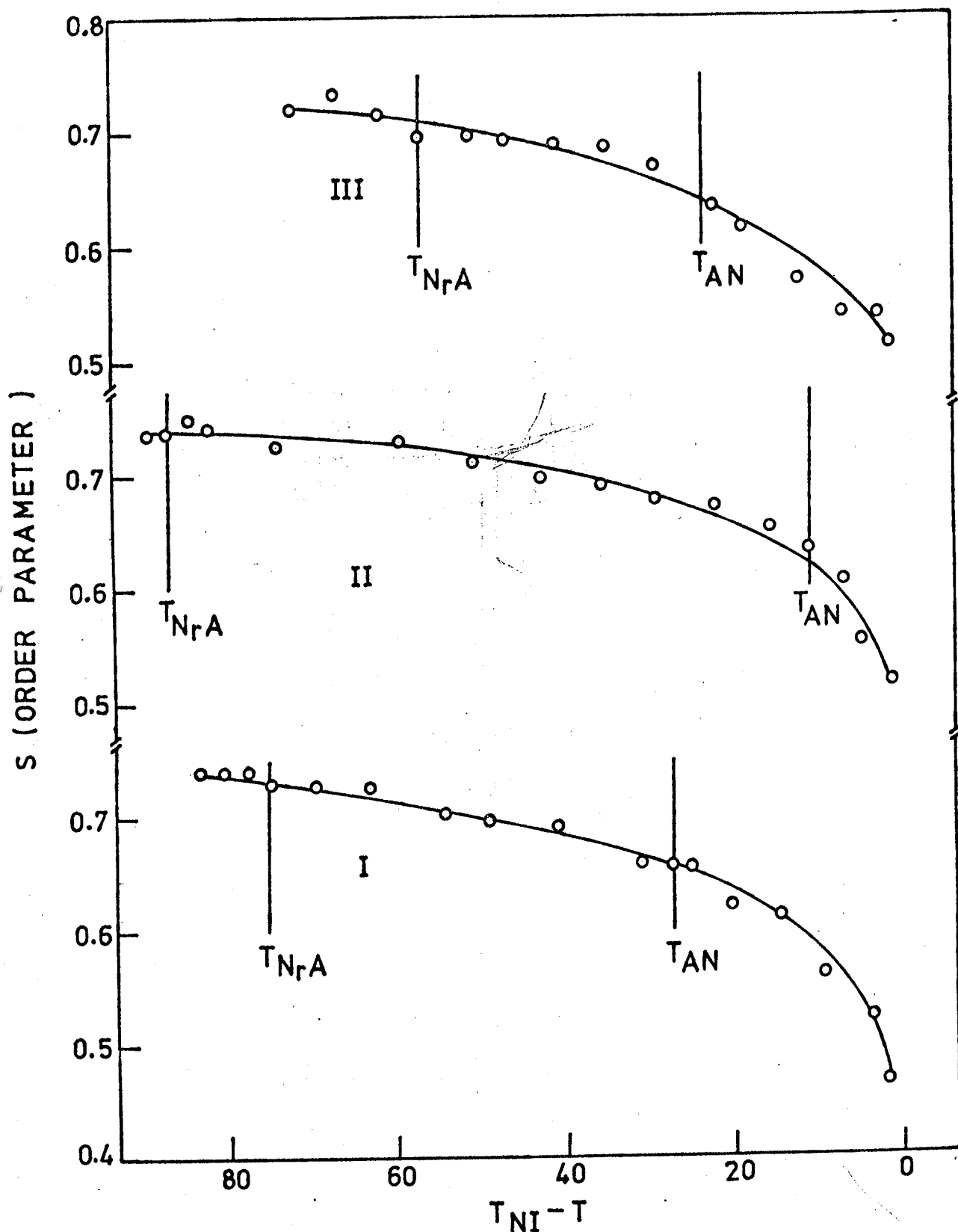


FIGURE 3.7

Variation of order parameter with temperature as measured by the IR dichroism method. (I) 11 CPMBB, (II) 12 CPMBB, and (III) mixture of 11 CPMBB and 10 OMCPG (molar ratio 45 : 55).

phases as the sample was being cooled from the isotropic phase.

These values are plotted against temperature in diagrams 3.8, 3.9 and 3.10 for 11 CPMBB, 12 CPMBB and the mixture respectively. The corresponding values are tabulated in tables 3.2, 3.3 and 3.4. Measurements were carried out on two independent samples and the values obtained in the two cases are in good agreement with each other within the limits of experimental error. The error was estimated to be about $\pm 1\%$. This error arises mainly due to the uncertainty in the measurement of thickness of the sample.

