CHAPTER VII

EFFECT OF SKEWED CYBOTACTIC STRUCTURE ON THE DIELECTRIC CONSTANTS AND CONDUCTIVITIES OF SOME BINARY MIXTURES EXHIBITING THE NEMATIC PHASE

7.1 Introduction

&. we have seen in chapters V and VI the effect of smectic like short range order is known to have direct influence on the conductivity anisotropy.[1] On the other hand, the effect of short range order an the Tow frequency dielectric constants is more difficult Po delineate This is because the values of the anisotropic dielectric constants depend an several factors, viz., (i) the principal polarizabilities of the molecules, (ii) the magnitude and mutual disposition of dipolar groups in the molecules, (iii) the orientational order, and (iv) the internal field which is not easy Po calculate for the highly anisotropic medium, and which also depends on the structure of the short range order.

As we mentioned in chapter I, smectic like short range order reveals itself in the Xray diffraction patterns.[2] The domains which possess short range translational order in the molecular arrangement are called

cybotactic groups. If the angle between the nematic
director and the smectic like layer is not equal to 90°,
the groups are referred to as skewed cybotactic groups.

Recently, Madhusudana et al[3] have studied the
influence of such skewed cybotactic groups on the optical
properties of the nematic compound 2-cyano-4-heptylphenyl-
4'-pentyl-4-biphenylcarboxylate [7P(2CN)5BC]. This
compound has a cyano group making a large angle ($\sim$60°)
with the long axis of the molecule. The tilt angle of
the skewed cybotactic structure decreases from $\sim$48° to
$\sim$40° as the temperature is raised from 25°C to 87°C.
Further, this has a significant influence on the tempe-
rature variation of its ordinary refractive index (n_o)[3,4],
n_o decreases first, attains a broad minimum and then
unusually increases as the temperature is lowered in the
nematic phase.   This was accounted for on the basis of
the tilt angle variation of the skewed cybotactic
structure. We have undertaken measurements on the
dielectric and conductivity properties of this substance
with a view to finding the effect of tilt angle variation
on these properties. The effect of the variation of the
short range order on the thermal evolution of the con-
ductivity anisotropy is quite obvious   But the dielectric
constants do not have any unusual temperature dependence.

However, the subtle effect of short range order on
the dielectric constants is manifested when we mix
7P(2CN)5BC with 4'-n-heptyl-4-cyanobiphenyl (7CB), a
nematogen with high positive dielectric anisotropy,
so as to get a very small net anisotropy. The results
are presented in this chapter.

7.2   Experimental

7P(2CN)5BC was obtained from E.Merck (Darmstadt)
and used without further purification. 7CB was synthe-
sized in our chemistry laboratory. The molecular
structures of the two compounds are given in fly. 7.1.
The phase diagram of their mixtures is shown in fig.7.2.
The transition temperatures were determined using a
Mettler hot stage (FP52) in conjunction with a polarising
microscope.

The experimental technique employed to measure
static dielectric constants $\varepsilon_{||}$ and $\varepsilon_{\perp}$ has already been
described in chapter IV.

The principal conductivities $\sigma_{||}$ and $\sigma_{\perp}$ were
measured over a range of frequencies from 300 Hz - 30 KHz
using the wayne Kerr bridge (B642) with an external
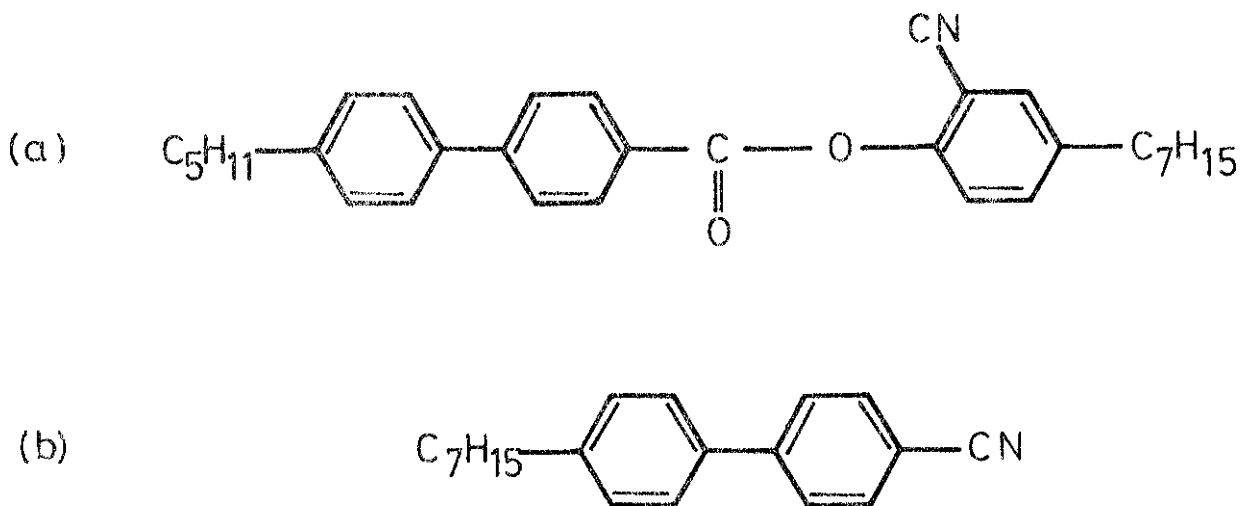source (systronics LF Oscillator) and detector (Lock-
in-amplifier, Model PAR186).

FIGURE 7.1

Structural formula of (a) 2-cyano-4-heptylphenyl-4'-pentyl-
4-biphenylcarboxylate [7P(2CN)5BC] and (b) 4-n-heptyl-4'-
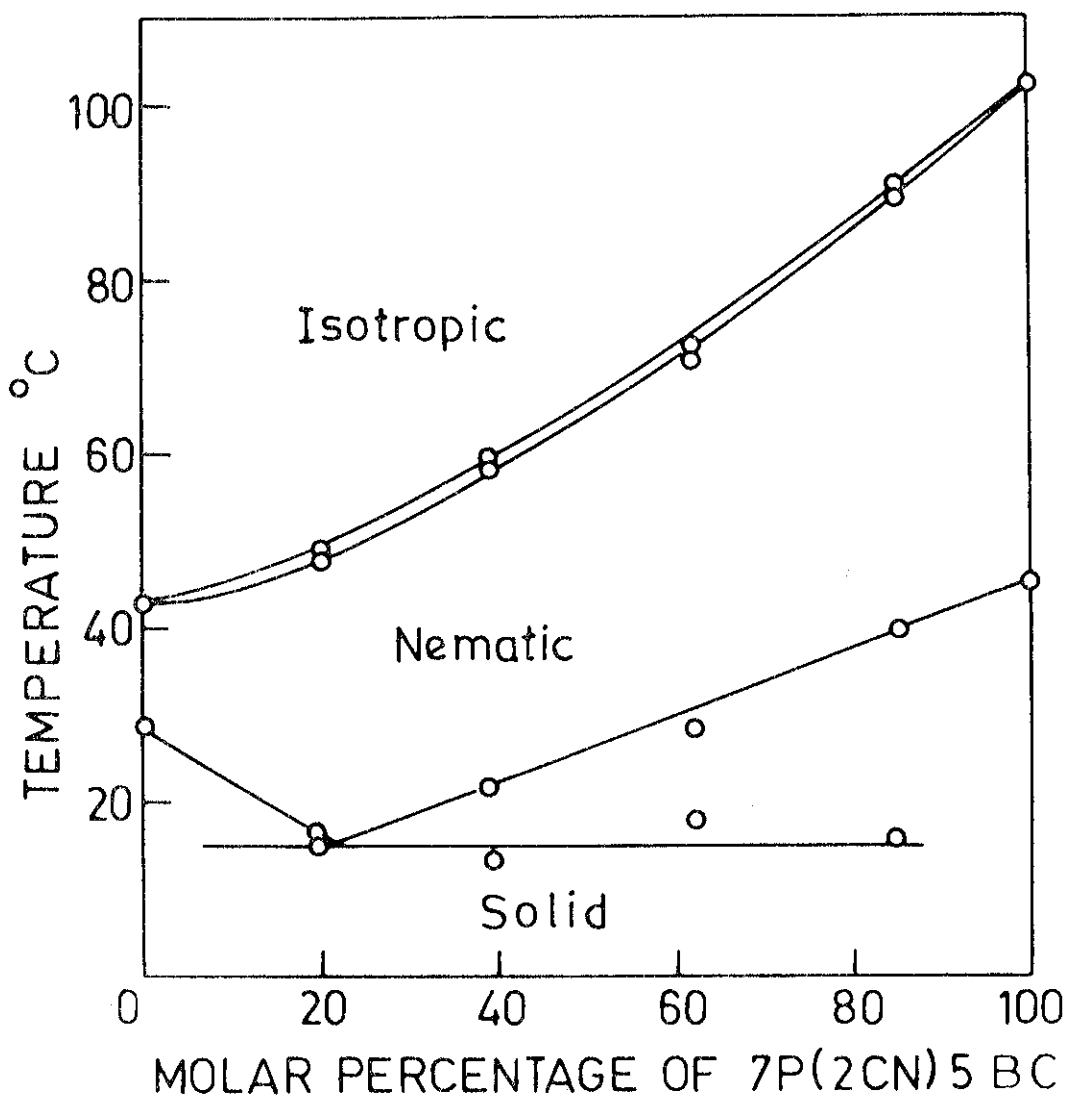cyanobiphenyl (7CB).

FIGURE 7.2

Phase diagram of mixtures of 7P(2CN)5BC and 7CB.
(Reproduced from Ref.4).

Dielectric and conductivity measurements were made on the following systems (percentages indicate mole per cent of the components):

    i)   7P(2CN)5BC
    ii)   15% 7CB + 85% 7P(2CN)5BC
   iii)   40% 7CB + 60% 7P(2CN)5BC
   iv)   61% 7CB + 39% 7P(2CN)5BC
    v)   80% 7CB + 20% 7P(2CN)5BC.

