

CHAPTER VI

STUDIES ON 2-CYANO-4-HEPTYLPHENYL-4'-PENTYL-4-BIPHENYL CARBOXYLATE AND SOME OF ITS MIXTURES WITH 4-HEPTYL-4'- CYANOBIPHENYL

6.1 Introduction

In the last few chapters, we have discussed studies on some interesting phenomena like the occurrence of the re-entrant nematic phase and induced smectic mesomorphism. These phenomena are closely associated with the presence of cyano end groups whose dipole moments are pointing almost exactly along the major axis of the molecule. Compounds consisting of such molecules have large positive dielectric anisotropy. In this chapter we present some observations made on a compound consisting of molecules having the cyano-group at a large angle with respect to the long axis of the molecule. Such a compound will have a large negative dielectric anisotropy.

We have measured the refractive indices and splay elastic constants of the compound at different temperatures. The ordinary refractive index shows an unusual trend in its temperature variation. In order to confirm the temperature variation of order parameter deduced from birefringence data, we measured the order parameter by an independent method, viz., by the wide-line nuclear magnetic resonance (NMR) method.

We have also studied the phase diagram of mixtures of this compound with 7OB which consists of molecules having the terminal cyano-group, almost along the long axis. The order parameters and splay elastic constants of some of these mixtures have also been determined.

6.2 Experimental

The compound 2-cyano-4-heptylphenyl-4'-pentyl-4-biphenyl carboxylate [7P(2CN)5BC] was obtained from E.Merck (Darmstadt) and was used without further purification. The structural formula of the compound is given in figure 6.1. The compound exhibits nematic phase over a wide temperature range. The crystal melts at 45.5°C to the nematic phase and becomes isotropic at 102°C . But it can be easily supercooled and measurements can be taken right down to room temperature. The Merck catalogue gives a value of -4.0 for the dielectric anisotropy of this compound (presumably at room temperature).

The refractive indices were determined by the prism method described in chapter V. The splay elastic constants were determined by the Freedericksz transition method (see chapter IV).

The NMR studies. The wide-line NMR technique has been extensively used to determine the order parameters of liquid crystals (Spence et al 1953, Lippmann and Weber 1957, Saupe and Maier 1961, Ghosh 1972). When a nematic liquid crystal with positive diamagnetic anisotropy is placed in the magnetic field

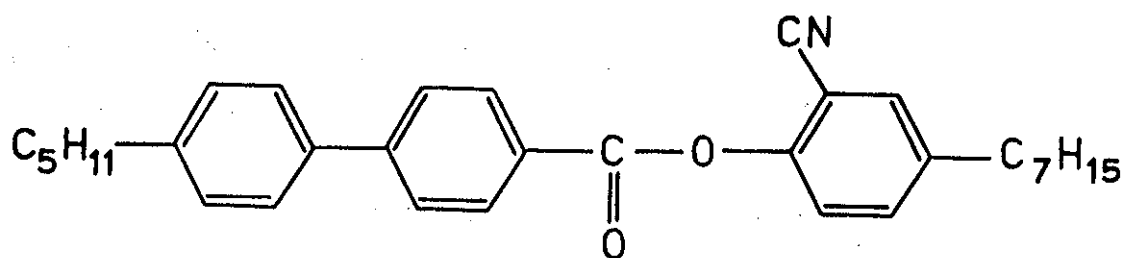


FIGURE 6.1

Structural formula of 2-cyano-4-(heptyloxy)phenyl 4-(5-pentylphenyl)carboxylate [7P(2CN)5BC]

(of the NMR spectrometer) the director aligns along the field. For a typical mesogen, the line joining the ortho protons of the benzene ring is approximately parallel to the long axis of the molecule. Each ortho proton is coupled to the dipolar field of the other ortho proton, in addition to being coupled to the external magnetic field. It is also coupled to all the other protons present in the molecule. But these couplings are usually very weak in comparison with the coupling between the ortho protons. The dipole-dipole coupling between the ortho protons results in a doublet splitting of the NMR signal when the compound is in the mesophase. The doublet spacing is directly proportional to the order parameter in a nematic liquid crystal. In the isotropic phase, since the molecule tumbles rapidly in all directions, the splitting vanishes. If r is the distance between the ortho protons and μ_p is the magnetic moment of the proton,

$$s = \frac{1419}{\mu_p} r^3 \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)^{-1} \Delta\omega \quad (6.1)$$

where $\Delta\omega$ is the frequency shift in hertz (i.e., half the separation between the peaks) and θ is the angle between the line joining the ortho protons and the long axis of the molecule. On substituting the values of μ_p and r (2.45 Å), equation 6.1 reduces (Boilini and Ghosh 1975) to

$$s = 8.16 \times 10^{-2} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right)^{-1} \Delta\omega \quad (6.2)$$

where $\Delta\omega$ is in KHz.

In the actual analysis one has to consider not only the interaction between the ortho protons but also the interaction between each ortho proton and all other protons present in the molecule. In other words, to get accurate values of δ , one has to make a line shape analysis of the NMR spectrum (Ghosh 1972). As our main interest was to study the temperature variation of δ we have not made a line shape analysis of the NMR signal.

The NMR spectra were recorded using an FT-NMR spectrometer (Bruker WM-270). The frequency of operation was 270 MHz. The sample was taken inside an NMR tube of internal diameter ~ 4 mm. It was heated by blowing dry, hot nitrogen. The temperature could be controlled and measured to an accuracy of $\pm 0.5^\circ$. Before conducting the experiment, temperature calibration was done using the known temperature variation of the chemical shift of ethylene glycol. For the purpose of locking the signal heavy water (D_2O) taken in a sealed capillary tube was placed inside the sample tube. In the nematic phase of the sample, the NMR spectra were recorded at different steady temperatures. One typical set of recordings is shown in figure 6.2.

The value of ϕ was estimated by constructing a geometrical model of the molecule. The line joining the centres of the extreme phenyl rings of the molecule was taken as the long axis and the angle ϕ was found to be $\sim 7^\circ$. One of the benzene rings of the molecule (see figure 6.1) contains an ortho cyano group.

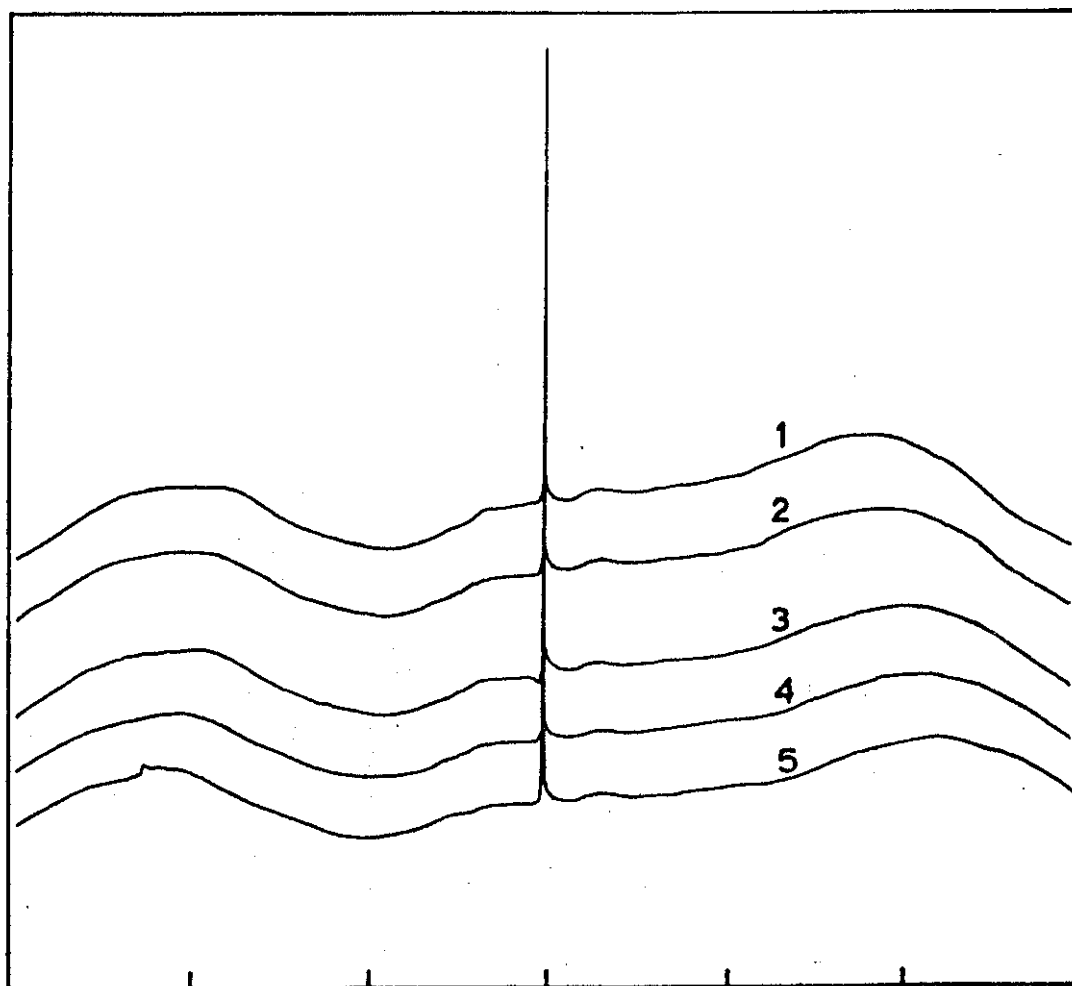


FIGURE 6

Traces of wide-line NMR spectra of 7P(2CN)5BO at different temperatures in the nematic phase (1) 100.5°C, (2) 98.5°C, (3) 96°C, (4) 94.5°C, (5) 92°C. The central sharp line arises from a small amount of water present in D₂O sample used for locking the signal.

Due to the influence of this and also due to the influence of protons other than the ortho protons, the NMR lines appear to be somewhat broad .

6.3 Results and discussion

a. Binary mixtures The phase diagram of the binary mixtures of 7CB and 7P(2CN)5BC is given in figure 6.3. These mixtures do not exhibit induced smectic mesomorphism unlike other binary mixtures of nematogens of which only one component has a terminal cyano-group. The mixtures show only the nematic mesophase. The thermal range of the nematic phase increases as the percentage composition of 7P(2CN)5BC increases. The eutectic temperature of the system was found to be $\sim 21^{\circ}\text{C}$ and the eutectic composition is 21.5% of 7P(2CN)5BC. The van Laar equation (see chapter V) gives the eutectic temperature as 18°C and eutectic composition as 24% 7P(2CN)5BC. These values are in fair agreement with the observed values.

Among the various interactions between a molecule of 7CB and another of 7P(2CN)5BC, the dipole-dipole interaction between the terminal cyano group of 7CB and the lateral cyano group of 7P(2CN)5BC is the strongest. Quite obviously, this interaction does not favour the formation of layers which would give rise to induced smectic A phase in the mixtures.

b. Birefringence. The birefringence of the following systems were determined.