The order parameters were calculated from the birefringence data using the formula (see equation 1.8)

$$s = \frac{\bar{\alpha}}{\Delta\alpha} \frac{n_e^2 - n_o^2}{n^2 - 1} \quad (3.10)$$

To find the value of s using this relation we should know the value of $\bar{\alpha} / \Delta\alpha$. One can determine the value of $\Delta\alpha$ if the refractive indices and the structure of the crystal are known. As these were not known, we could not determine $\Delta\alpha$ directly.

In the case of 11 CPMBB and 12 CPMBB, the values of $\bar{\alpha} / \Delta\alpha$ were determined by normalising the value of $(n_e^2 - n_o^2) / (n^2 - 1)$ with the values of s obtained from the IR absorption measurements at the lowest temperature in the

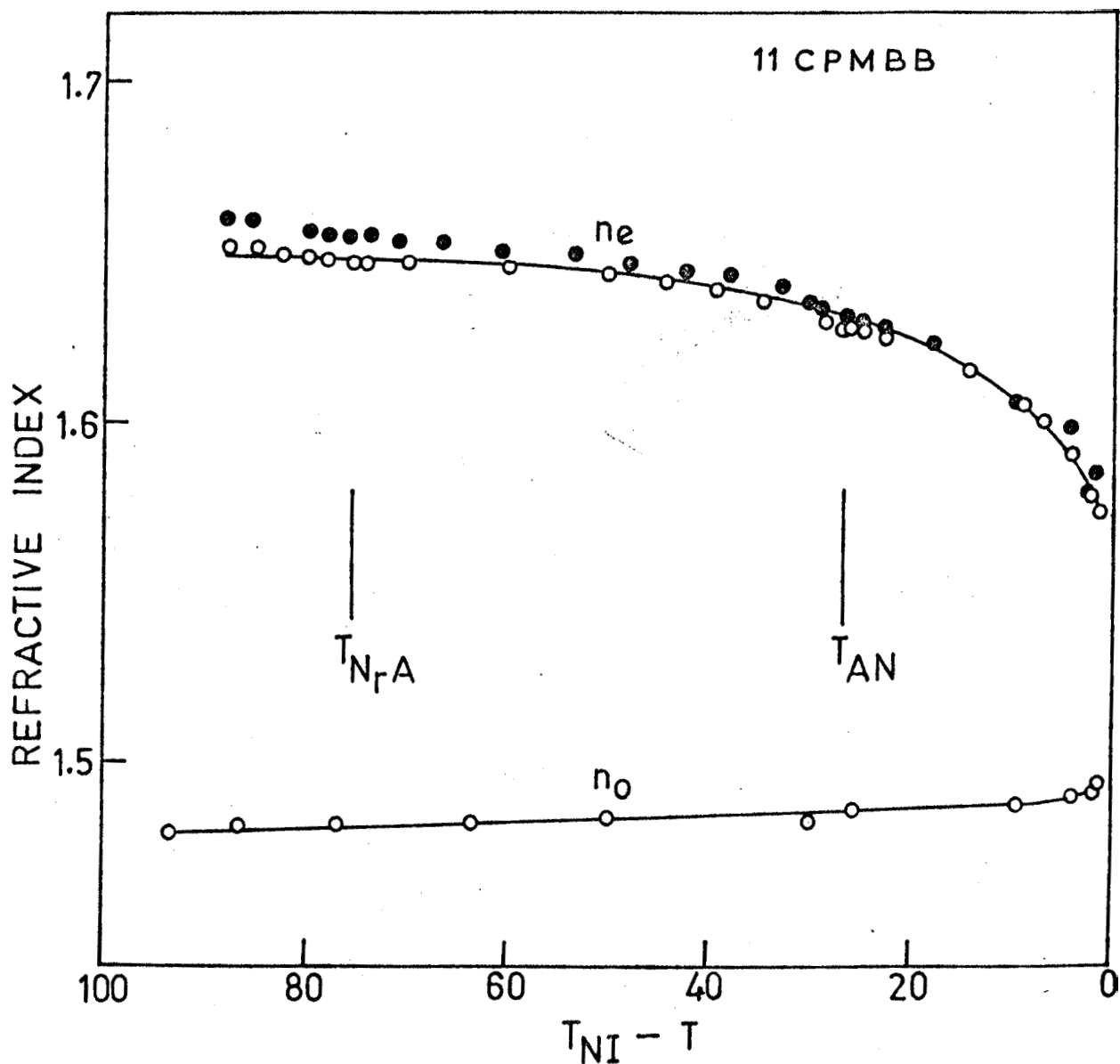
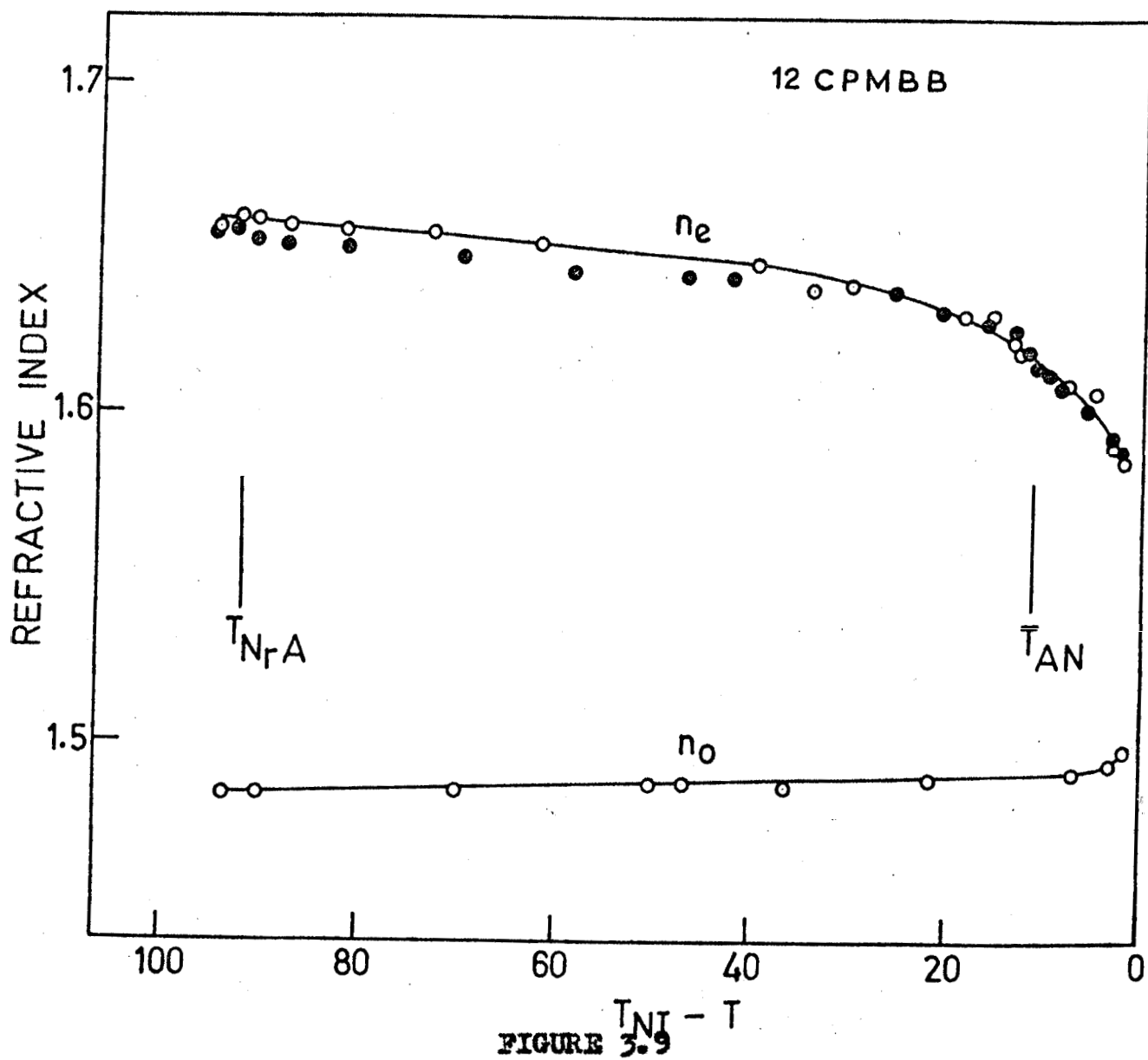