7.3   Results and Discussion

(a) Dielectric %&die&

The principal dielectric constants ($\varepsilon_{||}$ and $\varepsilon_{\perp}$) and the mean value $\bar{\varepsilon} = (\varepsilon_{||} + 2\varepsilon_{\perp})/3$ of the above systems are shown in figs.7.3-7.7 as functions of relative temperature ($T_{NI} - T$). The dielectric aniso-tropies ($\triangle\varepsilon$) of all these systems have been plotted in fig.7.8.

7P(2CN)5BC has a negative $\triangle\varepsilon$ (fig.7.3), because of a cyano group making an angle of $\sim 60°$ with the long axis of the molecule (fig.7.1). The $\bar{\varepsilon}$ value decreases with temperature throughout the nematic range, but these is a sudden increase of $\sim 2\%$ in its value at T_{NI}. This may be partly caused by a decrease in the anti-parallel correlation between the long axis components of the dipole moments of neighbouring molecules,[5,6] but
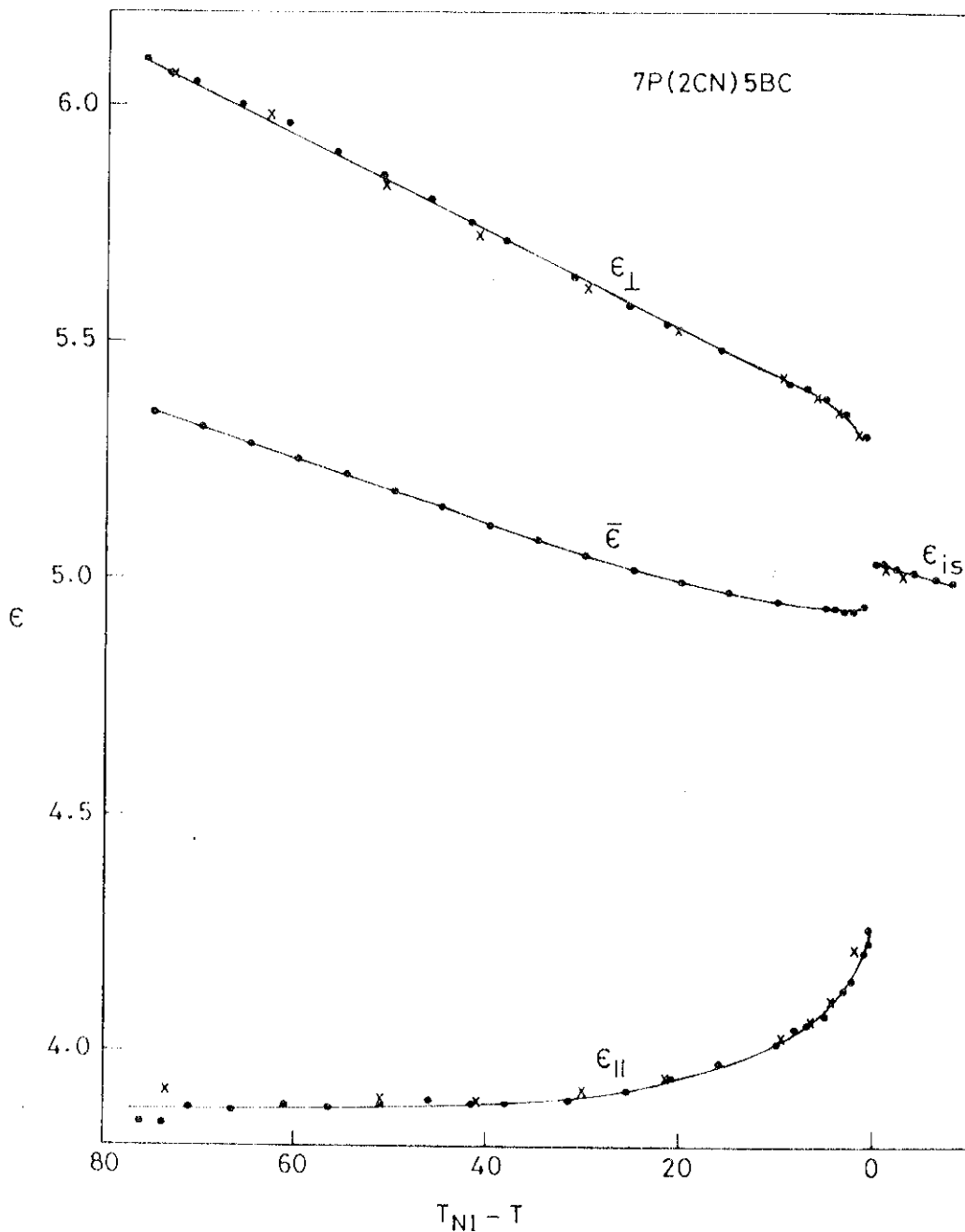
FIG.7.3: Temperature dependence of the low frequency dielectric oonatanta of 7P(2CN)5BC. $(T_{NI}-T)$ is the relative temperature. Different symbols show the results of independent meaaurementa.

another more probable reason will be discussed
later. It is interesting to note that $\varepsilon_\perp$ decreases
practically linearly as the temperature is increased
without any striking change in its rate of variation
near T_{NI}.

For mixtures with relatively high concentration
of 7CB, $\Delta\varepsilon$ is positive (fig.7.8). In the mixture with
60% 7P(2CN)5BO (fig.7.5) also, $\bar{\varepsilon}$ decreases with tempe-
rature, the rate of variation being smaller than that
in the purr compound. It also exhibits a positive
jump of comparatively lower magnitude at T_{NI}. Further,
$\varepsilon_\perp$ shows a broad minimum. In the mixture with 39%
7P(2CN)5BO, $\varepsilon_{||}$ and $\varepsilon_\perp$ show trends in their tempe-
rature variations which are usual for a material with
positive $\Delta\varepsilon$. $\bar{\varepsilon}$ remains practically constant (fig.7.6)
with decrease of temperature, showing a very slight
increase at the lowest temperatures. Further, $\bar{\varepsilon}$
exhibits practically no jump at T_{NI}. For mixtures
with higher concentrations of 7CB (for example 80% 7CB,
fig.7.7), $\bar{\varepsilon}$ increases with temperature. The latter
result is caused by a reduction in the antiparallel
correlation between neighbouring 7CB molecules with
increase of temperature,[5] as already discussed in the
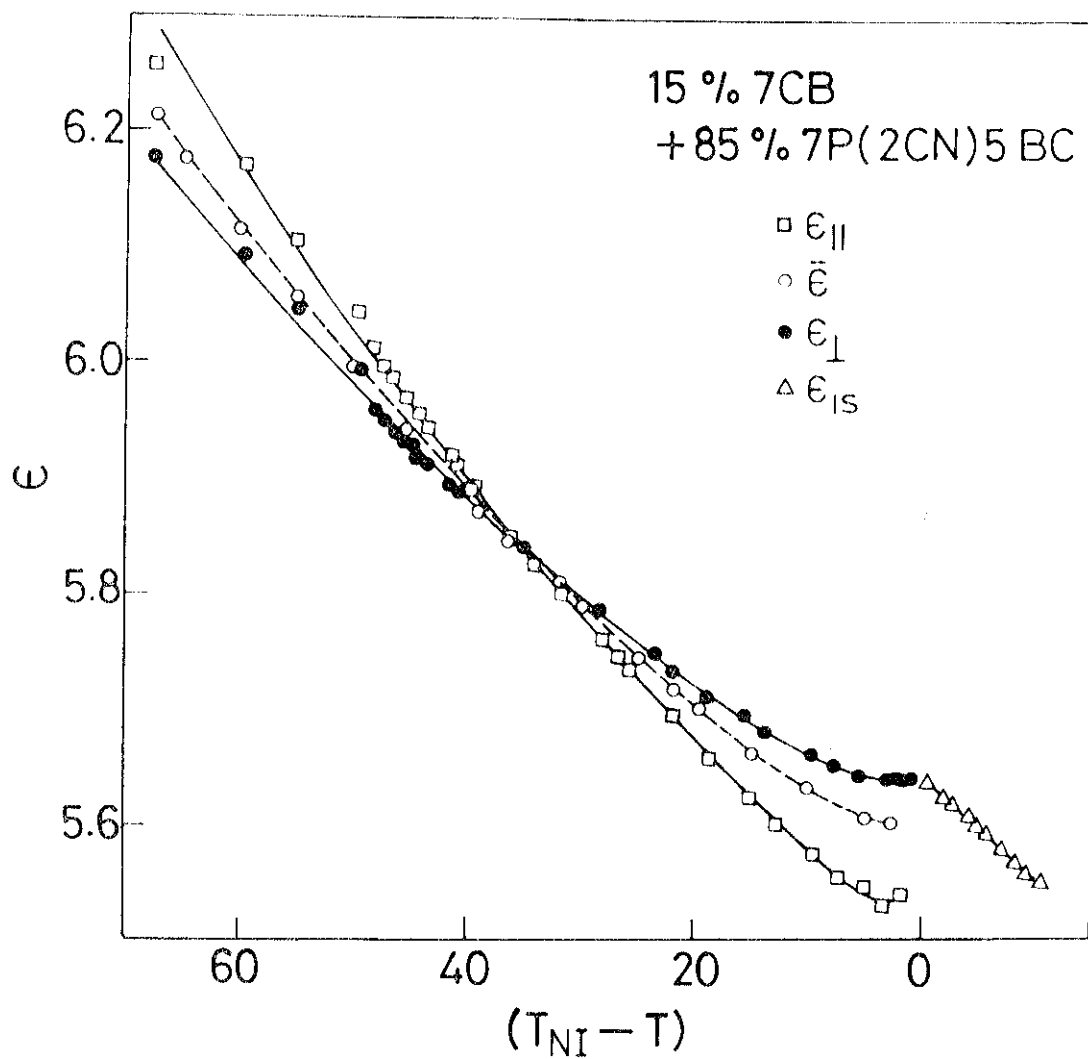previous chapters. We see that in the mixture with