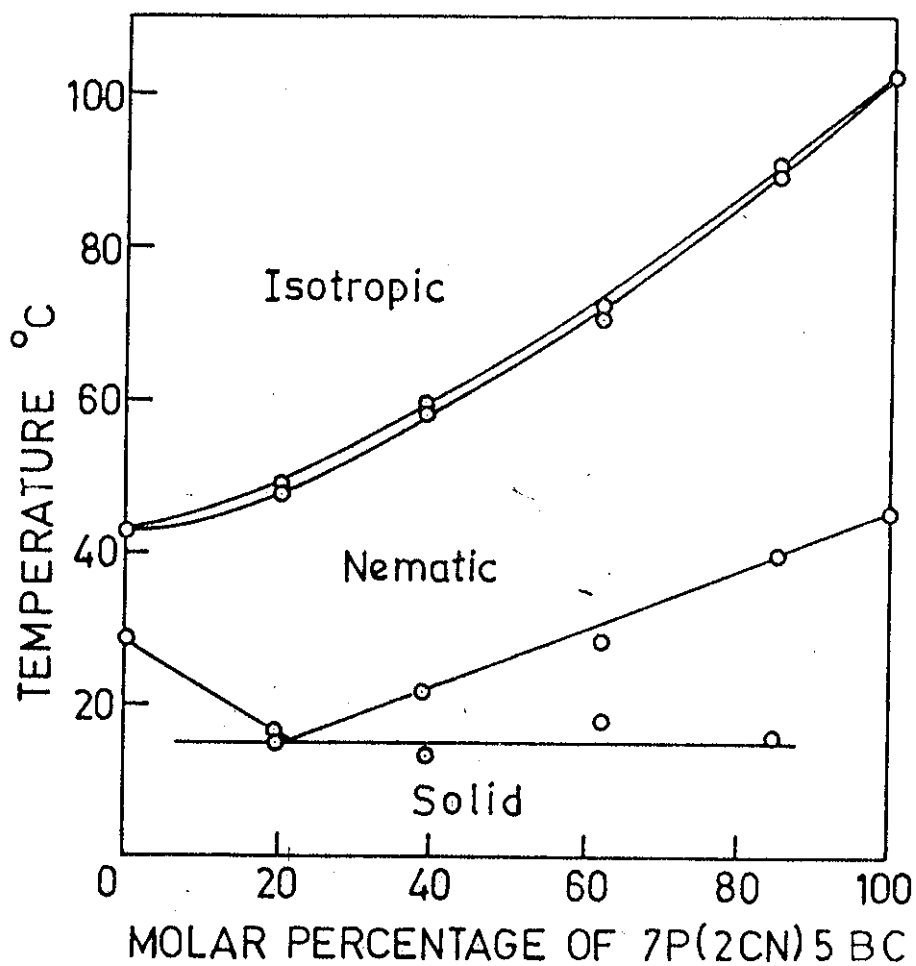


FIGURE 6.3

Phase diagram of mixtures of 7CB and 7P(2CN)5BC

- i) Pure 7P(2CN)5BC
- ii) Mixture 1 of 7CB and 7P(2CN)5BC (molar ratio 80:20)
- iii) Mixture 2 of 7CB and 7P(2CN)5BC (molar ratio 61:39)
- iv) Mixture 3 of 7CB and 7P(2CN)5BC (molar ratio 38:62)
- v) Mixture 4 of 7CB and 7P(2CN)5BC (molar ratio 15:85).

The transition temperatures of these systems are given in table 6.1.

The ordinary and extraordinary refractive indices (n_o and n_e) were measured for the wavelength 6326 Å. The values are given in tables 6.2-6.6 and are plotted against relative temperature in figures 6.4-6.8. The ordinary refractive indices of 7P(2CN)5BC and mixtures 3 and 4 show an unusual trend in temperature variation. As the sample is cooled down from T_{NI} , n_o decreases as usual but after reaching a broad minimum it shows a slight but significant increase with further lowering of temperature. n_e does not show any such unusual temperature variation. The temperature variation of n_e is much larger compared to that of n_o and hence the unusual variation of n_o hardly affects the temperature variation of birefringence. In fact, the birefringence decreases monotonically as the temperature increases, as in other nematics.

A plausible explanation for the unusual temperature variation of n_o is perhaps associated with some structural changes taking place in the medium as the temperature is varied. Indeed,

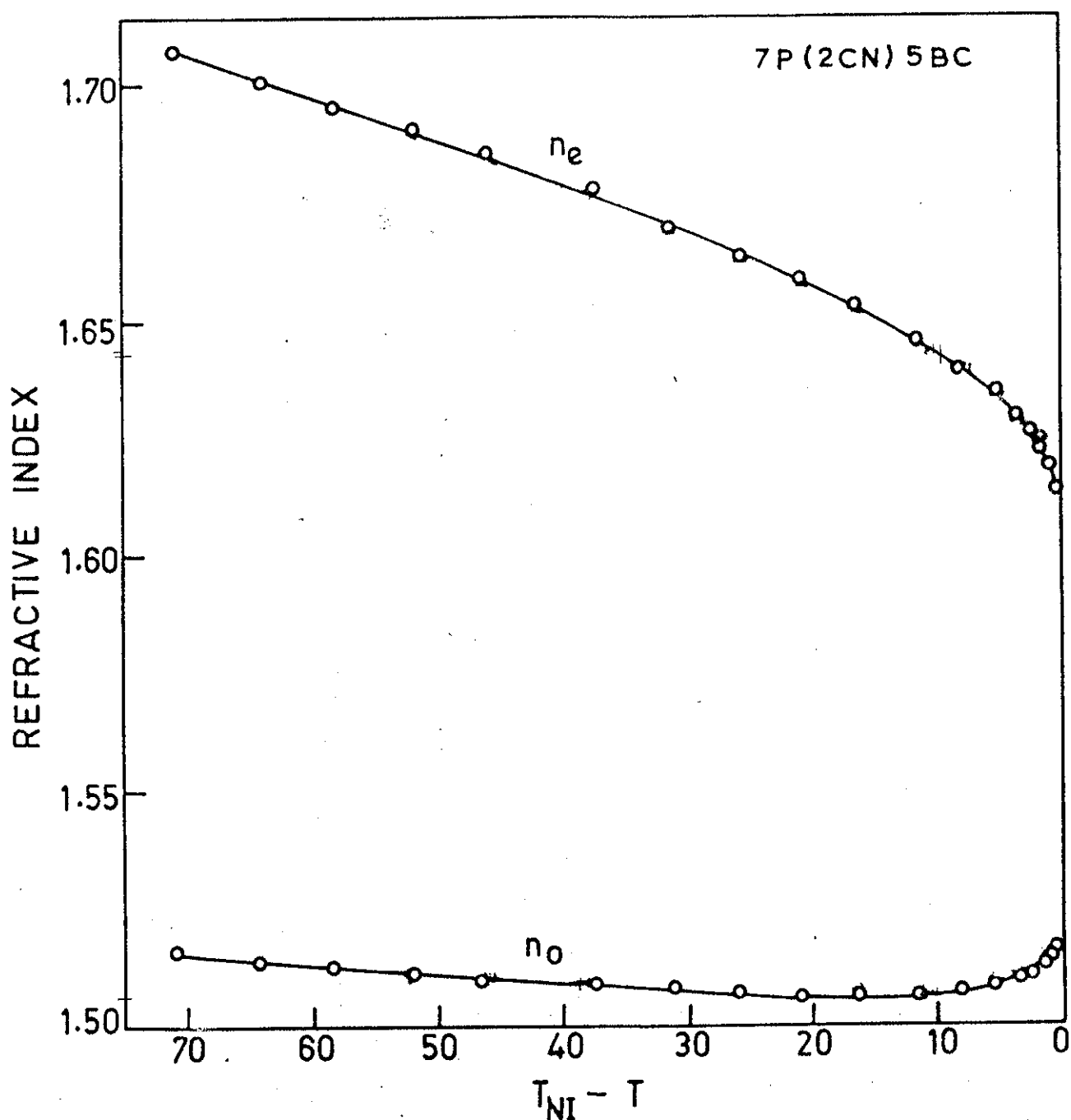


FIGURE 6.4

The ordinary and extraordinary refractive indices of 7P(2CN)5BC plotted against relative temperature, for $\lambda = 6328 \text{ nm}$.

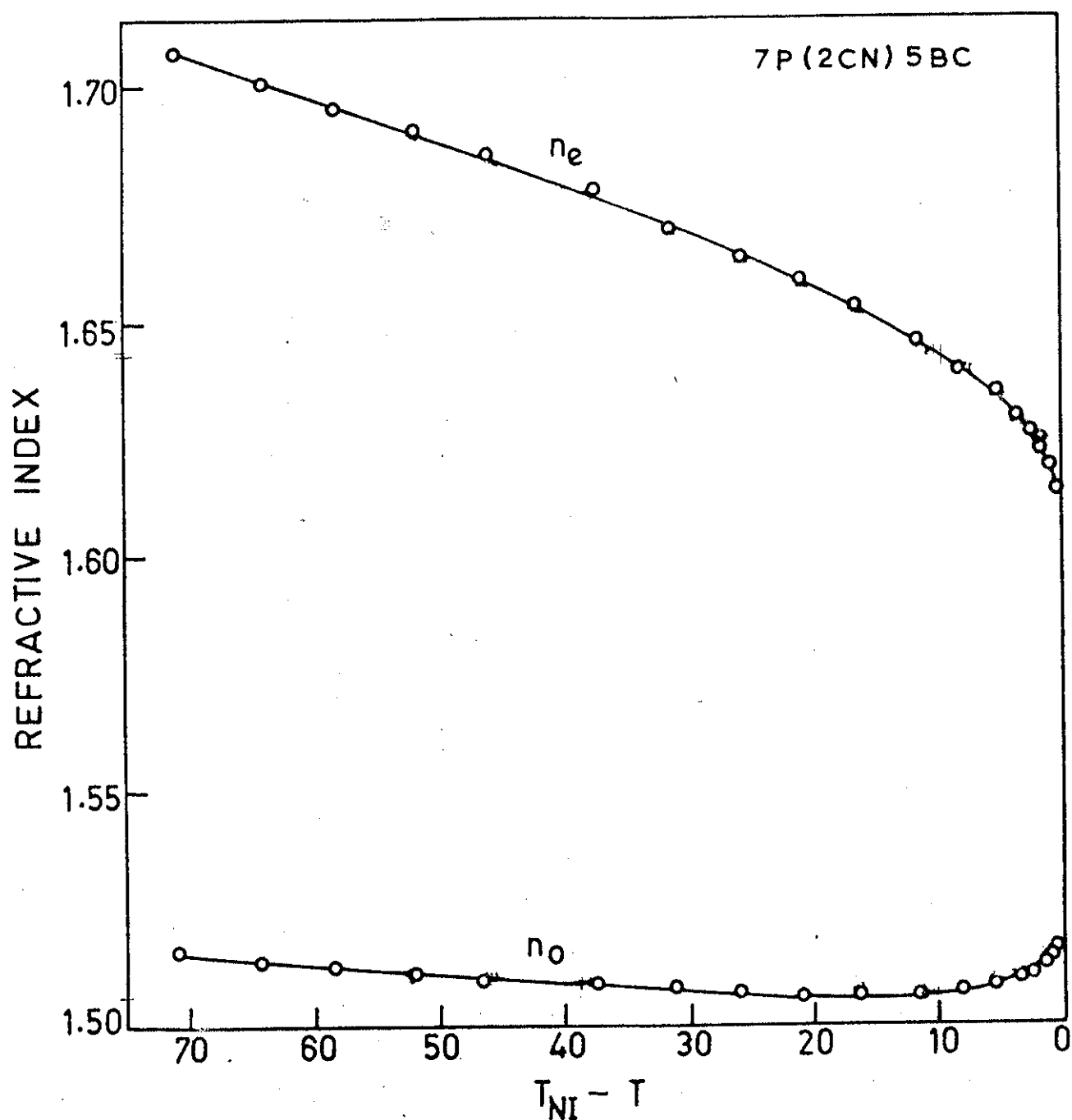


FIGURE 6.4

The ordinary and extraordinary refractive indices of 7P(2CN)5BC plotted against relative temperature, for $\lambda = 6328 \text{ nm}$.

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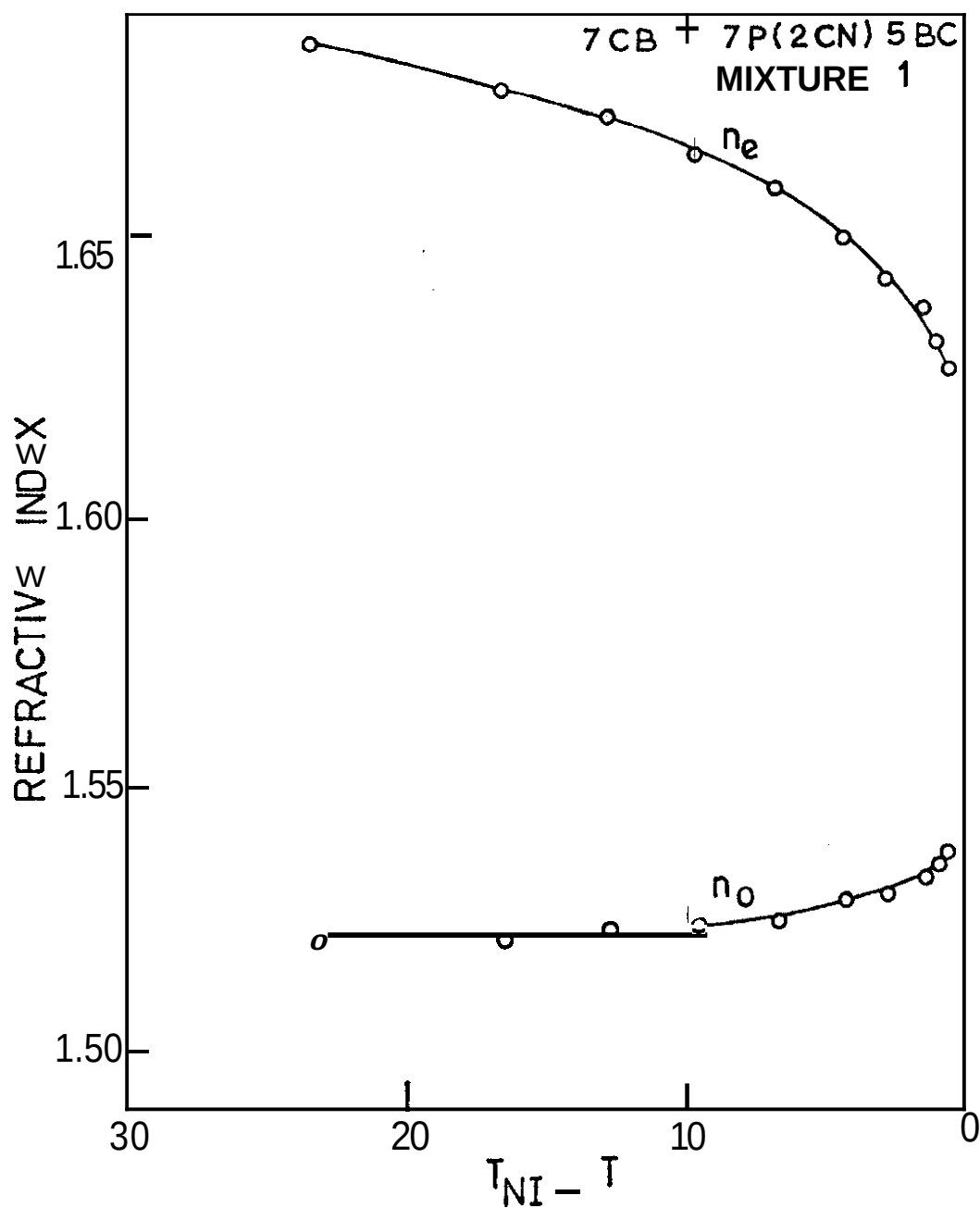