FIG. 3.8
FIGURE 3.8

Refractive indices of 11 CPMBB as functions of relative temperature. Filled and open circles represent measurements made on two independent samples.



Refractive indices of 12 CPMBB as functions of relative temperature. Filled and open circles represent measurements made on two independent samples.

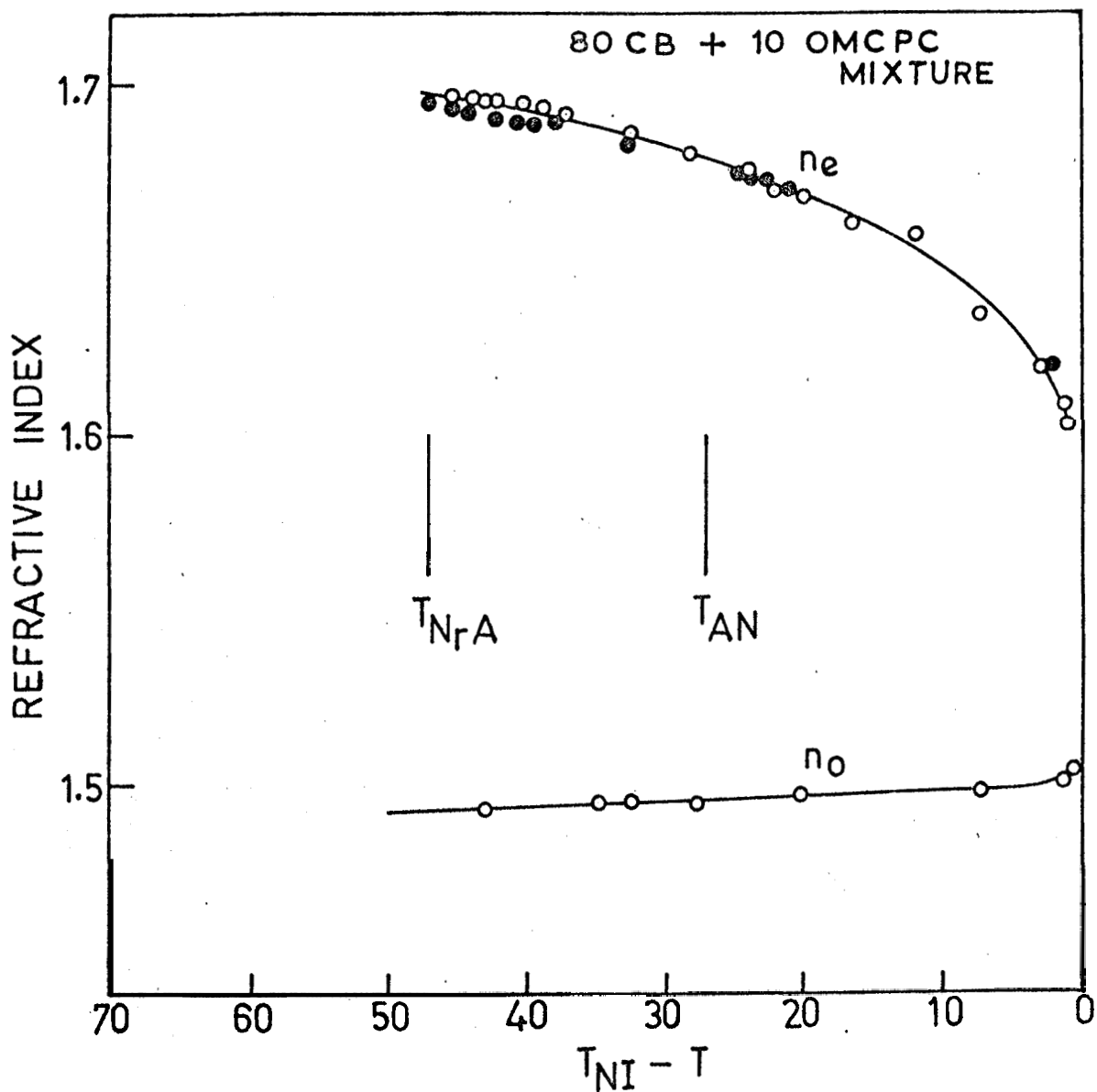


FIGURE 3.10

Refractive indices of the mixture of 80CB and 10 OMCP (molar ratio 45:55) as functions of relative temperature. Filled and open circles represent measurements made on two independent samples.

smectic phase. In the case of the mixture, $\Delta\alpha$ and $\bar{\alpha}$ were calculated using the additive law of polarisabilities (Chandrasekhar and Madhusudana, 1969). If $\Delta\alpha_1$ is the polarisability anisotropy of the component of mixture with mole fraction p_1 and $\Delta\alpha_2$ that for the other component with mole fraction p_2 , $\Delta\alpha = p_1 \Delta\alpha_1 + p_2 \Delta\alpha_2$. A similar formula holds good for $\bar{\alpha}$ of the mixture. The values of $\bar{\alpha}$ and $\Delta\alpha$ for the pure compounds 8 OCB and 10 OMCPG were taken from the data of Karat (1977). The polarisability data are given in table 3.5.

The values of orientational order parameters for 11 GPMBB, 12 GPMBB and the mixture are plotted as functions of temperature in figure 3.11 and the values are given in tables 3.2, 3.3 and 3.4.

Even with the improved accuracy obtained here we have not observed any discontinuous change in the value of s at the AN or AN_r transition points in 11 GPMBB and the mixture. This result is in agreement with the magnetic susceptibility measurements in some other pure compounds exhibiting re-entrant nematic phase reported by Hardouin et al (1979). However, in 12 GPMBB we have observed a slight increase in the value of s in the smectic A phase close to the AN_r transition point and subsequent decrease in the re-entrant nematic phase. Also there appears to be a slight change in the slope of the curve at the AN transition point.