FIG.7.4: Temperature dependence of the low frequency dielectric constants of a mixture of 85 mole per cent of 7P(2CN)5BC with 15 mole per cent of 7CB.
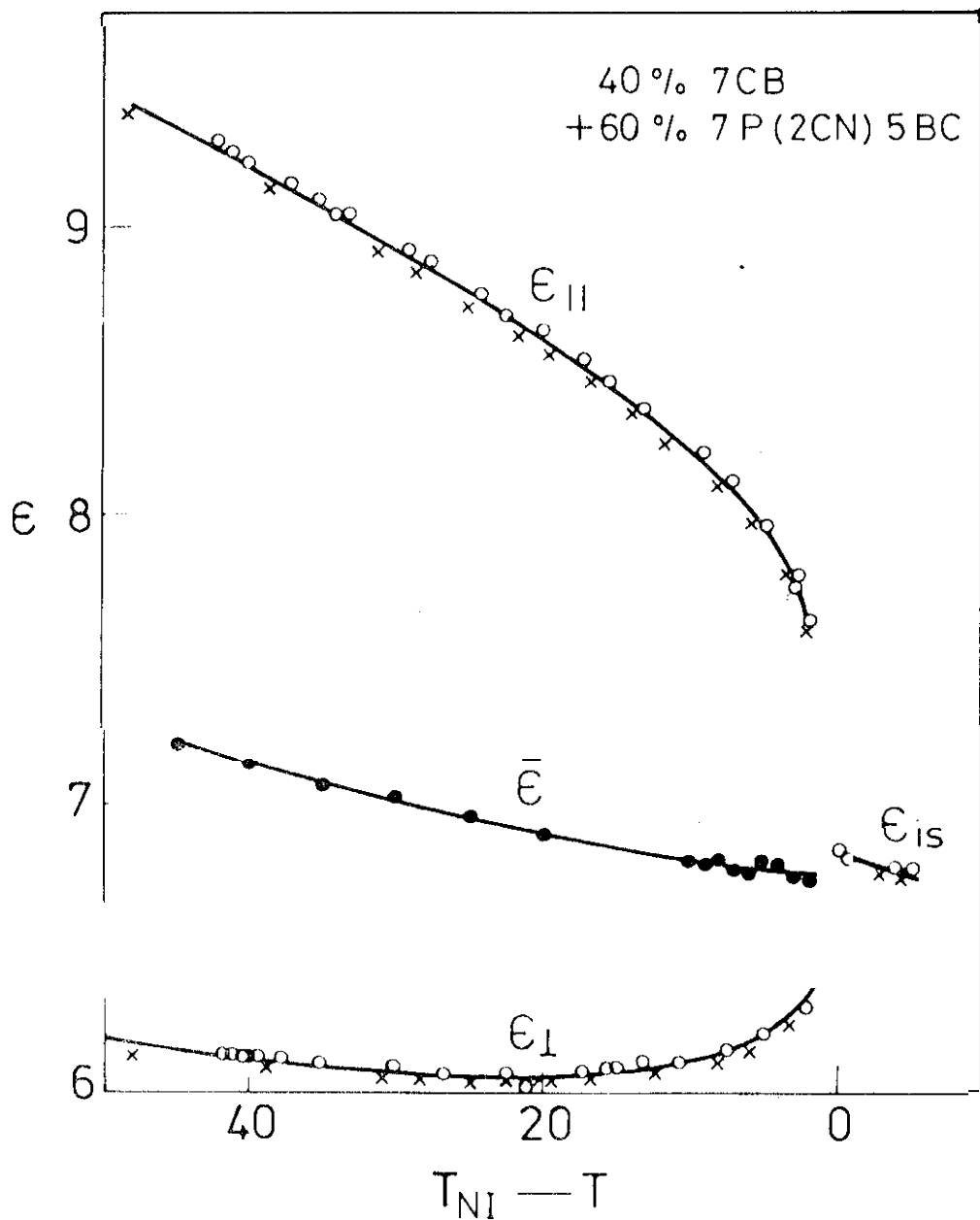
FIG.7.5: Temperature dependence of the low frequency
dielectric constants for a mixture of 60 mole
per cent of **7P(2CN)5BC** with 40 mole per cent
of **7CB**. The different symbols indicate the
results of two independent measurements.

FIG.7.6: Temperature dependence of the low frequenoy
dielectric oonatante of mixture of 39 mole per cent
of 7P(2CN)5BC *with* 61 mole per oent of 7CB.
Different symbols indicate the results of independent
measurements.

80% 7CB
+ 20% 7P(2CN)5BC

$\epsilon_{\parallel}$

$\bar{\epsilon}$

ϵ_{is}

$\epsilon_{\perp}$

$T_{NI} - T$

PIG.7.7:   Temperature dependence of the low frequency
dielectric constants of a mixture of 20 mole
per cent of 7P(2CN)5BC with 80 mole per cent of
7CB.   The different symbols indicate the results
of independent measurements.