FIGURE 6.5

The ordinary and extraordinary refractive indices for mixture 1 plotted against relative temperature for $\lambda = 6328 \text{ \AA}$.

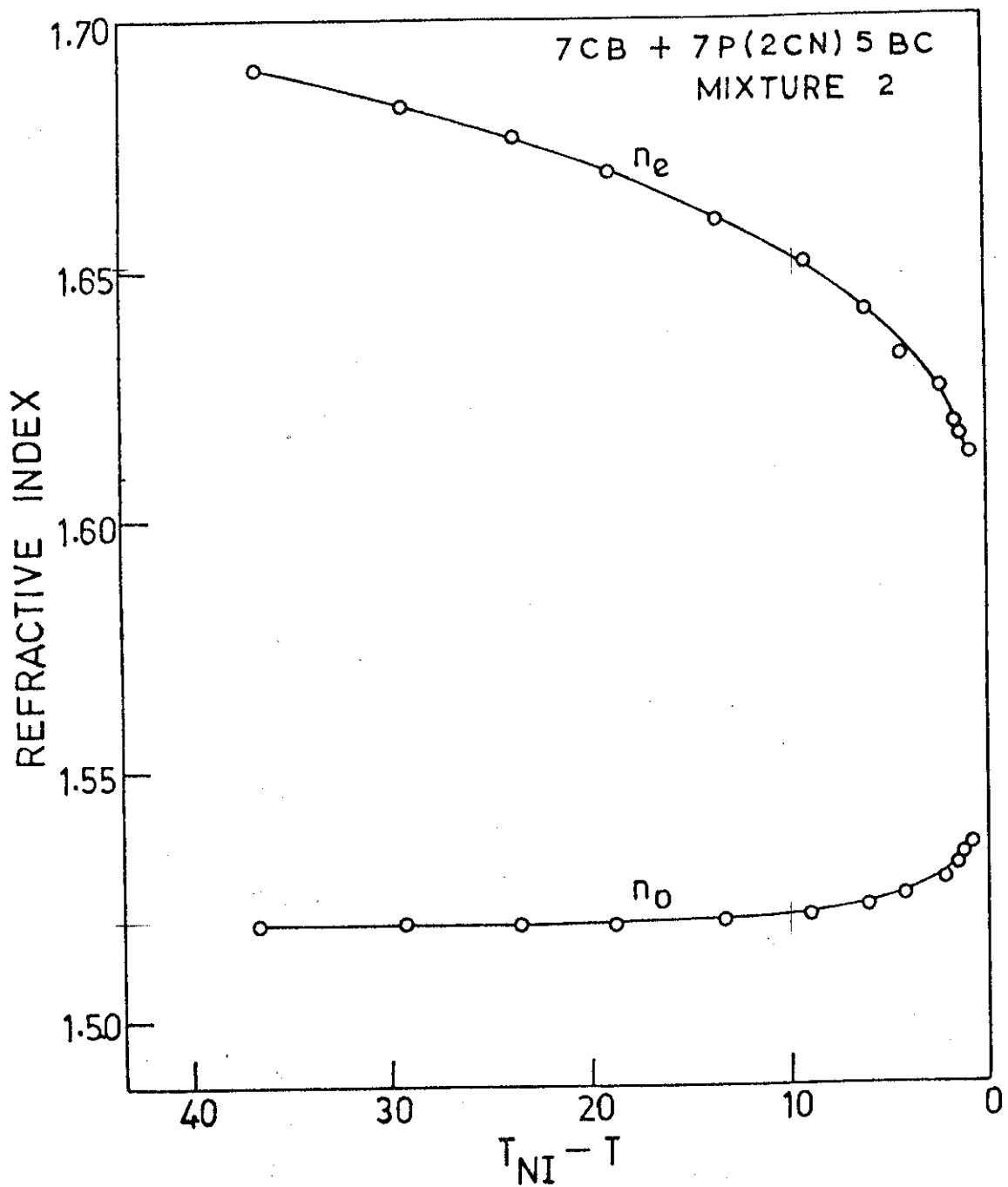


FIGURE 6.6

The ordinary and extraordinary refractive indices for mixture 2 plotted against relative temperature for $\lambda = 6328 \text{ \AA}$.

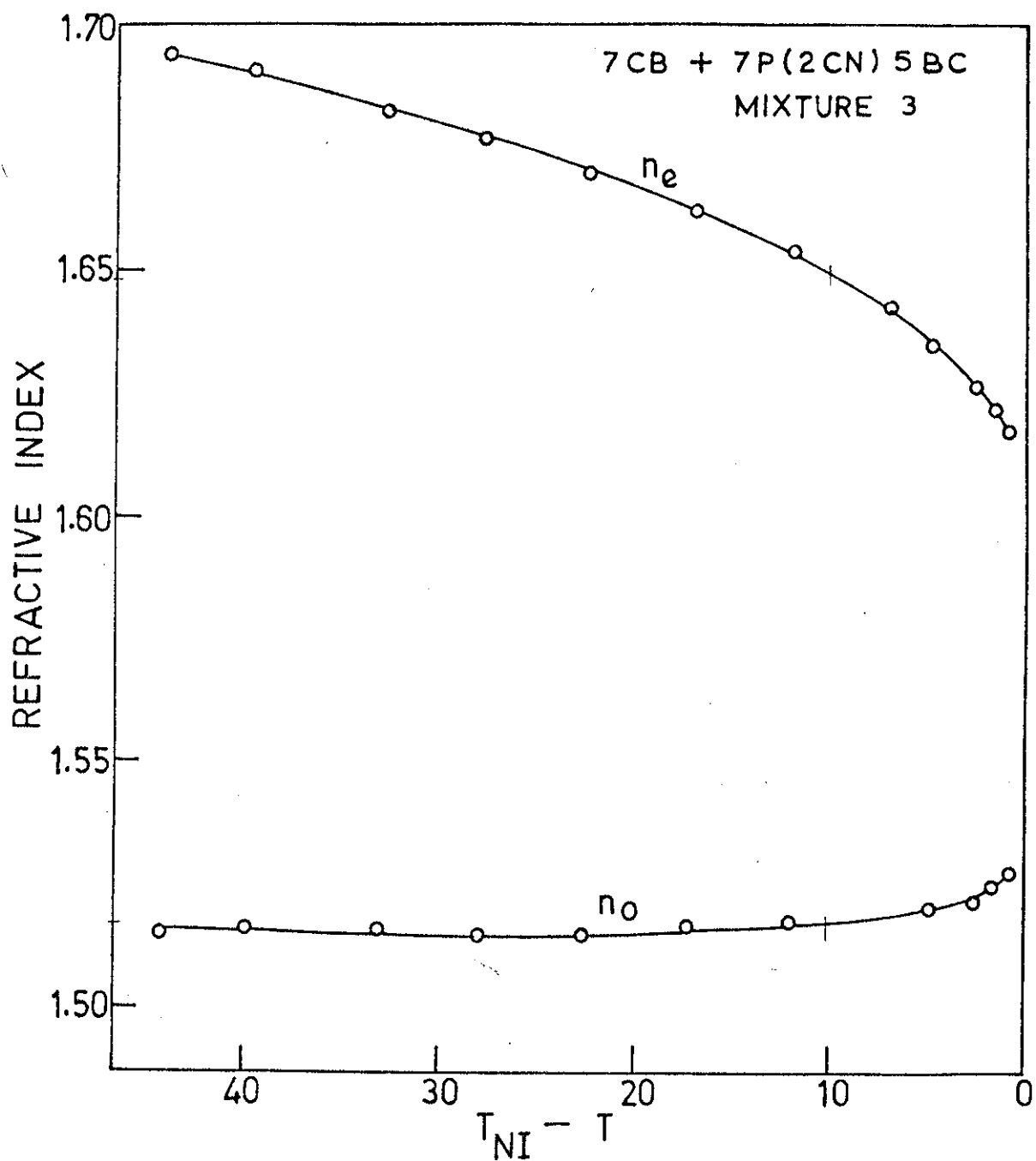


FIGURE 6.7

The ordinary and extraordinary refractive indices for mixture 3 plotted against relative temperature for $\lambda = 6328 \text{ \AA}$.

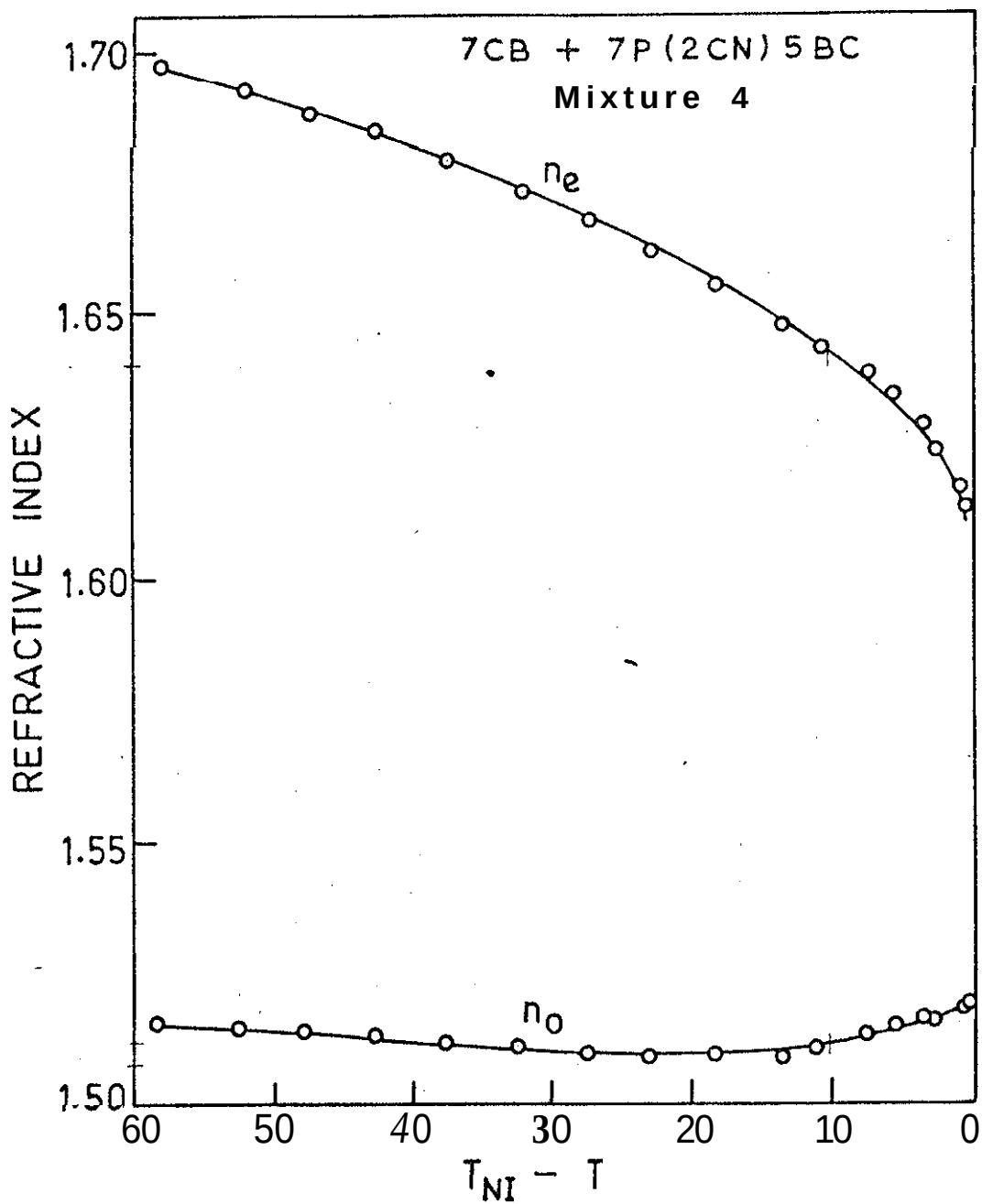


FIGURE 6.8

The ordinary and extraordinary refractive indices for mixture 4 plotted against relative temperature for $\lambda = 6328 \text{ \AA}$.