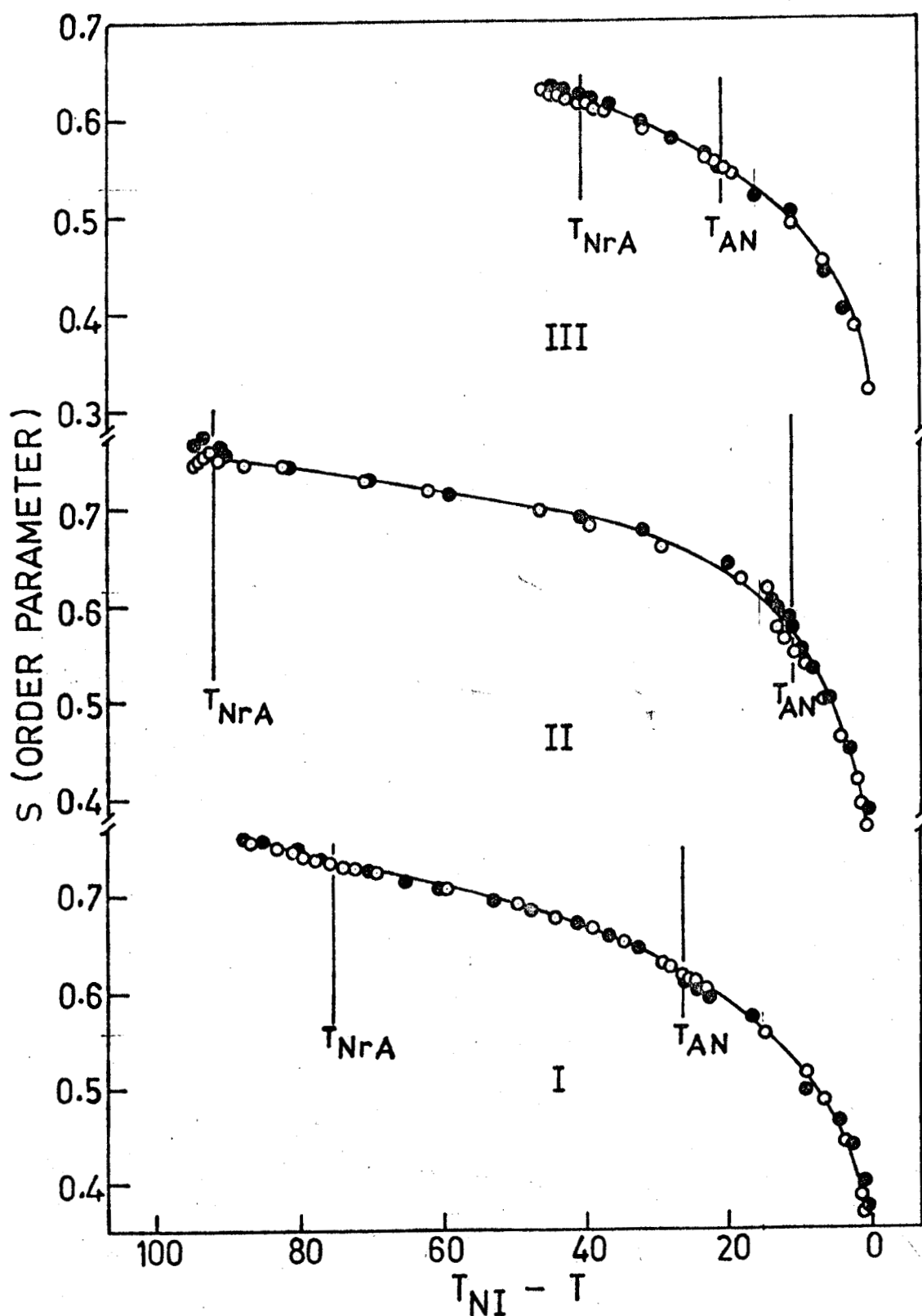


FIGURE 3.11

Order parameters (calculated using birefringence data).

(I) 11 OPMBB, (II) 12 OPMBB, and (III) mixture of 8 OCB and 10 OMCPG.

The heats of transition associated with AN and AN_x transitions of 12 CPMBB are much higher than the corresponding values of 11 CPMBB (see table 2.2). At the AN_x transition point of 12 CPMBB considerable scattering of light was observed due to the weak first order nature of the transition (see chapter IV). Though the heat of AN transition is higher than that of AN_x transition, not much scattering of light was observed at the AN transition in the cooling cycle. This is due to the fact that at the AN transition point the transition is taking place from the nematic phase to the smectic phase where the thermal fluctuations responsible for the scattering of light are considerably reduced. Also close to the AN_x transition point there is slight deterioration in the alignment of the sample. This may be responsible for the observed trend in the variation of s in the re-entrant nematic phase of 12 CPMBB.