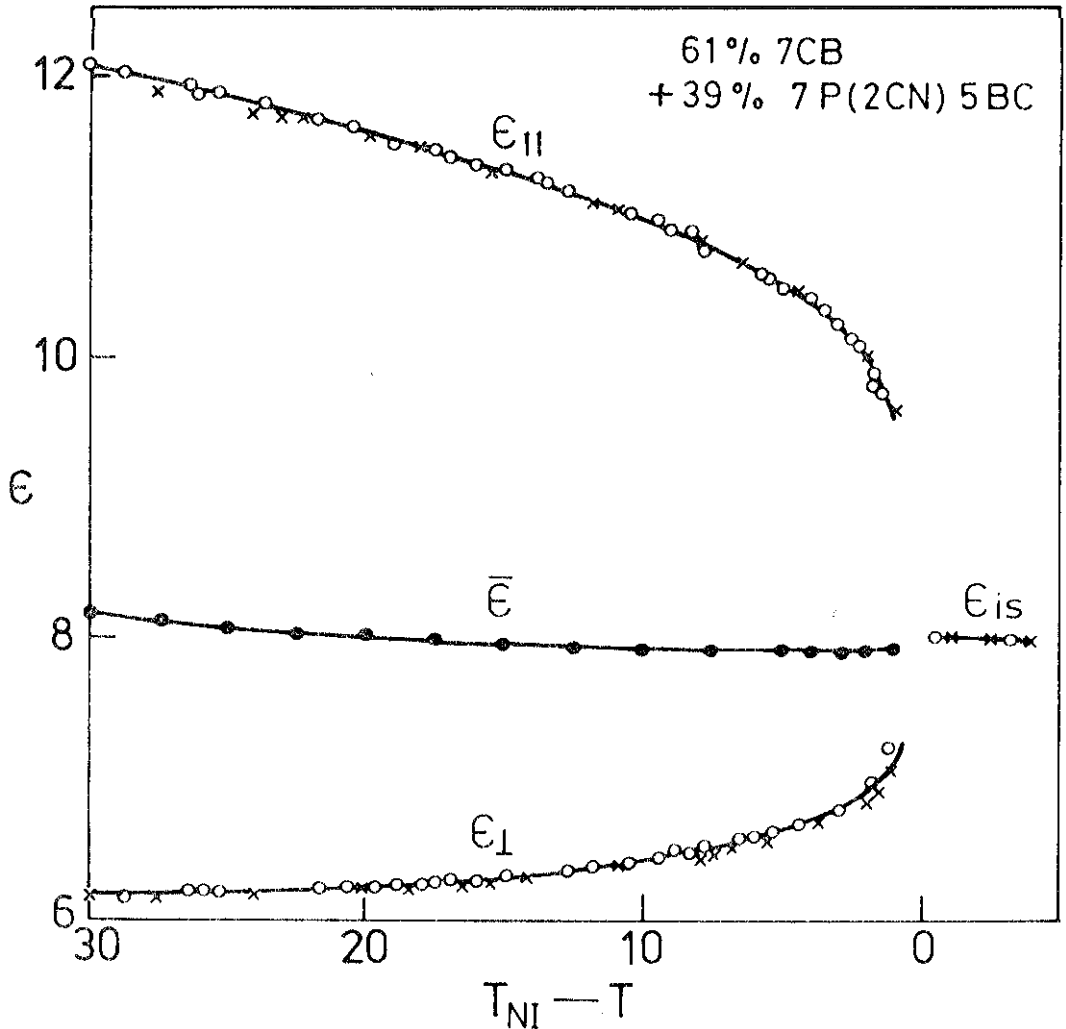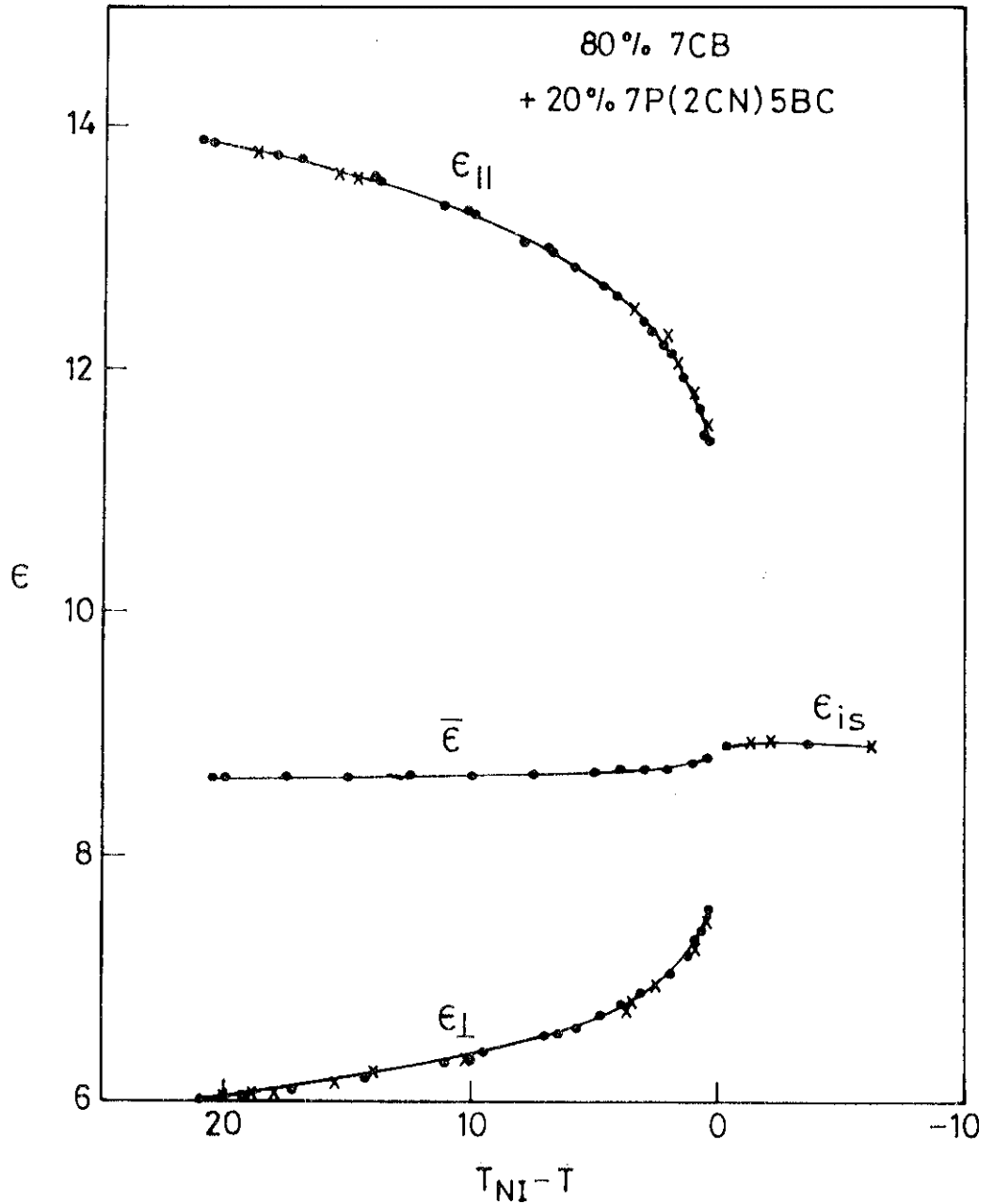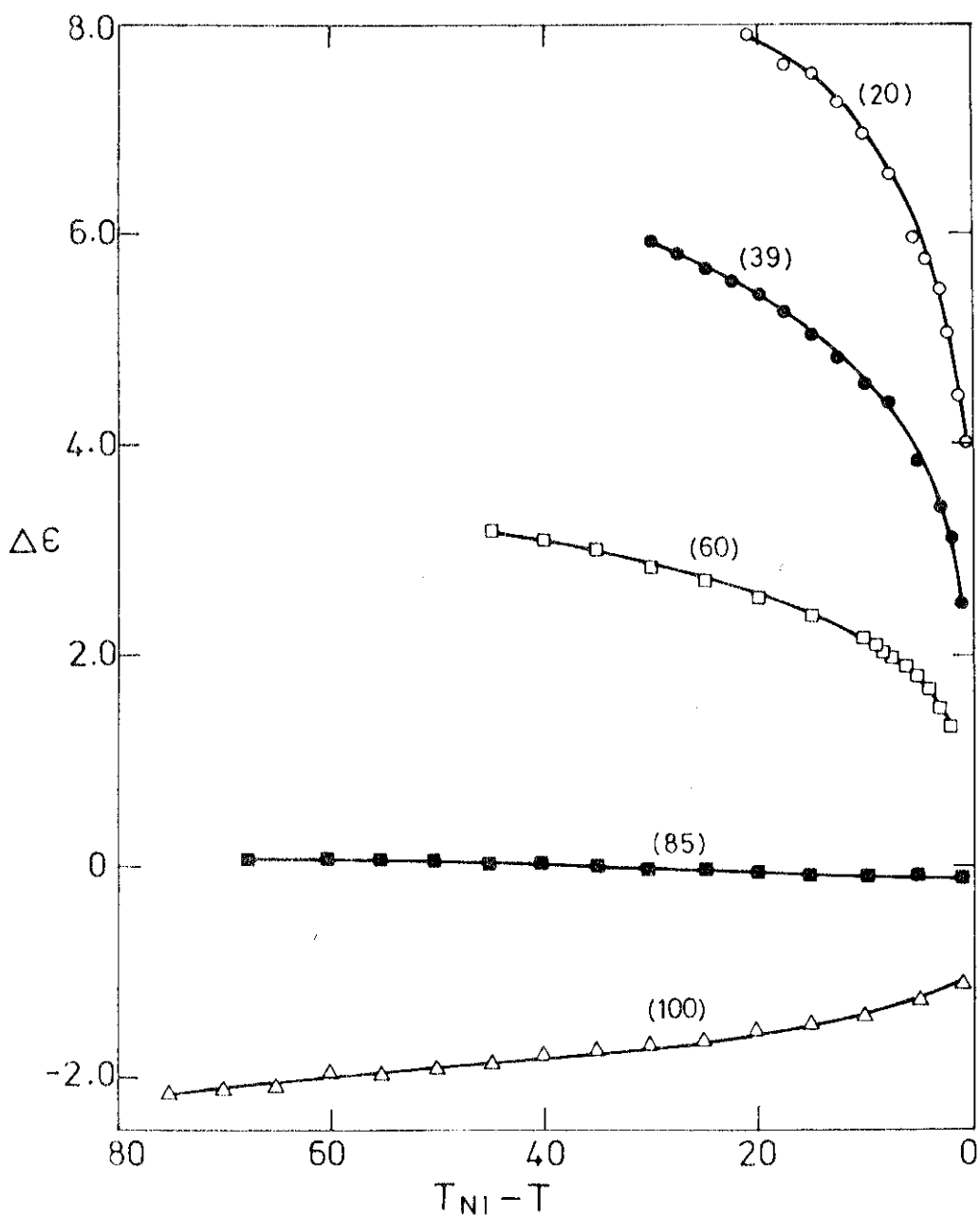FIG.7.8: Dielectric anisotropies of various mixtures of 7P(2CN)5BC with 7CB as functions of relative temperature. The numbers in brackets indicate the, mole percentage of 7P(2CN)5BC.

39% 7P(2CN)5BC (fig.7.6), the opposite trends
found in the temperature variation of $\bar{\varepsilon}$ of the pure
components ($\bar{\varepsilon}$ increases in 7CB and decreases An
7P(2CN)5BC with increase of temperature) appear to
balance leading to its practically constant value in
the temperature range of measurement.

In pure 7P(2CN)5BC and in mixtures with rela-
tively high concentrations of 7P(2CN)5BC, ε_{is} decreases
with temperature as in any other polar liquid. But in
mixtures with high concentrations of 7CB (fig.7.7),
ε_{is} slightly increases as the temperature is increased
above T_{NI}, and then decreases with temperature. This
initial increase close to T_{NI} is again due to the reduc-
tion in the antiparallel short range order in the
isotropic phase.

The mixture with 15% of 7CB exhibits very
striking and unusual features (fig.7.4) Firstly,
both $a_{,,}$ and $\varepsilon_{\perp}$ decrease with temperature in most of the
nematic range, $\varepsilon_{,,}$ increasing only close to T_{NI}. Such
a trend in which both $\varepsilon_{,,}$ and $\varepsilon_{\perp}$ decrease with increasing
temperature has been noted in several earlier studies.[7]
$\Delta\varepsilon$ is very small and changes sign as the temperature is
varied. But rather unusually, the sign is positive at
lower temperatures and negative ac higher temperatures.

This type of reversal (becoming negative at higher temperatures) has been found by us for the first time. We have _confirmed_ this result by making measurements on a mixture with 15.2% 7CB (fig.7.9). We see that the results are similar to those given in fig.7.4, except that the cross over occurs at a higher temperature.

This trend is opposite to the *on* expected an the basis of the theory of Maier and Meier[8] (chapter IV) which predicts that

$$\varepsilon_{\shortparallel} = 1 + 4\pi N h F\left\{ \bar{\alpha} + \frac{2}{3}\Delta\alpha S + \frac{\mu^2}{3k_B T}[1 - (1 - 3\cos^2 \beta)S]\right\}$$

$$\varepsilon_{\perp} = 1 + 4\pi N h F\left\{ \bar{\alpha} - \frac{1}{3} S\Delta\alpha + \frac{\mu^2}{3k_B T}[1 + \frac{1}{2}(1 - 3\cos^2 \beta)S]\right\}$$