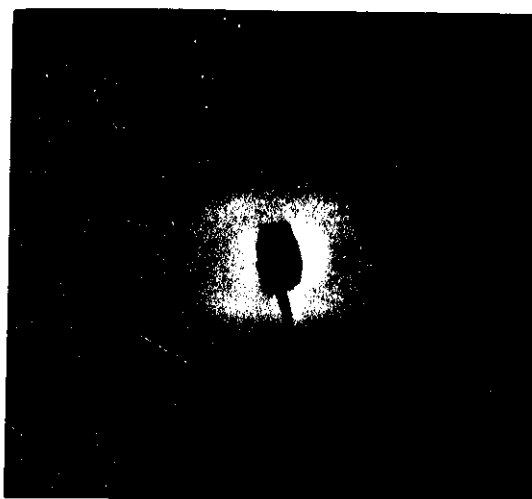
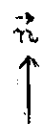
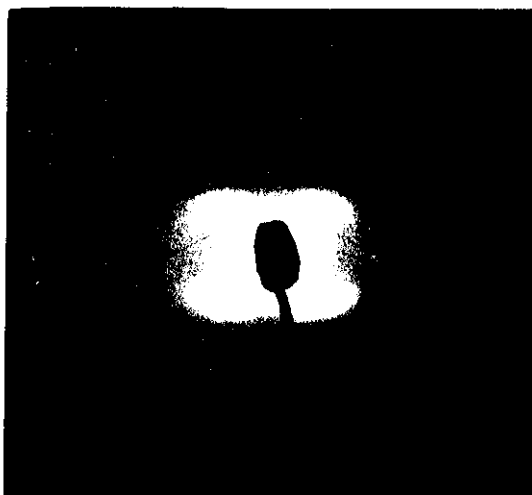
this appears to be the case as indicated by an x-ray investigation of the compound conducted in our laboratory.² The x-ray diffraction patterns photographed at two different temperatures in the nematic phase are shown in figure 6.9. These photographs were taken using monochromatic copper K_α radiation and the sample taken in a Lindemann capillary tube. The sample was aligned by applying a magnetic field of strength ~ 3 KGauss. The x-ray photographs clearly indicate the presence of skewed-cybotactic groups (i.e., smectic C type of short range ordering) in the sample (de Vries 1973). The tilt angle is 49° at 25°C and it decreases to $\sim 44^\circ$ as the temperature is increased to 70°C. At higher temperatures, the x-ray diffraction patterns become diffuse and measurement of the tilt angle is somewhat difficult.

We have made an attempt to understand the temperature variation of n_o in terms of the temperature variation of the tilt angle of the skewed cybotactic groups. For the sake of simplicity, we construct the skewed cybotactic structure in the following fashion. We will first assume that the cylindrically symmetrical molecules have their long axes normal to the layers as in a smectic A, but they are in a hexagonally close packed arrangement. We will now allow the molecules to slide parallel to their long axes such that a tilted arrangement as shown schematically in the right hand side of figure 6.10 is obtained.

²The author is grateful to Dr. K.A.Suresh for the results of the x-ray investigation.

FIGURE 6.9

X-ray diffraction photographs of a monodomain sample of 7P(2CN)5BC taken at (a) 25°C, and (b) 70°C. The direction of orientation of the director is indicated by an arrow mark. Four spots occurring in the diffraction patterns are characteristic of skewed cybotactic nematics.



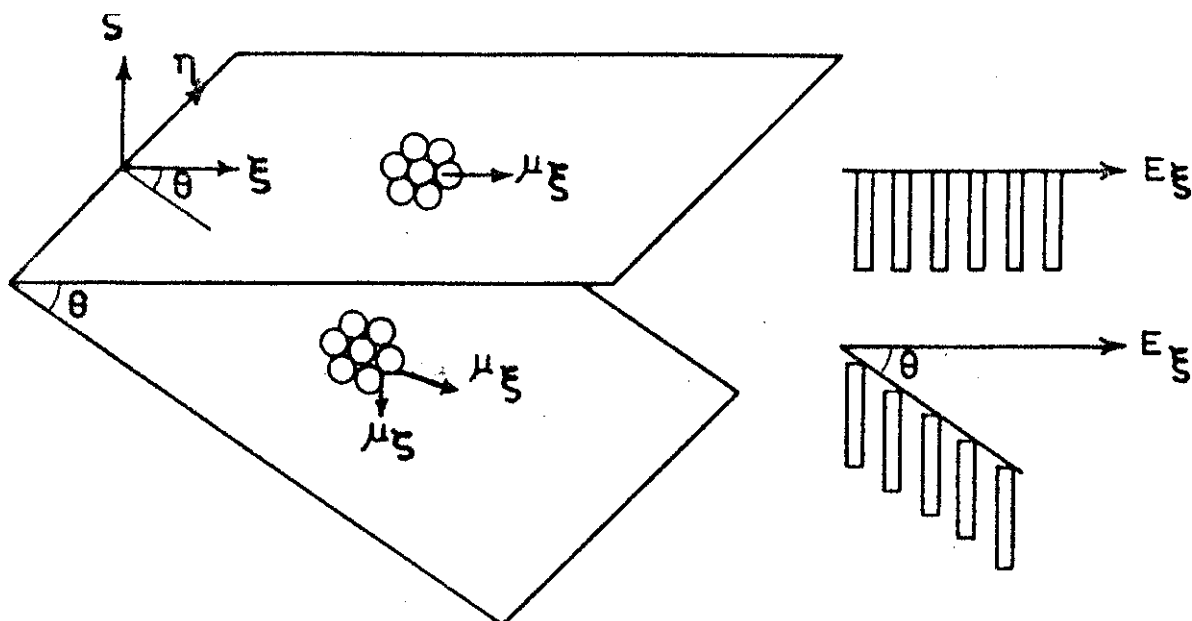


FIGURE 6.10

Schematic diagram of the molecular arrangement in cybotactic groups. The left side of the figure shows a sectional view of the layer and the right side a side view. In smectic A type of cybotactic groups an electric field E_{ξ} applied along the ξ axis gives rise to a dipole moment only along the ξ axis (upper part of the figure). In a skewed cybotactic arrangement shown in the lower part of the figure the molecules are tilted with respect to the layer normal at an angle θ . In this case an electric field applied along ξ axis gives rise to a dipole moment not only along the ξ axis but also along the ζ axis.

The long axes of the molecules are along the ζ axis and the angle of tilt, viz., the angle between the layer normal and the ζ axis is θ . We choose the ξ -axis such that it is in the plane containing the layer normal and the ζ -axis. If an external electric field is applied along the ξ axis (see figure 6.10) the induced dipoles μ_{ξ} will, due to the tilted structure of the cybotactic groups, produce an electric field along the ζ axis. Consequently, we have to consider the induced dipole moment μ_{ζ} also as shown in the figure. (We may note that $\mu_{\zeta} = 0$ when the tilt angle is zero). The local field at the site of a given molecule is calculated by taking into account the anisotropy of the molecular polarisability and the tilted structure in a manner almost similar to that given by Bragg (1924).

We consider a spherical region of known radius around the given molecule. The medium is supposed to be uniform beyond this region. The contributions to the local field at the centre due to the molecules within the spherical region are obtained following a detailed calculation. The local fields along the three axes ξ , η and ζ are

$$E_{1\xi} = E_{\xi} + \frac{4\pi}{3} P_{\xi} + \sum \frac{3\xi^2 - r^2}{r^5} \left(\frac{P_{\xi}}{2} \right) + \sum \frac{3\xi\zeta}{r^5} \left(\frac{P_{\zeta}}{2} \right)$$

$$E_{1\eta} = E_{\eta} + \frac{4\pi}{3} P_{\eta} + \sum \frac{3\eta^2 - r^2}{r^5} \left(\frac{P_{\eta}}{2} \right)$$

$$E_{1\zeta} = E_{\zeta} + \frac{4\pi}{3} P_{\zeta} + \sum \frac{3\zeta^2 - r^2}{r^5} \left(\frac{P_{\zeta}}{2} \right) + \sum \frac{3\xi\zeta}{r^5} \left(\frac{P_{\xi}}{2} \right)$$

where ξ , η and ζ are the coordinates of the molecules with respect to the centre of the spherical region and the summation is carried out over all the molecules within the region. (P is the dipole moment per unit volume and ν is the number of molecules per unit volume.)

Using the relation $P_{\xi} = \nu \alpha_{\xi} E_{1\xi}$, etc. (where α_{ξ} is a principal polarisability of the molecule'), and simplifying, we get,

$$E_{1\xi} = \frac{E_{\xi} + \frac{C_{\xi\xi} \alpha_{\xi} E_{\xi}}{1 - \alpha_{\xi} \left(\frac{4\pi}{3} \nu + C_{\xi\xi} \right)}}{1 - \alpha_{\xi} \left[\frac{4\pi}{3} \nu + C_{\xi\xi} + \frac{C_{\xi\xi}^2 \alpha_{\xi}}{1 - \alpha_{\xi} \left(\frac{4\pi}{3} \nu + C_{\xi\xi} \right)} \right]} = A E_{\xi} + B E_{\zeta}, \text{ say.}$$

$$E_{1\eta} = \frac{E_{\eta}}{1 - \alpha_{\eta} \left(\frac{4\pi}{3} \nu + C_{\eta\eta} \right)} = J E_{\eta}, \text{ say}$$

$$E_{1\zeta} = \frac{E_{\zeta} + \frac{C_{\xi\xi} \alpha_{\xi} E_{\xi}}{[1 - \alpha_{\xi} \left(\frac{4\pi}{3} \nu + C_{\xi\xi} \right)]}}{1 - \alpha_{\zeta} \left[\frac{4\pi}{3} \nu + C_{\zeta\zeta} + \frac{C_{\xi\xi}^2 \alpha_{\xi}}{1 - \alpha_{\xi} \left(\frac{4\pi}{3} \nu + C_{\xi\xi} \right)} \right]} = D E_{\zeta} + G E_{\xi}, \text{ say}$$

where $\alpha_{\xi\xi} = \sum \frac{3\xi^2 - r^2}{r^5}$, $\alpha_{\xi\zeta} = \sum \frac{3\xi\zeta}{r^5}$, etc.

Assuming that the director of the aligned nematic sample is along the z axis of a space fixed coordinate system and averaging the local fields over the Eulerian angles between the xyz system and $\xi\eta\zeta$ system, we can derive the principal refractive indices of the medium. Using the relation $D_z = n_z^2 E_z = E_z + 4\pi P_z$ and after some algebraic simplification we get,

$$\frac{n_z^2 - 1}{4\pi} = \frac{1}{3} \left[\frac{\alpha_{\xi} (A + J) + \alpha_{\zeta} D}{3} + \frac{2}{3} s(\alpha_{\zeta} D - \alpha_{\xi} \frac{A + J}{2}) \right] \quad (6.3)$$

Similarly,

$$\frac{n_x^2 - 1}{4\pi} = \frac{1}{3} \left[\frac{\alpha_{\xi} (A + J) + \alpha_{\zeta} D}{3} - \frac{1}{3} s(\alpha_{\zeta} D - \alpha_{\xi} \frac{A + J}{2}) \right] \quad (6.4)$$

where s is the order parameter, $n_z = n_o$ and $n_x = n_e$. The refractive indices depend on the structure of the cybotactic groups through the terms A , J and D .