Density. The density of 11 CPMBB as measured by the capillary tube method was 1.077 gm/cc at 127°C and that of 12 CPMBB was 1.086 gm/cc at 113°C. Substituting these values in equation (1.9) the polarisability $\bar{\alpha}$ was calculated in each case. For the mixture the values of $\bar{\alpha}$ was calculated using the additive law. If $\bar{\alpha}_1$ is the polarisability of the component having the mole fraction p_1 and $\bar{\alpha}_2$ that of the other component having mole fraction p_2 ,

$$\bar{\alpha} = \bar{\alpha}_1 p_1 + \bar{\alpha}_2 p_2 \quad (3.11)$$

Substituting the value of $\bar{\alpha}$, in equation (1.9), one can calculate the temperature variation of density.

The values of density plotted against relative temperature for the samples under study are shown in figure 3.12. The values are given in tables 3.2, 3.3 and 3.4. The n_0 values are accurate to only about $\pm 1\%$. Correspondingly the error in the values of density is about $\pm 2\%$. Hence we cannot come to any definite conclusions about the temperature variation of density in these systems.

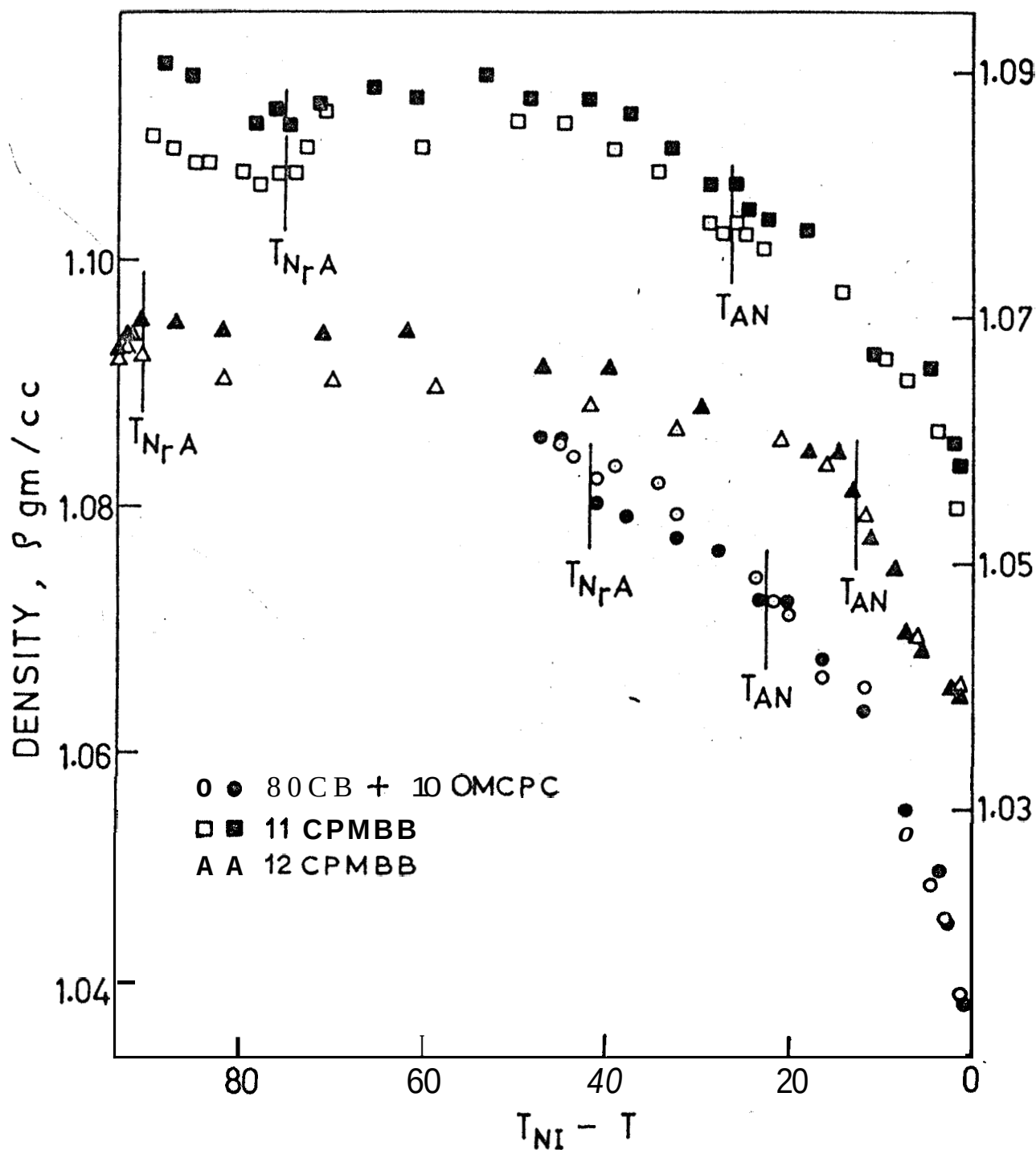


FIGURE 3.12

Densities of 11 CPMBB, 12 CPMBB and the mixture of 8 OCB and 10 OMCP (molar ratio 45:55) as functions of relative temperature. For 12 CPMBB and the mixture the scale of density is given on the left side and for 11 CPMBB, this is given on the right side. The open and filled symbols represent measurements made on independent samples.

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TABLE 3.1

Transition temperatures ($^{\circ}\text{C}$)

	Isotropic- nematic	Nematic- smectic A	Smectic A- reentrant nematic	Reentrant nematic - crystal
11 CPMBB	152.5	127.0	78.0	~ 65.0
12 CPMBB	148.5	138.0	59.8	~ 56.0
Mixture of 11 CPMBB and 10 OMCPG (molar ratio 45 : 55)	109.5	85.5	52.8	~ 33.0
Mixture of 8 OCB and 10 OMCPG (molar ratio 45 : 55)	73.2	52.0	32.0	~ 25.0