$$\ldots (7.1)$$

where $\Delta\alpha$ is the anisotropy of polarizability of a perfectly oriented medium, β is the angle made by the permanent dipole moment μ with the long axis of the molecule, $F = (1 - \bar{\alpha}f)^{-1}$, $f = \frac{4\pi N}{3}(\frac{2\bar{\varepsilon} - 2}{2\bar{\varepsilon} + 1})$ is the reaction field factor, $h = 3\bar{\varepsilon}/(2\bar{\varepsilon} + 1)$ is the cavity field factor, k_B the Boltzmann constant and S the orientational order parameter. If μ is sufficiently strong (as in cyano or nitro compounds), it is clear that the last term in the flower brackets in equation (7.1) prodominates and if β is large then _both_ $\varepsilon_{\shortparallel}$ and $\varepsilon_{\perp}$ can decrease with increase of temperature.
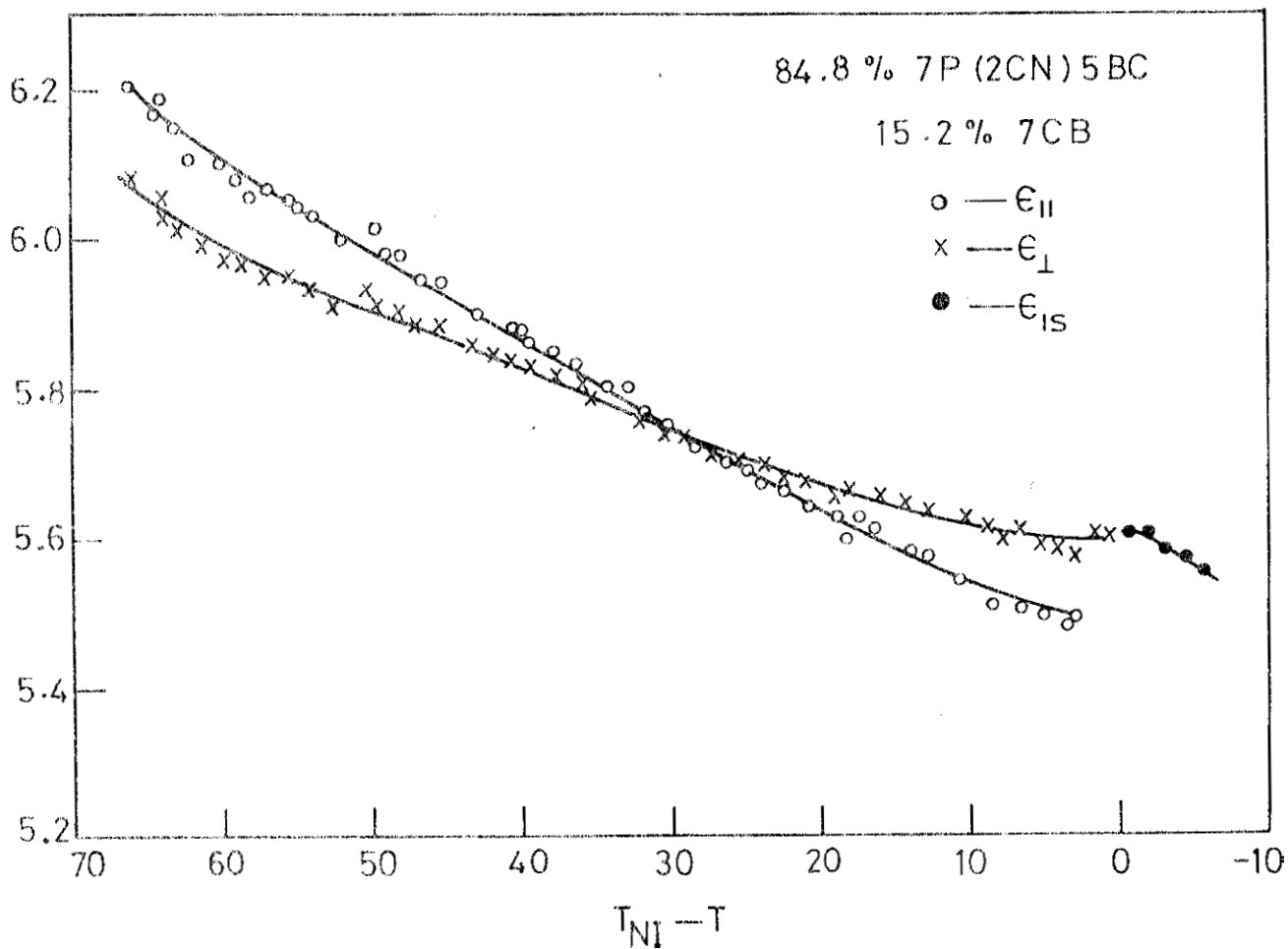
FIG.7.9: Temperature dependence of the low frequency dielectric constants of a mixture of 84.8 mole per cent of 7P(2CN)5BC with 15.2 mole per cent of 7CB.

We get for the anisotropy of the dielectric constant

$$\Delta\varepsilon = 4\pi N Fh \left\{ \Delta\alpha - \frac{F\mu^2}{2k_B T}(1 - 3\cos^2\beta) \right\} S \qquad (7.2)$$

If the two terms between the flower brackets in (7.2) are practically equal, kt is clear that $\Delta\varepsilon$ can change sign at some temperature T, and become positive at higher temperatures, as is indeed found in some systems.[9] A simple calculation with $\Delta\alpha = 50 \times 10^{-24}$ CC, $\bar{\alpha} = 30 \times 10^{-24}$ CC, $\mu = 4$ D, $\beta \simeq 60^0$, and assuming that F = 1, h = 1, for the sake of making an illustrative calculation, and the typical values of the order parameter S (temperature dependence) taken from ref.4, clearly indicates this expected trend as shown in fig. 7.10.

We therefore attribute the reverse trend observed in our studies to the temperature variation of the skewed cybotactic type of short range order found in 7P(2CN)5BO. Xray studies[3] reveal that the tilt angle of the skewed cybotactic structure decreases from ∼48[0] at 25[0]C to ∼40[0] at 87[0]C, the rate of decrease becoming stronger at higher temperatures (fig.7.11). Indeed Xray studies on the mixture with 15 mole per cent of 7CB also reveal a skewed cybotactic structure (fig.7.12), and just as in the case of 7P(2CN)5BO, the ordinary refractive index of this mixture also increases with decrease of temperature far below T_{NI}.[4]
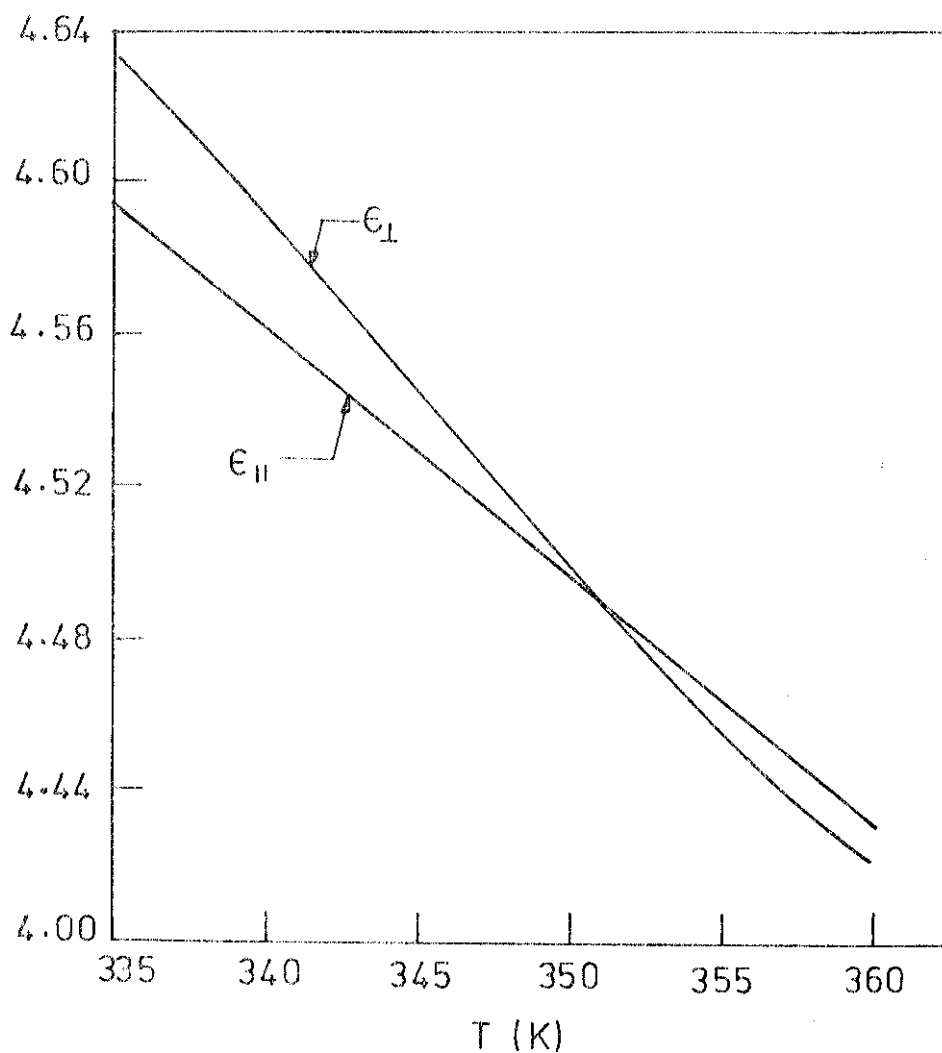
FIGURE 7.10: Curves showing the temperature
variations of the principal dielectric constants
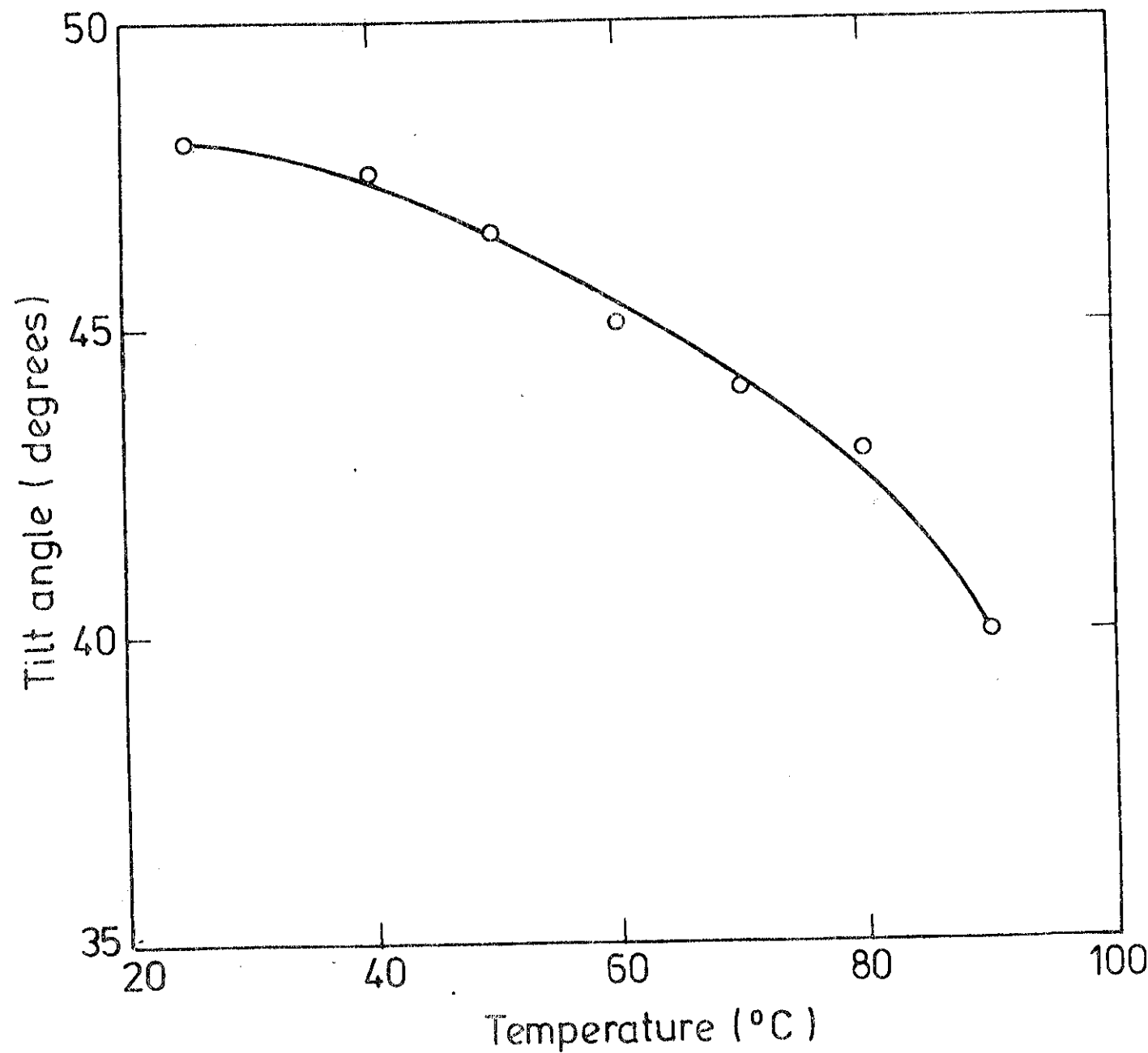calculated on the basis of the theory of Maier
and Meier.