In the above model, we have assumed that each molecule can be replaced by one centre of anisotropic polarisability with $a_{\zeta} > a_{\xi}$ ($= a_{\eta}$). However, the molecules forming liquid crystals are highly conjugated and further the density of the medium is quite high. Consequently, the assumption of a single centre is a very crude approximation. We have tried to improve the model by replacing each molecule by two centres of anisotropic polarisability. The formulae will then be somewhat more

complicated and will not be reproduced here. For a better approximation we have to replace each molecule by a much larger number of centres. But even with *tho* two oentre approximation we find that for certain range of parameters, the experimental trend in the variation of n_e and n_o can be reproduced. For example, for molecules of length 20 Å, diameter 5 Å, considering a spherical region of radius 25 Å and assuming $s = 0.4$, density = 1 gm/cc, $\alpha_{\Xi} = 15 \times 10^{-24}$ cc, $\alpha_s = 75 \times 10^{-24}$ cc we get the following values.

θ	n_e	n_o
36°	1.351	1.280
32°	1.321	1.278
28°	1.300	1.281

Hence as θ decreases, n_o can decrease, attain a minimum and then increase. However, for a detailed comparison with the experimental results, temperature variations of s and density will have to be taken into account. Nevertheless, the above calculations serve to illustrate that the temperature variation of θ can, in principle, lead to *tho* observed variation in n_o .

The presence of skewed cybotactic groups in 7P(2ON)5BC and the temperature variation of tilt angle is perhaps associated with the presence of the strongly polar cyano group making a large angle with the long axis of the molecules. Here, we may point out that de Vries and Qadri (1980) have found a similar

temperature variation of tilt angle of skewed cybotactic groups
 In a compound consisting of molecules with ^alateral chlorine atom.
 L

c. Densities. The density of pure 7P(2CN)5BC was measured at a known temperature—a (1.079 gm/cc at 41°0) by the capillary tube method. Substituting this value in equation 1.9, $\bar{\alpha}$ was calculated. Using this value of $\bar{\alpha}$, the values of density at different temperatures were calculated from the birefringence data. For the mixtures, $\bar{\alpha}$ were calculated using the molar additive law (table 6.7). The values of density are given in tables 6.2-6.6 and are plotted against relative temperature in figure 6.11. It can be seen that at any given relative temperature, the density of 7P(2CN)5BC is greater (by a factor of ~ 1.04) than that of 7CB. Mixtures have densities which are intermediate between those of the pure compounds.

d. Order parameters. In the light of the above discussion, it may not be very proper to use Yuks' formula in evaluating s from the birefringence data. However, as there is no hope of an exact calculation of the temperature dependence of internal field correction, we have made use of the Yuks formula. The equation used is

$$s = \frac{\bar{\alpha}}{\Delta\alpha} \frac{n_e^2 - n_o^2}{n^2 - 1} \quad (6.5)$$

The value of $\frac{\bar{\alpha}}{\Delta\alpha}$ was obtained using the extrapolation method described in chapter V. For 7P(2CN)5BC, the best fit

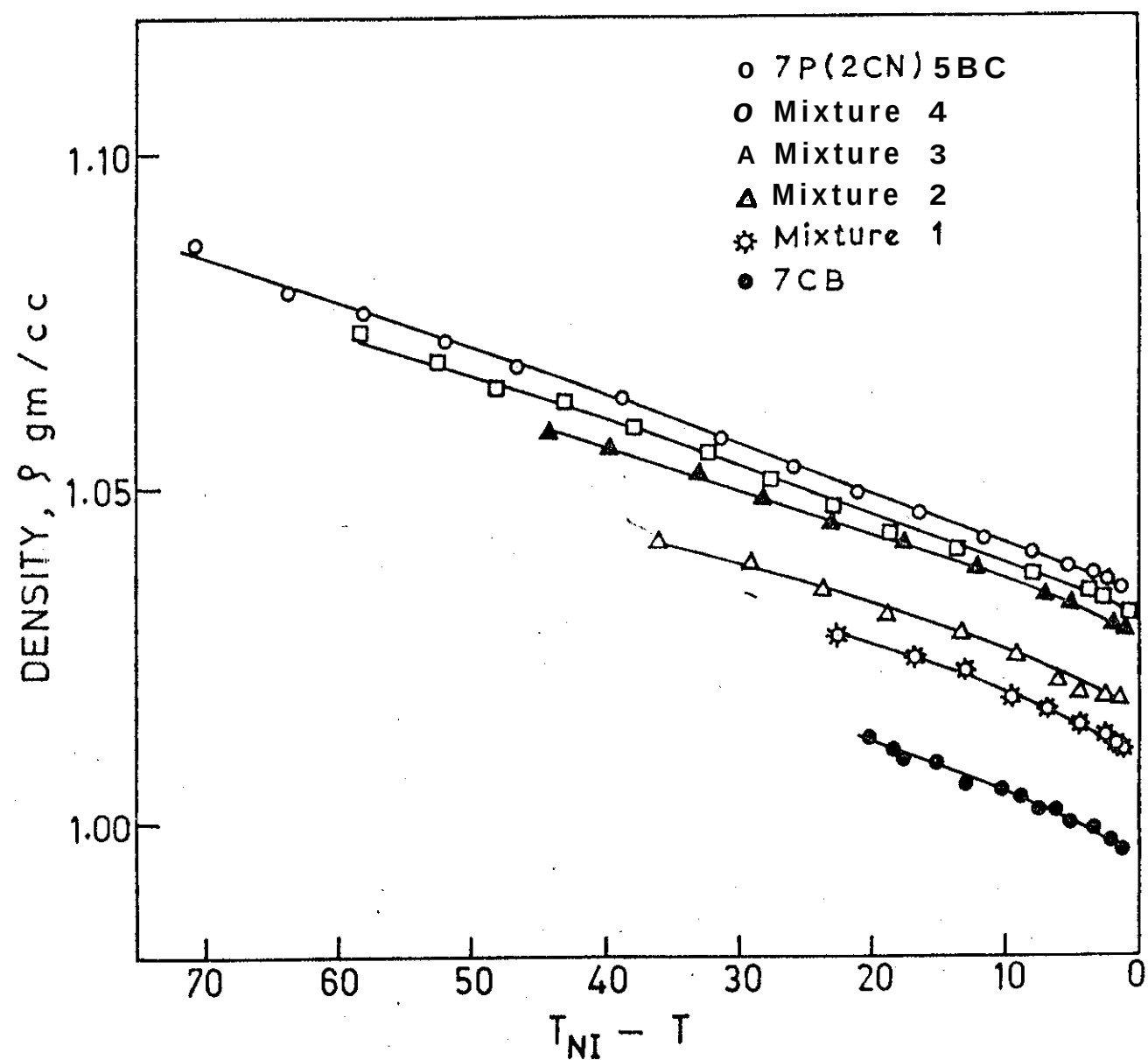


FIGURE 6.11

The densities of 7CB, mixture 1, mixture 2, mixture 3, mixture 4 and 7P(2CN)5BC plotted against relative temperatures.

to the straight line was obtained for $T_{NI}^H - T_{NI} = 1.2^\circ$ (figure 6.12). The order parameter has been plotted against relative temperature in figure 6.13 and the values are given in table 6.6.

In view of the unusual variation of n_o , we also calculated the values of a_a and α_o independently using the equation 1.7, i.e.,

$$\frac{n_1^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \gg \alpha_1 \quad (6.6)$$

to find whether the polarisabilities show any peculiar temperature variation. It was found that α_o and α_e vary with temperature in the usual manner. In particular, α_o increases monotonically with increase of temperature. The same trend was observed when Neugebauer's formula (see, for example, Saupe and Maier 1961) was used to calculate α_o . Hence the use of the following equations

$$\left. \begin{aligned} \alpha_o &= \bar{\alpha} - \frac{s}{3} \Delta\alpha \\ \alpha_e &= \bar{\alpha} + \frac{2s}{3} \Delta\alpha \end{aligned} \right\} \quad (6.7)$$

in evaluating s appears justified even in the present case.

In order to confirm that the temperature variation of order parameter obtained from birefringence data is reliable, we made an independent measurement of s . This compound has a cyano-group making a large angle with the long axis of the molecule. Hence it is very difficult to align it homeotropically.

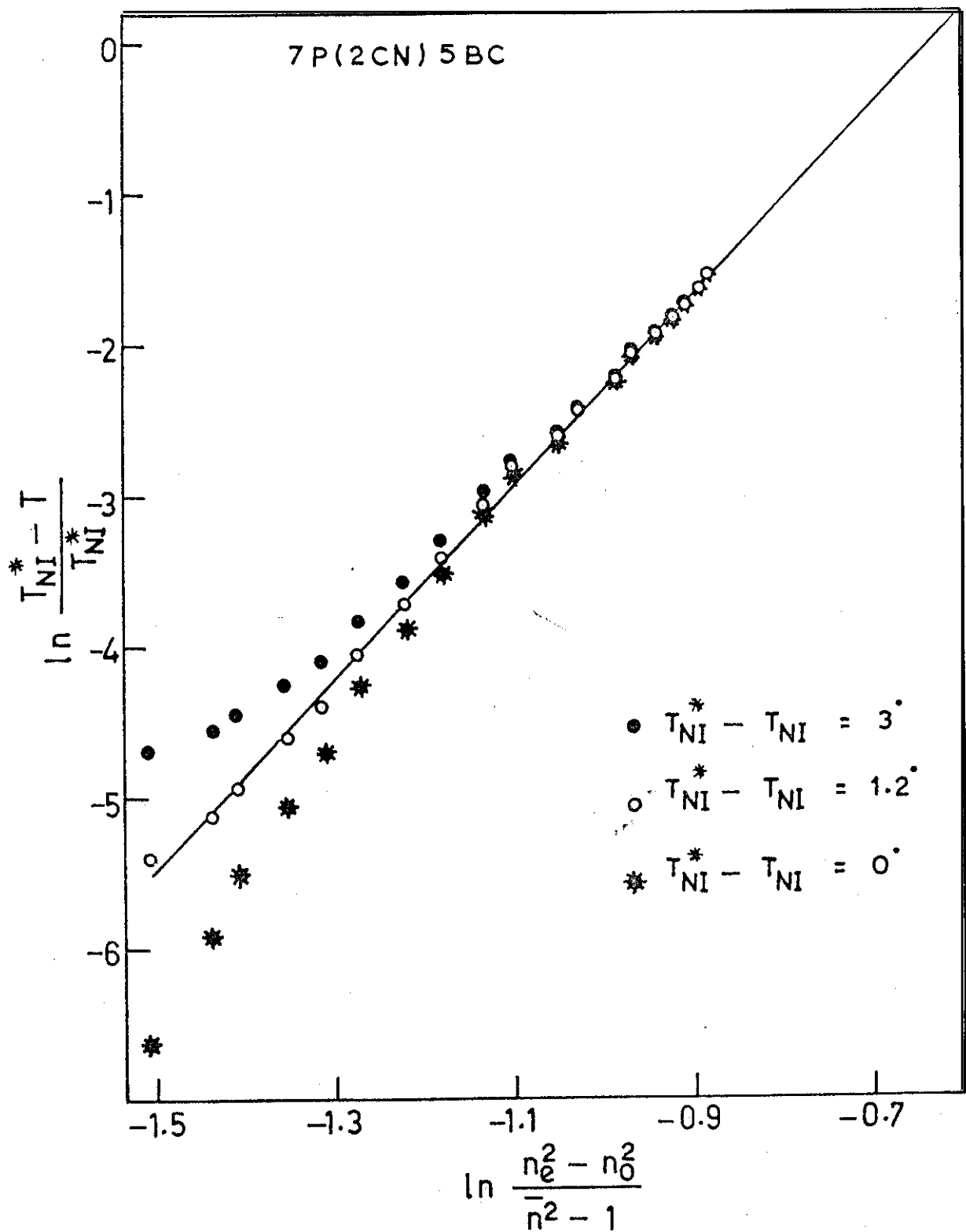


FIGURE 6.12

$\ln \left[\frac{T_{NI}^* - T}{T_{NI}^*} \right]$ plotted against $\ln \left[\frac{n_e^2 - n_o^2}{n^2 - 1} \right]$ for 7P(2CN)5BC