TABLE 3.2

Refractive indices, order parameters and densities of 11 CPMBB
(Note: Refractive index values correspond to $\lambda = 6328 \text{ \AA}$)

$T_{NI} - T$	n_o	n_e	s	$\rho_{gm/cc}$
<u>Trial No. 1</u>				
1.5	1.492	1.574	0.363	1.053
2.0	1.491	1.578	0.385	1.054
4.0	1.490	1.591	0.447	1.061
7.0	1.489	1.600	0.488	1.065
9.5	1.488	1.606	0.519	1.067
14.5	1.487	1.616	0.563	1.072
23.0	1.486	1.625	0.605	1.076
25.0	1.486	1.626	0.612	1.077
26.0	1.486	1.627	0.616	1.078
27.0	1.485	1.627	0.621	1.077
28.5	1.485	1.629	0.628	1.078
29.5	1.485	1.630	0.631	1.078
34.5	1.485	1.636	0.655	1.082
39.5	1.485	1.640	0.670	1.084
44.5	1.485	1.642	0.682	1.086
50.0	1.484	1.644	0.693	1.086
60.0	1.482	1.646	0.709	1.084
70.0	1.480	1.647	0.726	1.083
73.0	1.480	1.648	0.731	1.084
74.0	1.479	1.647	0.732	1.082
76.0	1.479	1.648	0.733	1.082
78.0	1.478	1.648	0.738	1.081
80.0	1.478	1.648	0.741	1.082
83.5	1.478	1.651	0.750	1.083
87.5	1.478	1.652	0.758	1.084
<u>Trial No. 2</u>				
1.25	1.494	1.579	0.361	1.056
2.0	1.492	1.586	0.375	1.060
2.75	1.492	1.596	0.442	1.066
4.75	1.490	1.600	0.464	1.066
10.25	1.488	1.606	0.499	1.067
17.75	1.487	1.625	0.578	1.077
22.75	1.486	1.628	0.597	1.078
24.75	1.486	1.630	0.604	1.079
25.75	1.486	1.631	0.609	1.080
26.75	1.486	1.632	0.614	1.081
27.75	1.485	1.632	0.619	1.081
29.75	1.485	1.636	0.630	1.082
32.75	1.485	1.640	0.649	1.084
41.75	1.485	1.647	0.673	1.087
48.25	1.484	1.648	0.685	1.088
53.25	1.484	1.651	0.695	1.088
60.75	1.482	1.652	0.707	1.088
70.75	1.480	1.654	0.724	1.087
73.75	1.480	1.655	0.731	1.086
75.75	1.479	1.655	0.735	1.087
76.75	1.479	1.656	0.738	1.087
78.75	1.478	1.656	0.744	1.086
80.75	1.478	1.658	0.752	1.088
85.75	1.478	1.662	0.768	1.090
88.25	1.478	1.664	0.775	1.091

TABLE 3.3

Refractive indices, order parameters and densities of 12₂CPMBB
 [Note: Refractive index values correspond to $\lambda = 6328 \text{ \AA}$]