FIG.7.11: Tilt angle variation of the skewed cybotactic
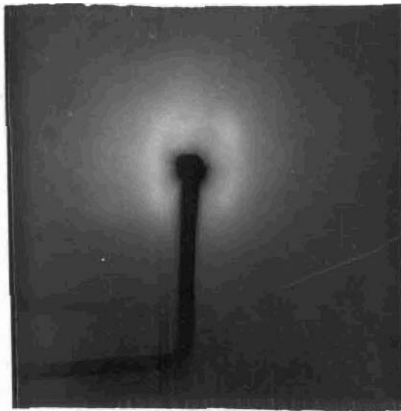structure of 7P(2CN)5BC. (Reproduced from ref.3).

FIGURE 7.12

X-ray diffraction photographs of a monodomain
sample of a mixture of 85 mole per aent of
7P(2CN)5BC with 15 mole per aent of 7CB taken at
25°C. Four spots seen in the diffraction pattern
are characteristic of a skewed cybotactic nematic.

Benguigui[10] has developed a theoretical model
of the dielectric constants lo the smectic C phase.
According to this theory, the permanent dipolar contri-
butions to the dielectric constants are given by

$$\varepsilon_{\shortparallel} - \varepsilon_{\shortparallel}^{\infty} = 3\bar{\varepsilon}/(2\bar{\varepsilon} + \varepsilon_{\shortparallel}^{\infty}) \frac{4\pi N}{k_B T} \mu^2 \cos^2 \beta \left\{ 1 - \frac{3\mu^2 \cos^2 \beta}{r^3 k_B T}(3\cos^2 \delta - 1)\right\}$$

$$\varepsilon_{\perp} - \varepsilon_{\perp}^{\infty} = 3\bar{\varepsilon}/(2\bar{\varepsilon} + \varepsilon_{\perp}^{\infty}) \frac{4\pi N}{k_B T} \frac{\mu^2 \sin^2 \beta}{2} \left\{ 1 + \frac{3}{4} \frac{\mu^2 \sin^2 \beta}{r^3 k_B T}(3\cos^2 \delta - 1)\right\}$$

.. (7.3)

where " and ⊥ refer to directions which are parallel
and perpendicular to the long axes of the molecules which
are assumed to have perfect orientational order, ε^{∞} is
the value at a frequency beyond the lowest relaxation
frequency, N the number of molecules per unit volume, δ
the tilt angle and r an intermolecular distance in the
layer.

We can expect that relations (7.3) are valid for
skewed cybotactic groups with a smectic C type of short
range order also. It is then clear that as δ decreases
In 7P(2CN)5BC with temperature, the contribution to $\varepsilon_{\shortparallel}$
is reduced while that for $\varepsilon_{\perp}$ is increased. In pure
7P(2CN)5BC, $\beta \simeq 60°$ and the medium has a moderately
strong negative $\triangle \varepsilon$ and the contribution from the
temperature variation of S ominates over that of δ.

However, if might explain the practically linear decrease of $\varepsilon_\perp$ with temperature, without any pronounced increase in its rate of variation near T_{NI} (fig.7.3). The rate of decrease of $\varepsilon_\perp$ should have increased near T_{NI} if it depended only on that of the order parameter. However, the tilt angle sf the cybotactic structure also decreases rapidly near T_{NI}, and the effect due to this appears ta compensate for the order parameter variation in 7P(2CN)5BO. It is also easy to verify from the eqn.(7.3) that if δ decreases with a jump at T_{NI}, it can contribute to the observed positive jump in $\bar{\varepsilon}$.

In the mixture with 15% 7CB, $\Delta\varepsilon$ has been reduced to a small value and the effect of temperature variation of δ is immediately obvious. For the sake of argument, we assume that the effective value of $\beta \simeq 54°$, so that $\cos^2 \blacksquare = \frac{1}{3}$. We further assume that $(2\bar{\varepsilon} + \varepsilon_{||}^\infty) \simeq (2\bar{\varepsilon} + \varepsilon_\perp^\infty)$. It is easy to verify that the small difference between $\varepsilon_{||}^\infty$ and $\varepsilon_\perp^\infty$ leads to an error of only $\sim 2-3\%$ in this relation. Using eqns.(7.3), we can now write that the temperature dependent part of the dielectric anisotropy

$$\Delta\varepsilon \propto - \frac{(3\cos^2 \delta - 1)}{T^2} \qquad (7.4)$$

Using the observed variation of δ with temperature, $(3\cos^a \delta - 1)$ increases more strongly than T^2 and hence

$\Delta\varepsilon$ should become more negative as the temperature is increased, in agreement with the result found lor the mixture with 15% 7CB (fig.7.8). It is interesting to compare the measured values of $\Delta\varepsilon$ and $\bar{\varepsilon}$ of the mixtures with those calculated on the basis of an additive law of the typo $\Delta\varepsilon_{mix} = X_1 \Delta\varepsilon_1 + X_2 \Delta\varepsilon_2$, where X_1 is the mole fraction of tho component 1, etc. The results are shown in table 7.1. The calculated values of $\Delta\varepsilon$ are larger than the measured ones, whereas $\bar{\varepsilon}$ values have the opposite trend. Using eqns.(7.3), both these results can be explained by assuming that the tilt angle of the skewed cybotactic structure la the mixture is less than that implied by an additive law. The interactions between 7P(2CN)5BC and 7CB molecules can be expected to lead to this result. This assumption also explains the observation that $\varepsilon_\perp$ values of some mixtures ore higher than those 04 both the pure components (figs. 7.3 - 7.7).

(b) Conductivity Studies

The principal conductivities $\sigma_{\parallel}$ and $\sigma_\perp$ were measured on all the systems over the frequency range 300 Hz - 30 KHz. The conductivities for a typical case is shown in fig.7.13. The important results obtained are summarized below.
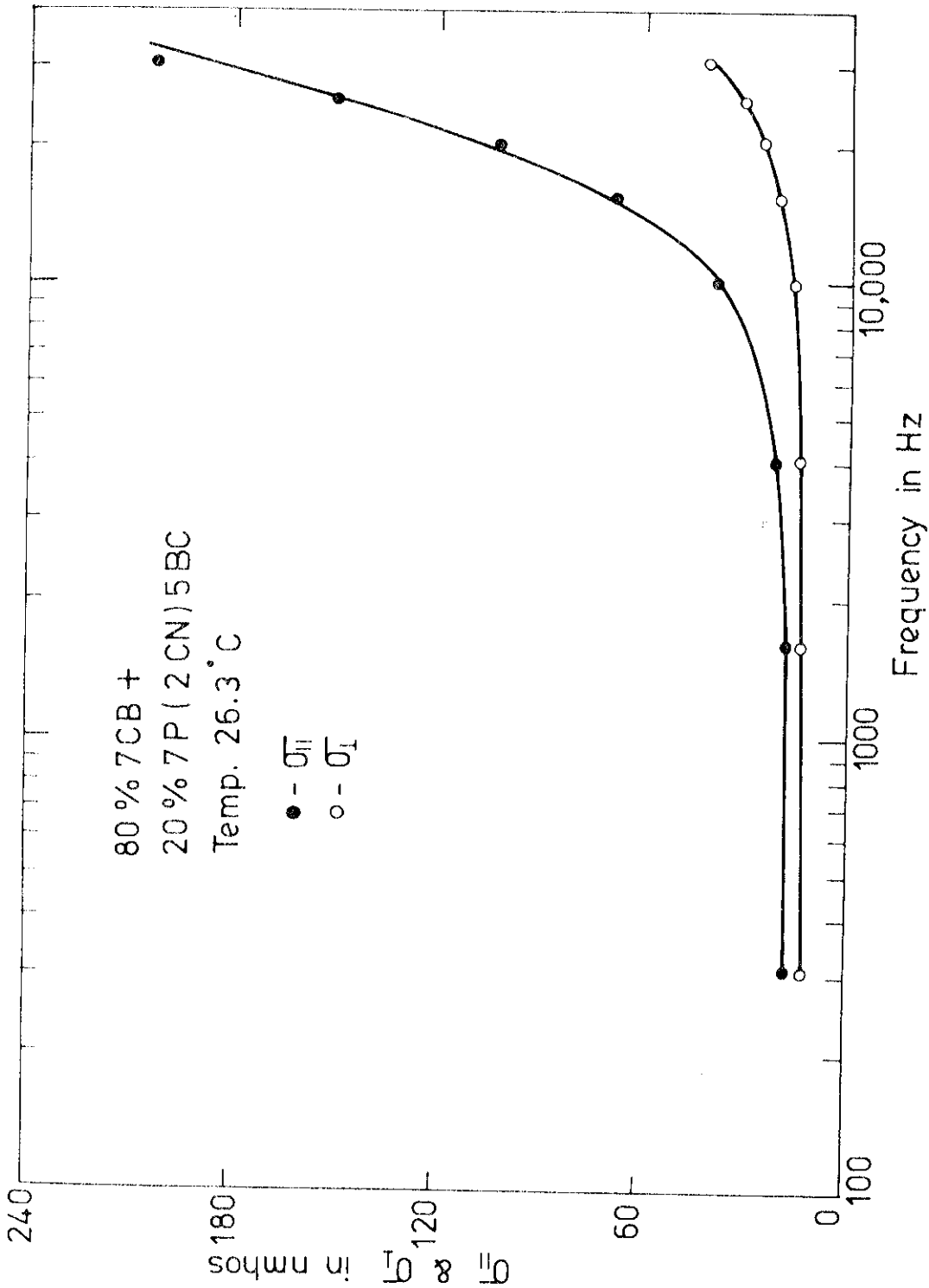
FIG.7.13: Frequency dependence of the principal conductivities of a mixture of 80 mole per cent of 7CB with 20 mole per cent of 7P(2CN)5BC at 26.3°C.