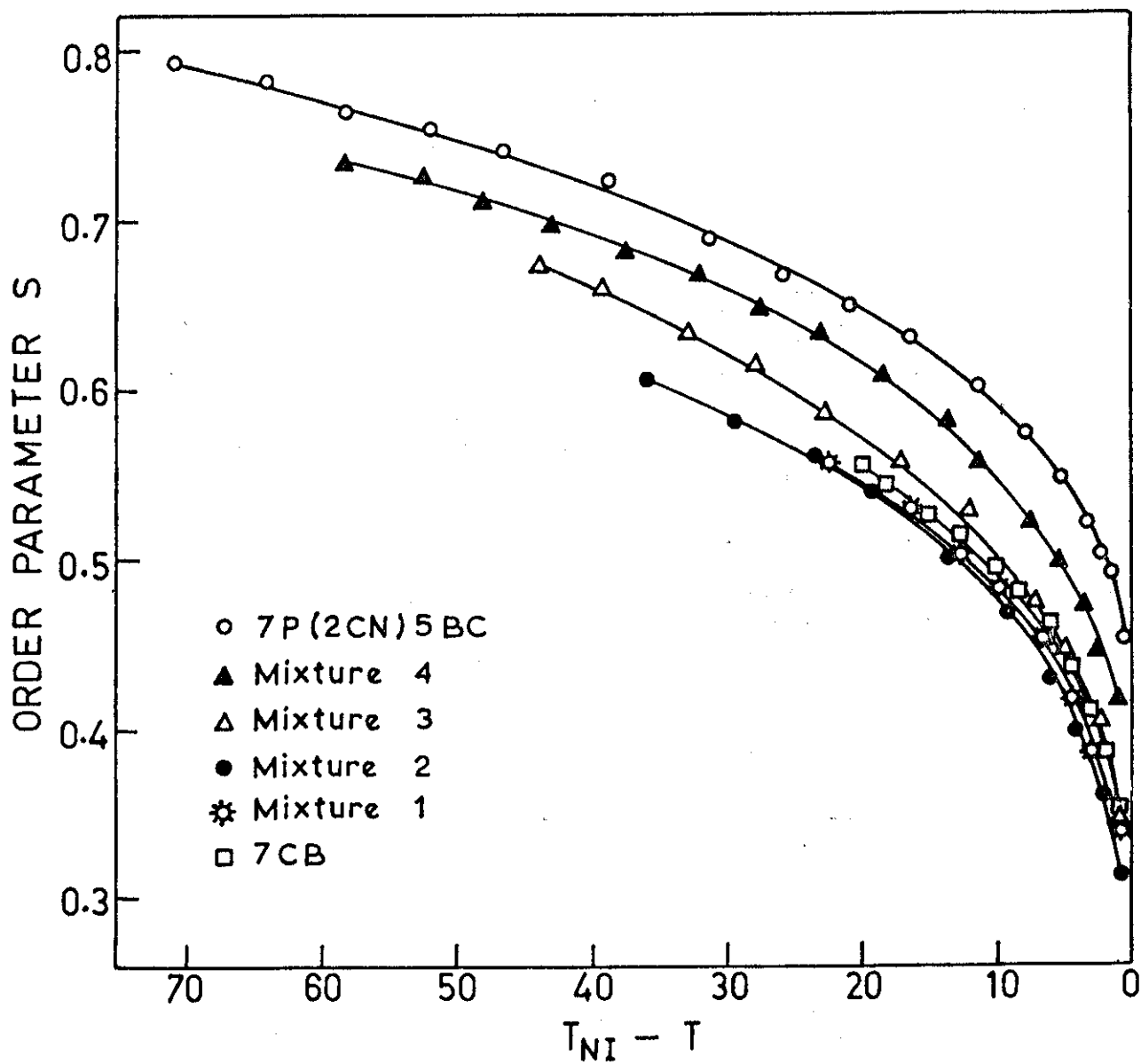


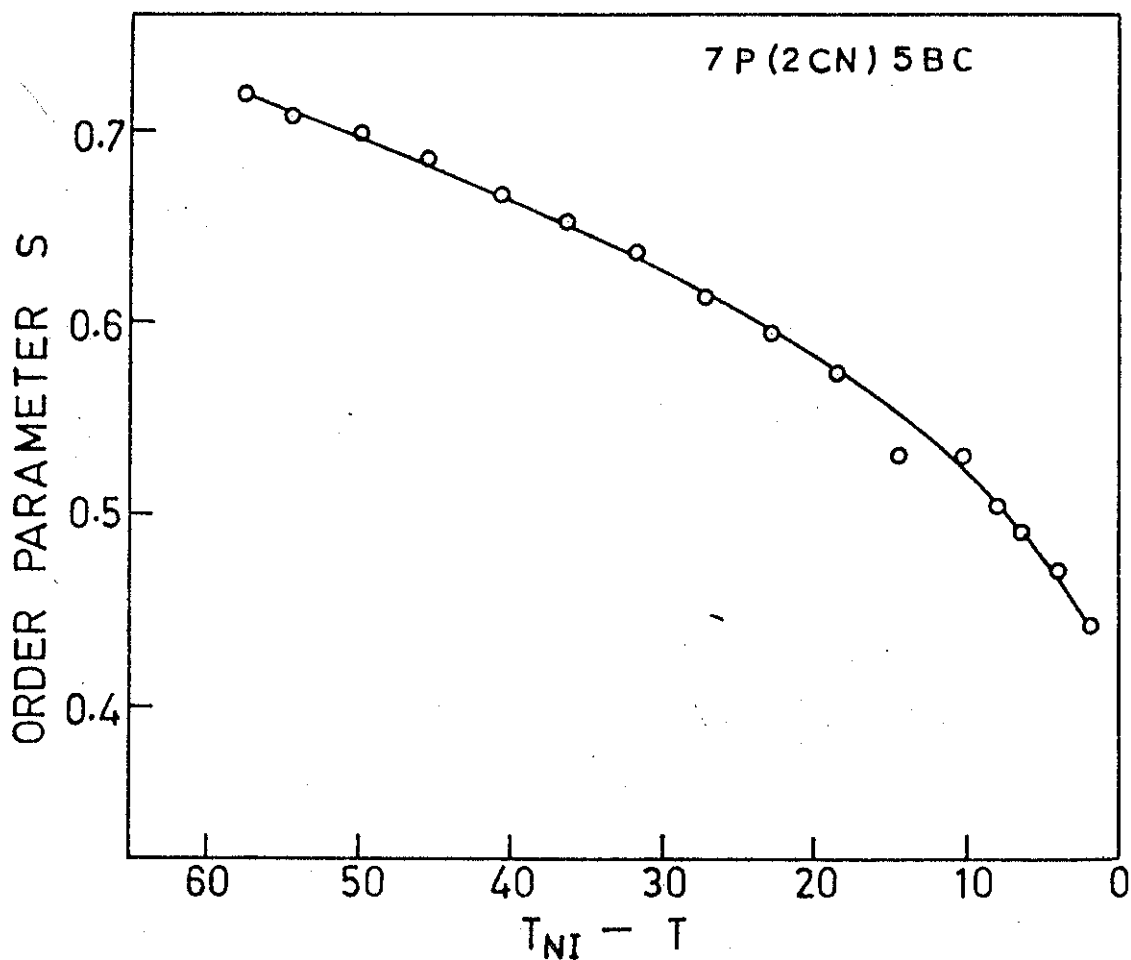
FIGURE 6.13

Order parameters derived from birefringence data of 7CB, mixture 1, mixture 2, mixture 3, mixture 4 and 7P(2CN)5BC plotted against relative temperatures.

Therefore we did not use the IR dichroism method described in chapter III to determine s . The values of s were determined by the wide-line NMR technique and the values obtained are plotted against relative temperature in figure 6.14. The error involved in these measurements is somewhat high ($\sim 8\%$) due to the uncertainties in the measurement of temperature and also due to the fact that no line-shape analysis of the NMR spectrum was conducted. The values of s obtained from the NMR data is lower (by ~ 0.07) compared to those obtained from optical data. As we mentioned earlier, Boilini and Ghosh (1975) used $r = 2.45 \text{ \AA}$ for the distance between the orthoprotons. If r is taken to be $2.48 \text{ \AA}$ as given by Raman measurements (Longseeth and Stoicheff 1956) the s -values evaluated from NMR data go up by $\sim 4\%$. In any case, the temperature variations are similar in the two cases. Hence we have used the birefringence data to find the order parameters of all the mixtures.

The values of $\bar{\alpha}$ and $\Delta\alpha$ for the mixtures were calculated using molar additive laws (see equation 3.11). These values are given in table 67. The s values for the mixtures are given in tables 6.3-6.6 and are plotted against relative temperature in figure 6.13.

7P(20N)5BC has got s values which are higher (~ 1.1 times) than those of 7CB. Mixtures 1 and 2 which have high concentrations of 7CB have values of s which are slightly lower than those of



.C.

FIGURE 6.14

Order parameter of 7P(2CN)5BC obtained from NMR data plotted against relative temperature.

7CB. For mixtures 3 and 4, the values of α are intermediate between those of 7CB and 7P(2CN)5BC. Quite obviously, the molar additive law does not hold good for order parameters in mixtures of 7CB and 7P(2CN)5BC.

e. Splay elastic constants. The splay elastic constants of the systems mentioned above were measured as functions of temperature by the Fredericksz transition technique. The calculations were done using equation 5.5. The value of ΔK for 7P(2CN)5BC was calculated following Flygare's (1974) procedure described in chapter IV. For the mixtures the values of ΔK were obtained using the molar additive law and these values are given in table 6.8. The values of k_{11} are given in tables 6.9-6.13 and are plotted in figures 6.15 and 6.16. It can be seen that the k_{11} values for mixtures 1 and 2 are less than those of pure 7CB which itself is much lower (~ 0.75 times) than the k_{11} values of 7P(2CN)5BC. Mixtures 3 and 4 have values of k_{11} which are intermediate between those of the pure components.

We have fitted these data to the relation $k_{11} = Cn^X$ by following the procedure given in chapter V. The values of X and C so obtained are given in table 6.14. The index X is found to increase as the concentration of 7CB decreases, the only exception being pure 7P(2CN)5BC which has got a value less than that of mixture 4.

In figures 6.17 and 6.18 we have plotted the values of

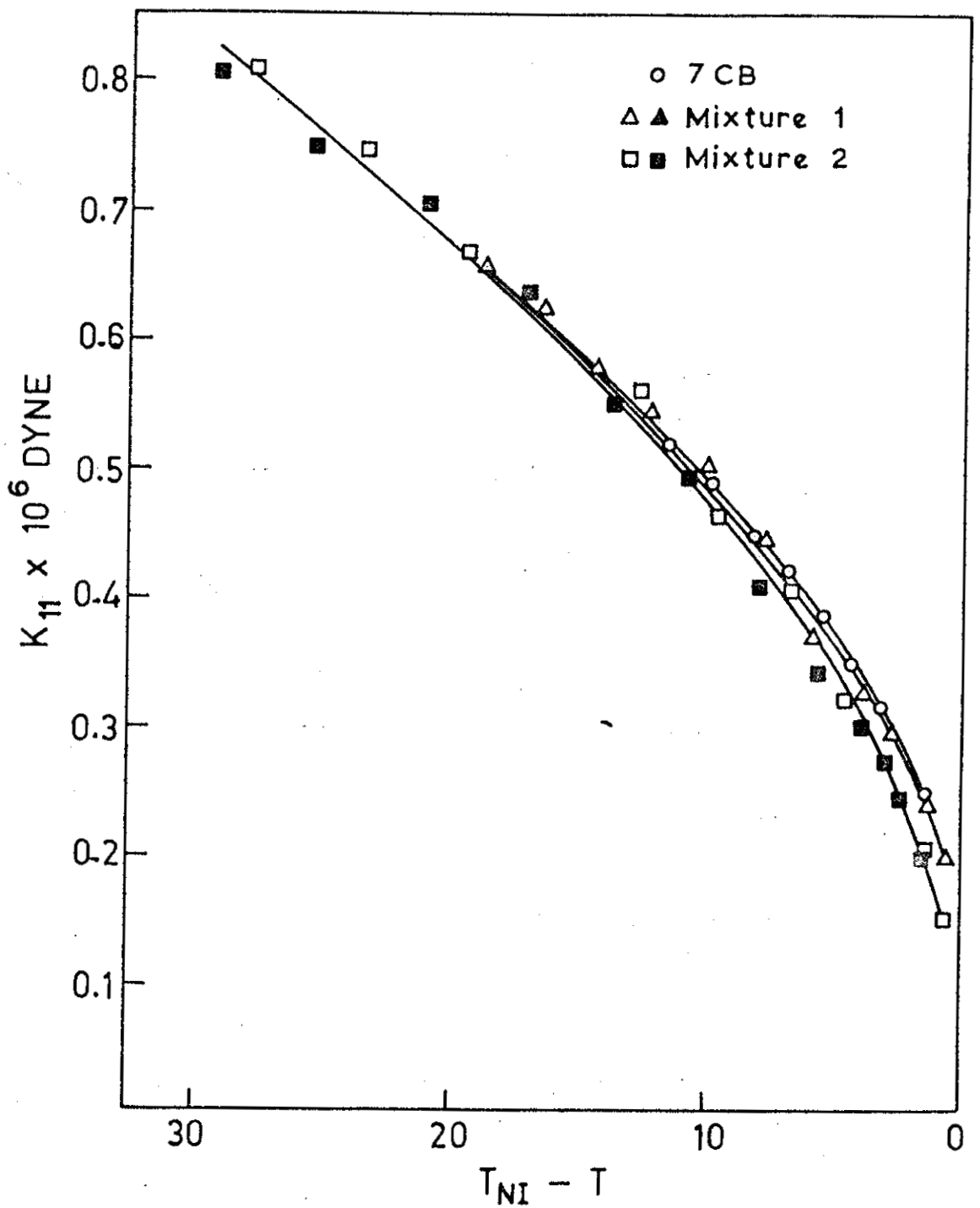


FIGURE 6.15

The splay elastic constants of 7CB, mixture 1 and mixture 2 plotted against relative temperature.