$T_{NI} - T$	n_o	n_e	s	$\rho_{gm/cc}$
Trial No.1				
0.5	1.500	1.578	0.358	1.064
1.0	1.498	1.583	0.391	1.065
2.0	1.497	1.589	0.421	1.067
3.5	1.494	1.593	0.453	1.066
6.0	1.492	1.602	0.503	1.069
8.5	1.491	1.608	0.537	1.072
10.0	1.491	1.613	0.558	1.075
11.0	1.491	1.615	0.567	1.076
12.0	1.491	1.621	0.590	1.079
13.0	1.491	1.625	0.610	1.082
16.0	1.490	1.629	0.632	1.083
21.0	1.490	1.633	0.646	1.085
32.5	1.488	1.638	0.679	1.086
41.5	1.488	1.641	0.692	1.088
59.0	1.487	1.645	0.712	1.089
70.25	1.486	1.648	0.730	1.090
81.5	1.485	1.650	0.745	1.090
90.5	1.485	1.653	0.756	1.092
91.5	1.485	1.656	0.770	1.094
92.5	1.484	1.656	0.777	1.093
93.5	1.484	1.656	0.774	1.092
95.25	1.484	1.655	0.774	1.092
Trial No.2				
1.25	1.498	1.581	0.369	1.064
2.00	1.497	1.586	0.393	1.065
3.00	1.495	1.590	0.421	1.066
4.80	1.493	1.599	0.467	1.068
7.0	1.491	1.604	0.500	1.069
10.5	1.491	1.613	0.540	1.077
11.8	1.491	1.619	0.561	1.079
13.25	1.491	1.623	0.580	1.081
18.5	1.489	1.633	0.628	1.084
30.0	1.488	1.640	0.664	1.088
40.0	1.488	1.645	0.685	1.091
47.0	1.487	1.648	0.699	1.091
62.0	1.487	1.653	0.719	1.094
71.0	1.486	1.654	0.731	1.094
82.0	1.485	1.656	0.742	1.094
87.5	1.485	1.657	0.748	1.095
91.0	1.485	1.658	0.753	1.095
92.0	1.485	1.659	0.756	1.094
93.0	1.484	1.659	0.761	1.093
94.5	1.484	1.656	0.747	1.093

TABLE 3.4

Refractive indices, order parameters and densities of a
mixture of 8 OCB and 10 OMCPG
[Note: refractive index values correspond to $\lambda = 6328 \text{ \AA}$]

	T NI - T	n_o	n_e	s	$\rho_{gm/cc}$
Trial	0.50	1.506	1.595	0.292	1.039
No.1	1.25	1.502	1.604	0.332	1.040
	2.75	1.500	1.620	0.392	1.046
	4.75	1.499	1.625	0.411	1.049
	7.25	1.498	1.636	0.446	1.053
	11.75	1.498	1.657	0.510	1.065
	16.75	1.497	1.661	0.525	1.067
	20.25	1.497	1.669	0.548	1.071
	21.75	1.497	1.671	0.555	1.072
	22.75	1.496	1.672	0.563	1.072
	24.25	1.496	1.675	0.571	1.074
	28.25	1.496	1.680	0.587	1.079
	32.75	1.495	1.686	0.607	1.083
	39.25	1.495	1.693	0.626	1.083
	40.25	1.494	1.693	0.628	1.083
	41.25	1.494	1.693	0.631	1.082
	42.25	1.494	1.694	0.634	1.083
	43.25	1.494	1.695	0.637	1.084
	45.25	1.494	1.697	0.642	1.085
Trial No.2					
	0.50	1.506	1.595	0.293	1.039
	1.00	1.503	1.603	0.326	1.040
	2.75	1.500	1.620	0.389	1.046
	7.25	1.498	1.639	0.455	1.055
	11.75	1.498	1.653	0.499	1.063
	16.75	1.497	1.662	0.528	1.067
	20.25	1.497	1.669	0.550	1.072
	21.75	1.497	1.671	0.556	1.072
	22.75	1.496	1.672	0.561	1.072
	23.75	1.496	1.673	0.566	1.072
	24.75	1.496	1.675	0.572	1.074
	28.25	1.496	1.680	0.585	1.076
	32.75	1.495	1.683	0.598	1.077
	38.00	1.495	1.689	0.612	1.079
	39.75	1.495	1.690	0.618	1.079
	40.75	1.494	1.689	0.620	1.080
	42.25	1.494	1.690	0.623	1.080
	44.25	1.494	1.692	0.627	1.082
	47.00	1.494	1.695	0.637	1.083

TABLE 3.5

$\bar{\alpha}$, and $\bar{\alpha}/\Delta\alpha$ for 11 CPMBB, 12 CPMBB and a mixture
of 8 OCB and 10 OMCPG

Sample	$\bar{\alpha} \times 10^{24} \text{ cm}^3$	$\bar{\alpha}/\Delta\alpha$
11 CPMBB	58.45	1.862
12 CPMBB	60.07	1.950
(8 OCB + 10 OMCPG) mixture	43.93	1.436