Table 7.1

Comparison of measured and calculated values

of $\Delta\varepsilon$ and $\bar{\varepsilon}$ for various mixtures at $T_{NI} - T = 20^{\circ}c$

Mole per cent of 7P(2CN)5BO	$\Delta\varepsilon$		$\bar{\varepsilon}$	
	Calculated value	Measured value	Calculated value	Measured value
100	–	– 1.60	–	4.99
85	0.43	– 0.05	5.62	5.71
60	3.80	2.55	6.66	6.90
39	6.64	5.40	7.54	8.00
20	9.20	7.85	8.33	8.65
7	–	11.90	–	9.77

In all the systems, $a_{,,}$ and $\sigma_{\perp}$ increase with frequency. In 7P(2CN)5BC (fig.7.14) both of them vary in practically the same manner. The dielectric absorption associated with dipolar relaxation contributes to the measured values of the conductivity,[11] and in the frequency range covered in our experiments, σ can be expressed as a quadratic function of ω (chapter V):

$$\sigma(\omega) = \sigma(do) + \epsilon_o(\epsilon - 1)\tau\omega^2 \qquad (7.5)$$

where τ is the relaxation time of orientational polarization.

Of course usually only the long axis component of the dipole moment relaxes at a relatively low frequency, i.e., the corresponding value τ_{λ} is long enough lo make an important contribution to the frequency dependence of a fa the low frequency range used in our measurements. As we have seen is earlier chapters, this contributes only to the frequency dependence of $a_{,,}$, . In 7P(2CN)5BC, on the other hand, the strong skewed cybotactic short range order in the medium leads τ_{λ} to contribute to the observed frequency dependence of $\sigma_{\perp}$ also (fig.7.14). For the sake of simplicity, we can assume that the orientational order <u>within</u> a cybotactic group
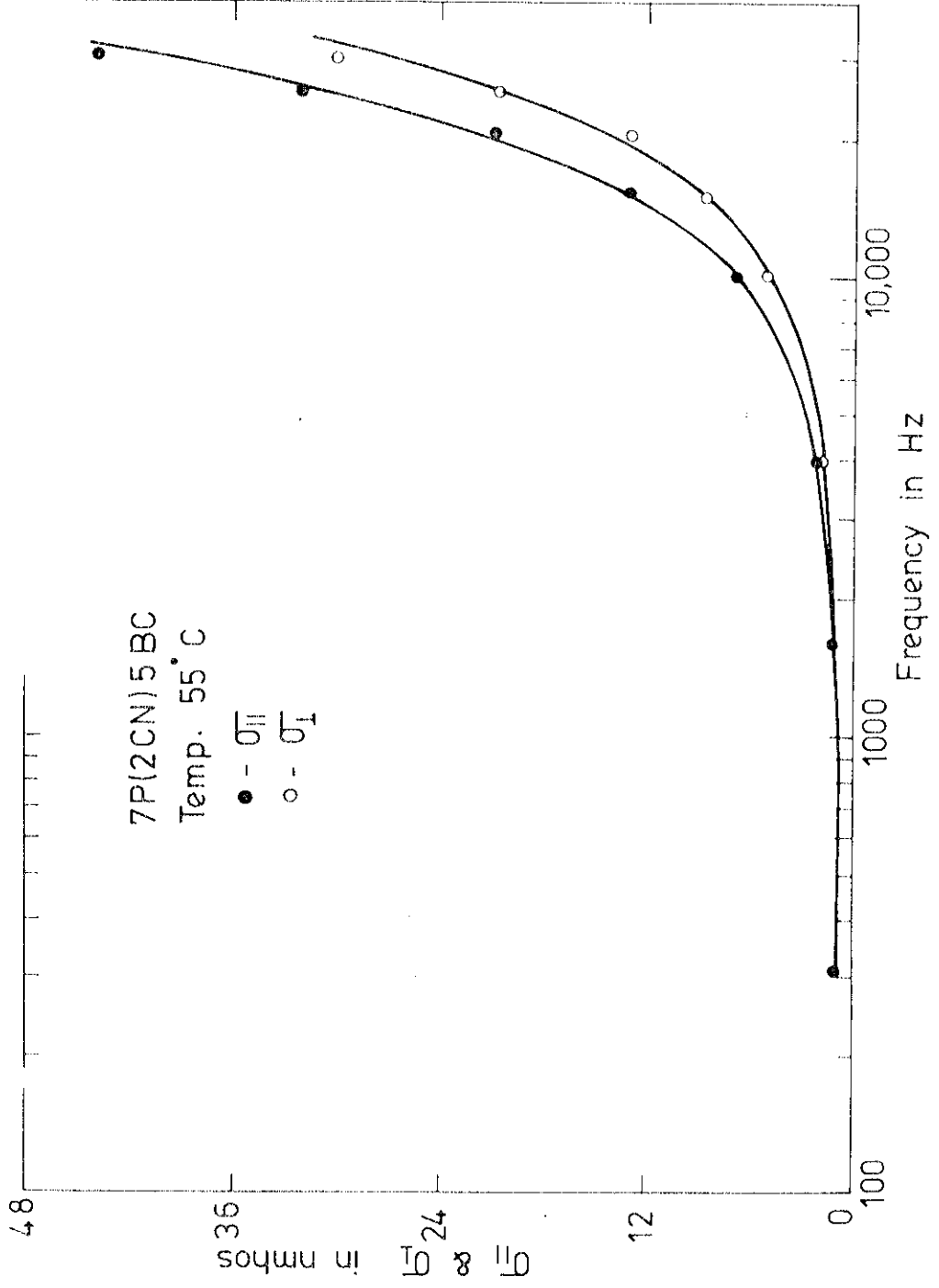
FIG.7.14: Frequency dependence of the principal conductivities of 7P(2CN)5BC   55°r

is perfect (i.e., all the molecules are parallel to one another) and associate a coordinate system $\xi\eta\zeta$ with the same as shown in fig.7.15 such that $\xi\zeta$ plane contains the normal $\underline{o}\,\underline{n}$ to the layers. The tilt angle δ is the angle between the ζ axis an4 $\underline{o}\,\underline{n}$. An electric field parallel to the ζ axis, say, leads to an electric conduction both parallel and normal to the layers. If the corresponding conductivities are given by σ_p and σ_n respectively, we can write[1]

$$\sigma_\zeta = \sigma_n \cos^2 \delta + \sigma_p \sin^2 \delta ,$$
$$\sigma_\xi = \sigma_n \sin^2 \delta + \sigma_p \cos^2 \delta ,$$
and $\quad \sigma_\eta = a_p$ \hfill (7.6)

we can now imagine a space fixed coordinate system XYZ such that the Z axis is along the nematic director $\vec{n}$. Defining the Eulerian angles in the usual manner between XYZ and $\xi\eta\zeta$ systems, and averaging over these angles taking into account the uniaxial symmetry of the nematic, we can write

$$a_{,,} = \left(\frac{a_n^* + 2\sigma_p}{3}\right) + \frac{2S}{3}\left(\frac{3\cos^2 6 - 1}{2}\right)(\sigma_n - \sigma_p)$$
and
$$\sigma_\perp = \left(\frac{\sigma_n + 2\sigma_p}{3}\right) - \frac{S}{3}\left(\frac{3\cos^2 \delta - 1}{2}\right)(\sigma_n - \sigma_p) \quad (7.7)$$

where S is the orientational order parameter ($= \overline{\frac{3\cos^2\theta - 1}{2}}$), θ being the Eulerian angle between Z and ζ axes. The
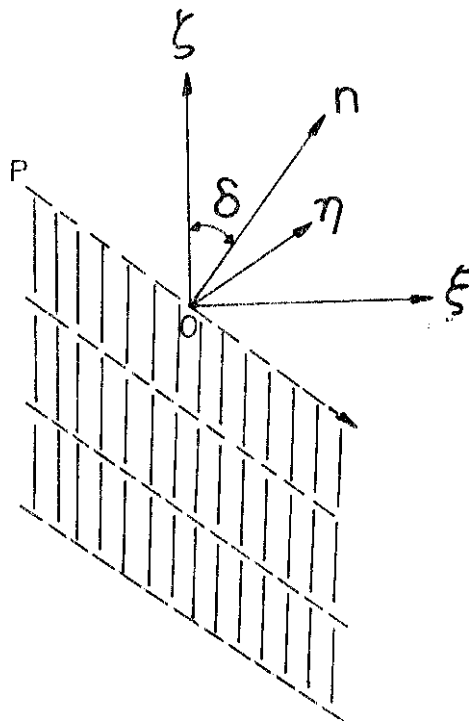
FIGURE 7.15

Schematic representation of a skewed
cybotactic group. $\underline{o}\,\underline{n}$ *is* the normal
to the boundary planes (layer normal)
and δ is the tilt angle.

tilt angle in 7P(2CN)5BC goes up to $\sim 50°$ as the temperature is lowered, and both $\sigma_n(\omega)$ and $\sigma_p(\omega)$ have contributions from the relaxation of $\mu_\perp$. This in turn leads to the observed similar frequency dependences of both $\sigma_{||}$ and $\sigma_\perp$.