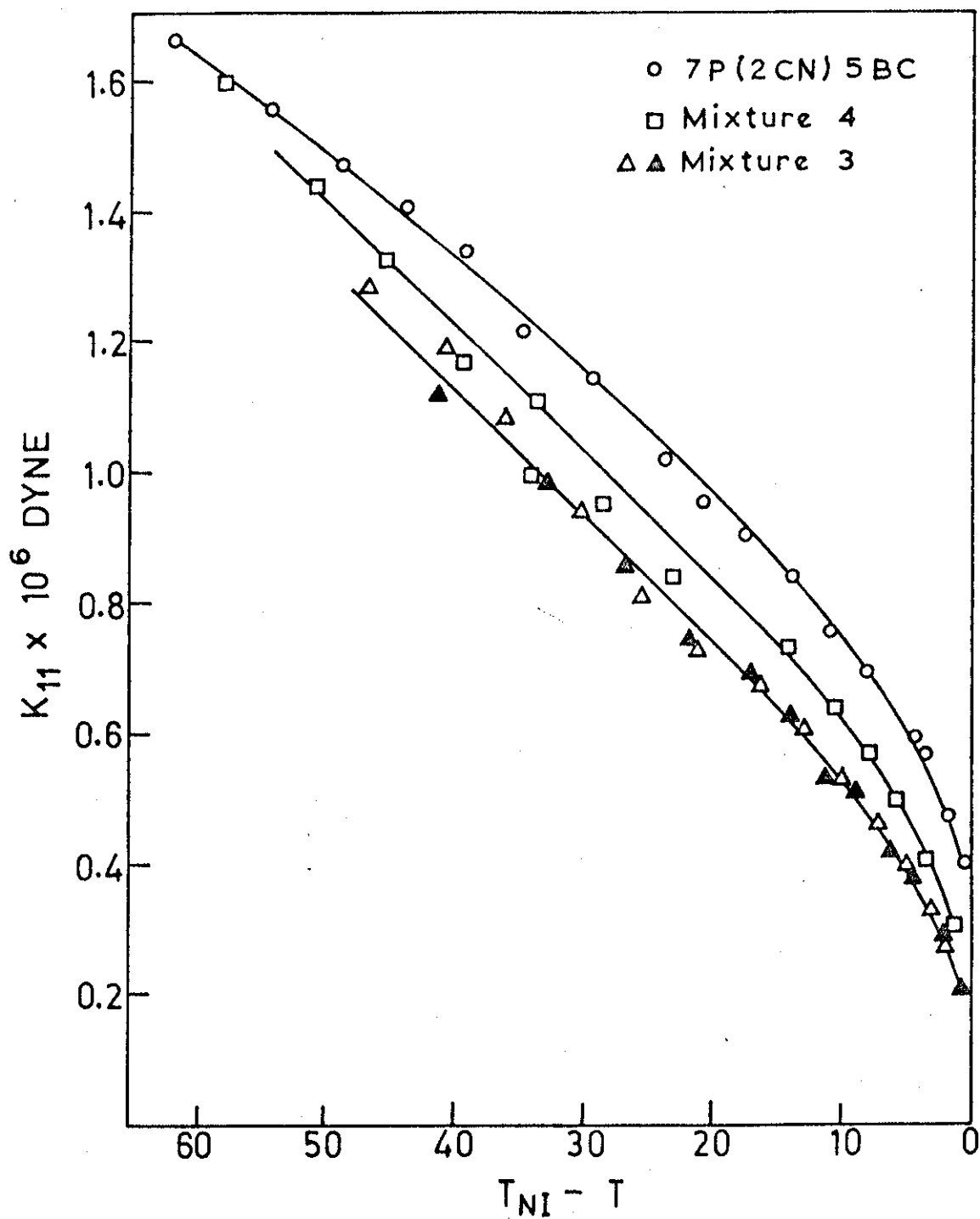


FIGURE 6.16

The splay elastic constants of mixture 3, mixture 4 and 7P(2CN)5BC plotted against relative temperature.

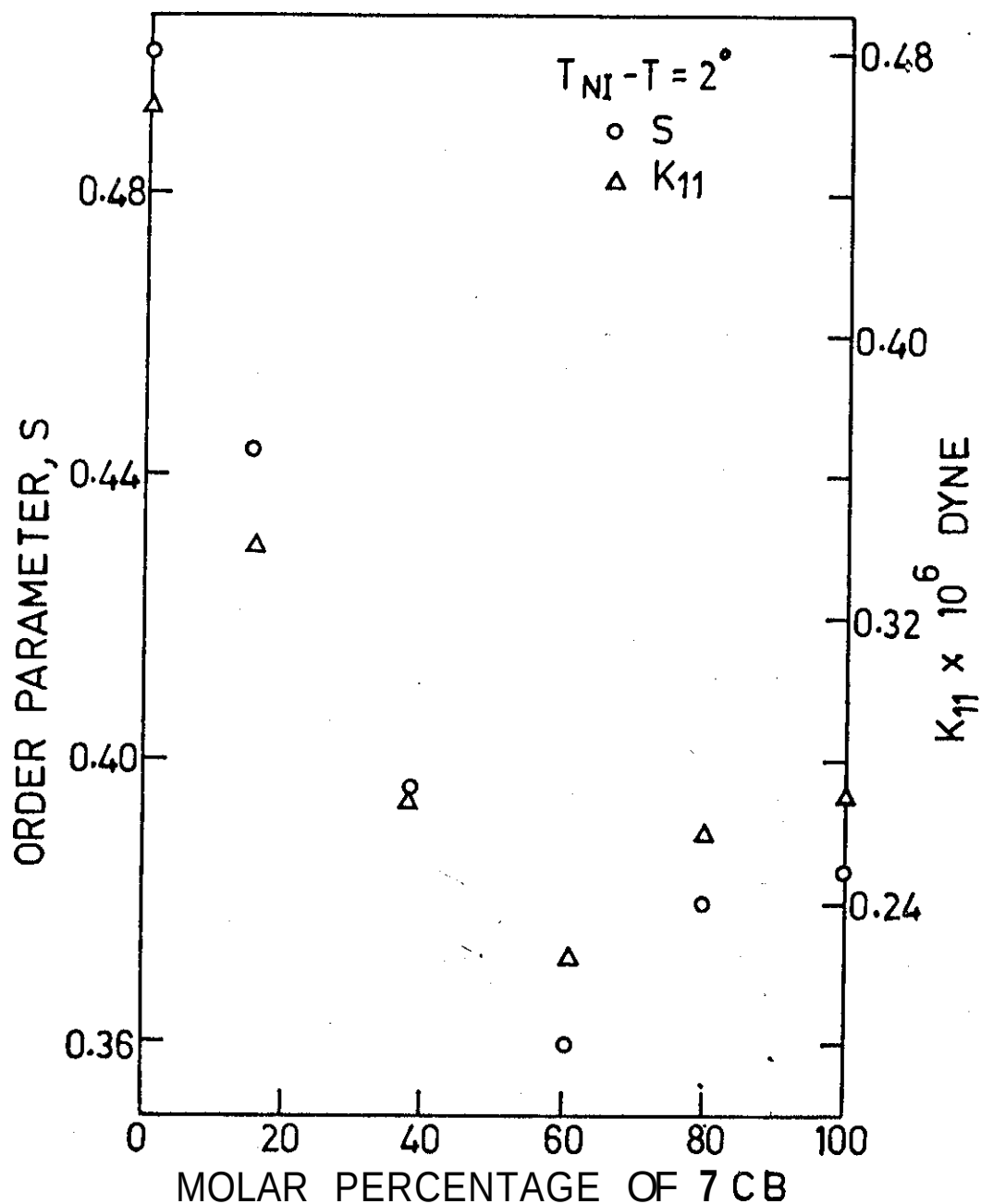


FIGURE 6.17

k_{11} and s plotted against the concentration of 7CB in mixtures of 7CB and 7P(2CN)5BC at $T_{NI} - T = 2^\circ$.

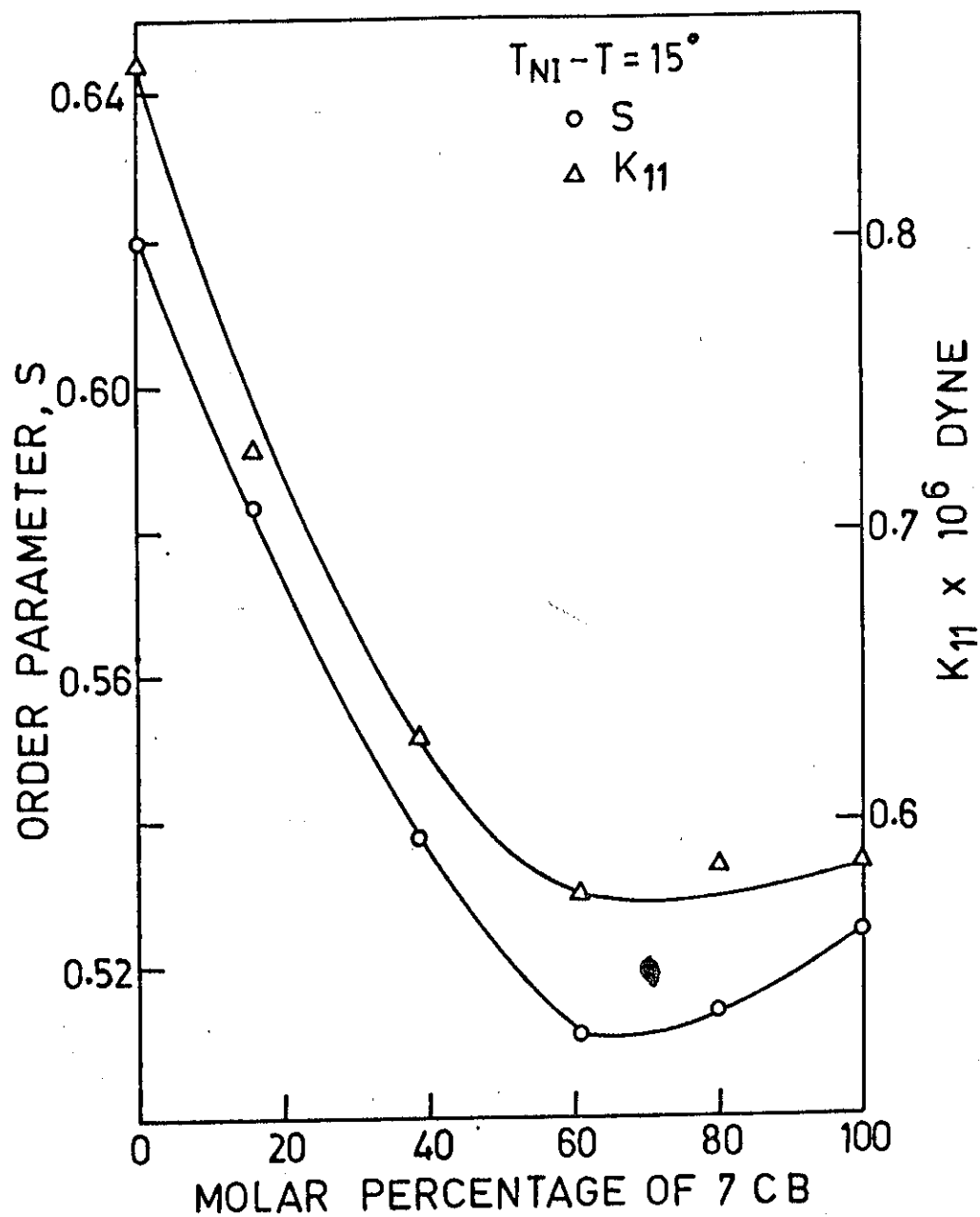


FIGURE 6.18

k_{11} and s plotted against the concentration of 7CB in mixtures of 7CB and 7P(2CN)5BC at $T_{NI} - T = 15^\circ$.

k_{11} and s corresponding to the same relative temperature against composition of the mixtures. At $T_{NI} - T = 2^\circ$ as well as at 15° , both k_{11} and s decrease as the percentage of 7CB is increased. They attain minimum values for ~ 60 per cent composition of 7CB and increase slightly as the concentration of 7CB is further increased.

We have not determined k_{33} for these systems as it was not possible to get a homeotropic alignment of 7P(2CN)5BC and some of the mixtures.

References

- Boilini, E. and Ghosh, S.K. 1975 J. App. Physics 46, 78.
- Bragg, W.L. 1924 Proc. Roy. Society 105, 370.
- de Vries, A. 1973 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1973, Ed. S. Chandrasekhar Pramana Supplement 1, 93.
- de Vries, A. and Qadri, S.B. 1980 Proceedings of the International Liquid Crystals Conference, Bangalore, December 1979, Ed. S. Chandrasekhar, Heyden, London, p. 179.
- Flygare, W.H. 1974 Chem. Rev. 74, 653.
- Ghosh, S.K. 1972 Solid State Commun. 11, 1763.
- Lippmann, H. and Weber, K.H. 1957 Ann. Physik 20, 265.
- Longseth, A. and Stoicheff, B.P. 1956 Can. J. Phys. 34, 350.
- Saupe, A. 1970 in Magnetic Resonance, Eds. Coogan, C.K., Ham, N.S., Stuart, S.N., Pithrow, J.R. and Wilson, G.V.H., Plenum.
- Saupe, A. and Maier, W. 1961 Z. Naturforsch. A16, 816.
- Spence R.D., Moses, H.A. and Jain, P.L. 1953 J. Chem. Phys. 21, 380.

TABLE 6.1

Transition Temperatures (°C)

Sample	Composition of 7CB:OH-EBBA	Solid- Nematic	Nematic- Isotropic
7CB		28.1	42.2
Mixture 1	80:20	~17 ^m	48-49
Mixture 2	61:39	~22 ^m	58-60
Mixture 3	38:62	~28 ^m	71-73
Mixture 4	15:85	40 ^m	89-90
7P(2CN)5BO		45.5	102.0

^m corresponds to liquidus point

TABLE 6.2

Refractive indices, densities and order parameters of Mixture 1

$T_{NI}-T$	n_e	n_o	$\rho_{gm/cc}$	s
0.6	1.626	1.530	1.011	0.318
1.0	1.631	1.529	1.011	0.338
1.5	1.637	1.528	1.012	0.360
2.9	1.643	1.527	1.013	0.384
4.4	1.651	1.525	1.015	0.415
6.8	1.660	1.523	1.017	0.451
9.6	1.667	1.521	1.019	0.480
12.8	1.674	1.521	1.023	0.501
16.5	1.679	1.520	1.025	0.528
22.6	1.688	1.519	1.028	0.551

[values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$]

TABLE 6.3

Refractive indices, densities and order parameters of Mixture 2

$T_{NI}-T$	n_e	n_o	ρ gm/cc	s
0.8	1.612	1.530	1.018	0.293
1.1	1.616	1.529	1.018	0.311
1.5	1.619	1.528	1.018	0.325
2.2	1.625	1.526	1.018	0.354
4.2	1.632	1.524	1.019	0.386
6.0	1.641	1.522	1.021	0.424
9.1	1.651	1.520	1.025	0.465
13.3	1.660	1.519	1.028	0.500
18.8	1.669	1.517	1.031	0.537
23.4	1.676	1.517	1.035	0.560
29.2	1.683	1.518	1.039	0.579
36.2	1.690	1.517	1.042	0.606

(values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$)**TABLE 6.4**

Refractive indices, densities and order parameters of Mixture 3

$T_{NI}-T$	n_e	n_o	ρ gm/cc	s
0.9	1.617	1.528	1.029	0.343
1.7	1.622	1.525	1.029	0.374
2.6	1.625	1.522	1.028	0.398
5.1	1.635	1.520	1.031	0.444
7.0	1.642	1.519	1.034	0.474
12.0	1.654	1.517	1.038	0.526
17.3	1.662	1.517	1.042	0.554
22.7	1.669	1.515	1.044	0.584
28.0	1.676	1.515	1.048	0.613
33.0	1.682	1.516	1.052	0.630
39.6	1.690	1.516	1.056	0.658
44.2	1.693	1.515	1.057	0.673

(values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$)

TABLE 6.5

Refractive indices, densities and order parameters of
Mixture 4

$T_{NI}-T$	n_e	n_o	ρ gm/cc	s
0.40	1.613	1.519	1.031	0.392
0.85	1.617	1.517	1.031	0.417
2.75	1.624	1.517	1.034	0.445
3.75	1.629	1.516	1.035	0.469
5.60	1.635	1.515	1.036	0.497
7.80	1.639	1.513	1.037	0.522
11.25	1.644	1.510	1.038	0.556
13.75	1.648	1.508	1.041	0.581
18.50	1.656	1.509	1.043	0.608
23.25	1.662	1.509	1.047	0.631
27.50	1.668	1.510	1.051	0.649
32.25	1.674	1.511	1.055	0.667
37.75	1.679	1.512	1.059	0.681
43.00	1.685	1.513	1.063	0.698
48.00	1.688	1.513	1.065	0.710
52.50	1.693	1.514	1.069	0.724
58.50	1.698	1.516	1.073	0.732

[values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$]

TABLE 6.6

Refractive indices, densities and order parameters of
7P(2CN)5BC

$T_{NI}-T$	n_e	n_o	ρ gm/cc	s
0.60	1.613	1.516	1.035	0.421
1.15	1.618	1.514	1.035	0.451
1.60	1.621	1.512	1.035	0.490
2.40	1.625	1.510	1.036	0.500
3.45	1.629	1.509	1.037	0.521
5.40	1.634	1.508	1.038	0.546
7.90	1.639	1.507	1.040	0.572
11.35	1.645	1.506	1.042	0.601
16.35	1.652	1.506	1.046	0.629
20.95	1.657	1.506	1.049	0.649
26.00	1.663	1.507	1.053	0.668
31.50	1.669	1.508	1.057	0.687
38.70	1.678	1.509	1.063	0.717
46.60	1.685	1.510	1.068	0.740
52.10	1.690	1.511	1.072	0.754
58.30	1.695	1.513	1.076	0.763
64.00	1.700	1.513	1.079	0.782
71.00	1.707	1.516	1.086	0.794

[values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$]

TABLE 6.7

 $\bar{\alpha}$ and $\bar{\alpha}/\Delta\alpha$ for the systems studied

Sample	$\bar{\alpha} \times 10^{24}$ cm ³	$\bar{\alpha}/\Delta\alpha$
7CB	36.13	1.390
Mixture 1	40.37	1.514
Mixture 2	44.26	1.623
Mixture 3	49.00	1.756
Mixture 4	53.85	1.867
7P(2CN)5BC	56.93	1.940

TABLE 6.9

Splay elastic constants of Mixture 1

 $x_0 = 32.2 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
1.30	2025	0.239
2.72	2175	0.295
3.90	2238	0.327
5.89	2300	0.370
7.67	2438	0.447
9.97	2550	0.506
12.22	2600	0.545
14.22	2650	0.582
16.63	2700	0.628
18.63	2738	0.668

TABLE 6.8

Anisotropy in molar diamagnetic susceptibilities

Sample	$\Delta K \times 10^6$ cm ³ /mole
7CB	39.00
Mixture 1	47.98
Mixture 2	56.20
Mixture 3	66.24
Mixture 4	76.49
7P(2CN)5BC	83.00

TABLE 6.10

Splay elastic constants of Mixture 2

 $x_0 = 31.8 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
0.58	1750	0.153
1.42	1950	0.211
2.95	2100	0.274
4.63	2188	0.320
6.72	2350	0.407
9.75	2400	0.463
12.72	2575	0.559
16.33	2650	0.626
19.55	2700	0.668
23.50	2800	0.745
27.92	2875	0.809

 $x_0 = 32.2 \mu$

0.70	1775	0.167
1.45	1875	0.202
2.50	1975	0.245
4.15	2125	0.300
5.75	2175	0.341
7.95	2283	0.410
10.75	2425	0.489
13.85	2500	0.549
17.25	2625	0.635
21.12	2725	0.705
25.42	2750	0.746
29.17	2825	0.806

TABLE 6.7

 $\bar{\alpha}$ and $\bar{\alpha}/\Delta\alpha$ for the systems studied

Sample	$\bar{\alpha} \times 10^{24}$ cm^3	$\bar{\alpha}/\Delta\alpha$
7CB	36.13	1.390
Mixture 1	40.37	1.514
Mixture 2	44.26	1.623
Mixture 3	49.00	1.756
Mixture 4	53.85	1.867
7P(2CN)5BC	56.93	1.940

TABLE 6.8

Anisotropy in molar diamagnetic susceptibilities

Sample	$\Delta K \times 10^6$ cm^3/mole
7CB	39.00
Mixture 1	47.98
Mixture 2	56.20
Mixture 3	66.24
Mixture 4	76.49
7P(2CN)5BC	83.00

TABLE 6.9

Splay elastic constants of Mixture 1

 $x_0 = 32.2 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
1.30	2025	0.239
2.72	2175	0.295
3.90	2238	0.327
5.89	2300	0.370
7.67	2438	0.447
9.97	2550	0.506
12.22	2600	0.545
14.22	2650	0.582
16.63	2700	0.628
18.63	2738	0.668

TABLE 6.10

Splay elastic constants of Mixture 2

 $x_0 = 31.8 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
0.58	1750	0.153
1.42	1950	0.211
2.95	2100	0.274
4.63	2188	0.320
6.72	2350	0.407
9.75	2400	0.463
12.72	2575	0.559
16.33	2650	0.626
19.55	2700	0.668
23.50	2800	0.745
27.92	2875	0.809

 $x_0 = 32.2 \mu$

0.70	1775	0.167
1.45	1875	0.202
2.50	1975	0.245
4.15	2125	0.300
5.75	2175	0.341
7.95	2283	0.410
10.75	2425	0.489
13.85	2500	0.549
17.25	2625	0.635
21.12	2725	0.705
25.42	2750	0.746
29.17	2825	0.806

TABLE 6.11

Splay elastic constants of Mixture 3

$x_0 = 31.5 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
1.92	2025	0.271
3.00	2112	0.324
5.13	2250	0.392
7.33	2350	0.459
9.92	2425	0.527
12.87	2550	0.608
16.58	2650	0.676
21.17	2700	0.732
25.50	2775	0.810
30.33	2925	0.940
36.25	3075	1.079
40.53	3175	1.193
46.83	3250	1.284

$x_0 = 32.4 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
0.58	1762	0.205
2.37	1975	0.285
4.42	2162	0.376
6.37	2212	0.416
8.83	2350	0.510
11.33	2400	0.527
14.08	2512	0.628
17.13	2600	0.694
21.78	2638	0.747
26.92	2750	0.857
33.00	2875	0.980
41.42	2875	1.112

TABLE 6.12

**Splay elastic constants
of Mixture 4**

$x_0 = 31.2 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
1.60	2000	0.304
3.50	2200	0.404
5.90	2350	0.496
7.90	2462	0.568
10.50	2550	0.636
14.00	2650	0.737
17.80	2688	0.783
23.00	2725	0.844
28.60	2850	0.955
34.60	2950	0.993
39.70	3050	1.164
46.00	3200	1.324
51.10	3300	1.436
58.10	3450	1.603

TABLE 6.13

**Splay elastic constants of
7P(2CN)5BO**

$x_0 = 27.4 \mu$

$T_{NI}-T$	H_0 gauss	$k_{11} \times 10^6$ dynes
0.80	2525	0.403
1.75	2638	0.477
3.60	2800	0.571
4.70	2800	0.594
8.20	2950	0.700
10.90	3000	0.754
14.10	3125	0.846
17.70	3175	0.904
20.95	3225	0.956
24.40	3300	1.025
29.80	3365	1.114
35.00	3475	1.215
39.50	3600	1.337
44.00	3650	1.404
49.15	3700	1.474
54.60	3762	1.554
61.90	3838	1.662

TABLE 6.14

The experimental values fitted to the
equation $k_{11} = CS^x$

Sample	x	C
7CB	2.20	2.28
Mixture 1	2.44	3.00
Mixture 2	2.42	2.89
Mixture 3	2.76	3.60
Mixture 4	3.01	3.74
7P(20N)5BC	2.69	3.20