In mixtures of 7P(2CN)5BC with 7CB, the conductivity anisotropy ratio $\sigma_R (= \sigma_{||}/\sigma_\perp)$ is always greater than one. In the mixture with 80% 7CB, at low temperatures $\sigma_{||}$ increases with frequency more rapidly than in the case of a, (fig.7.13), so that σ_R becomes large at high frequencies. As is illustrated in fig.7.16 for the mixture with 61% 7CB, with increase of temperature, the frequency dependences of $\sigma_{||}$ and $\sigma_\perp$ become similar and therefore σ_R dose not vary much in the frequency. This result can be easily understood in terms of the contributions to the conductivity from the law frequency $e_{||}$, relaxation of 7CB molecules which have a very large $\mu_\perp$ due to the cyano end groups. The tilt angle in these mixtures can be expected to be low ($\sim 0°$), and as the temperature is lowered, the relaxation time corresponding to $\epsilon_{||}$ relaxation increases and therefore increases faster than $\sigma_\perp$ as can be seen from the eqn.(7.5).
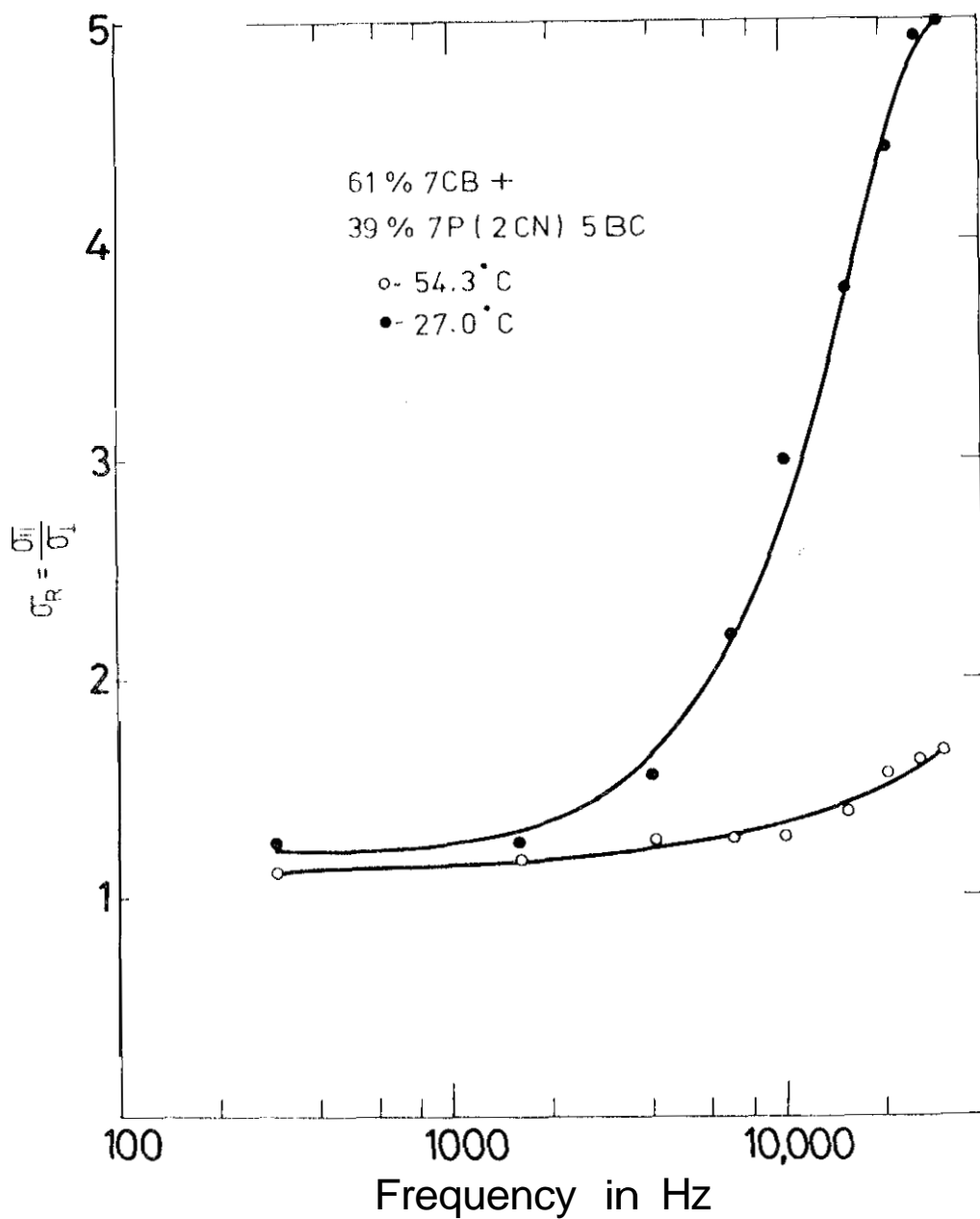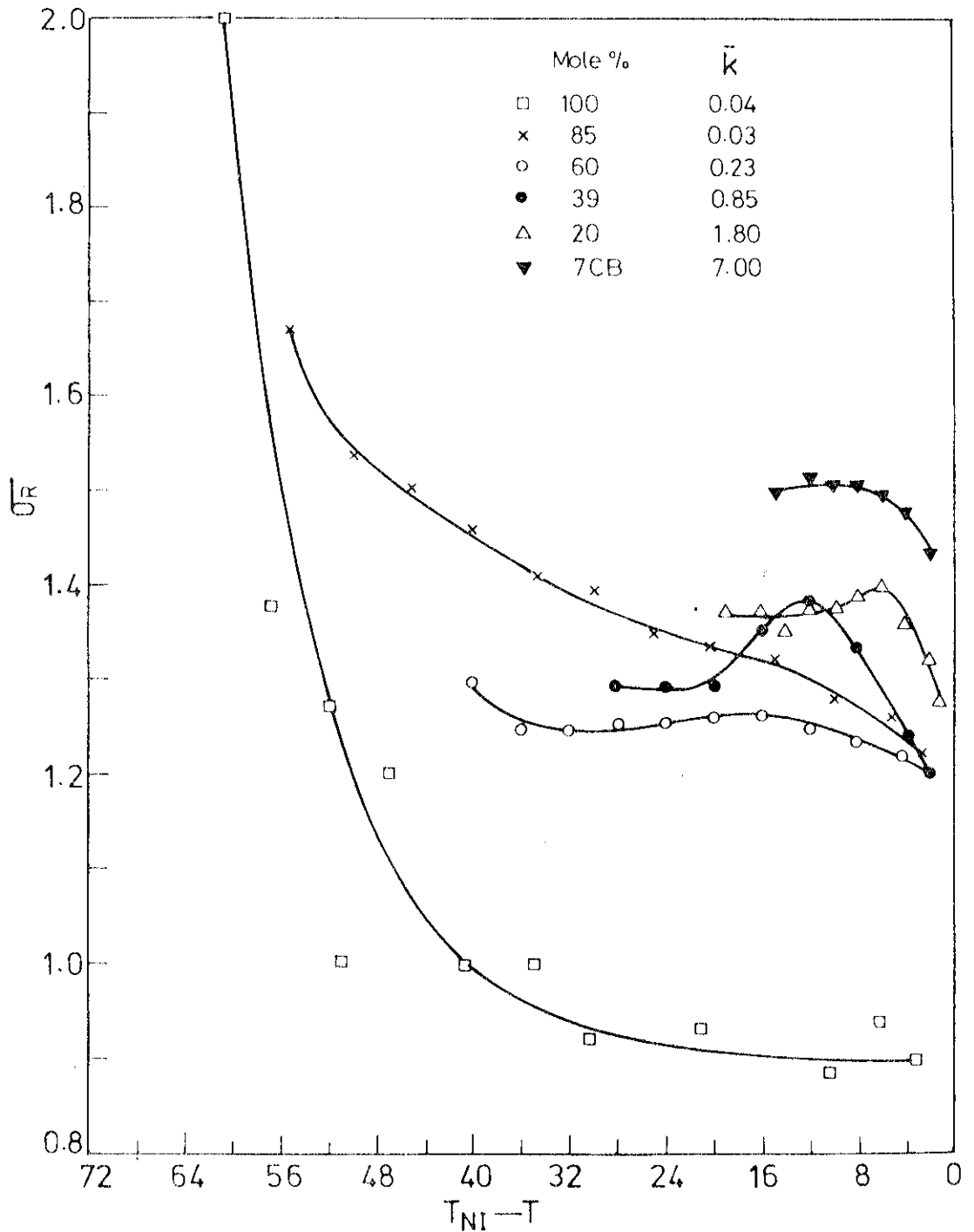
The temperature variations of the ratios of the

FIG.7.16: Frequency dependence of the ratio of the principal
conductivities (σ_R) of a mixture of 39 mole per cent
of 7P(2CN)5BC with 61 mole per cent of 7CB.

principal conductivities (σ_R) at 1592 Hz are shown
for all the systems studied in fig.7.17. As we men-
tioned earlier, σ_R is a sensitive function of the short
range order in the medium and also to some extent on
the nature and concentration of the ionic species,[12,13]
σ_R generally increasing with increasing conductivity of
the medium. Our samples contained some unknown conduc-
ting impurities. We have indicated the average specific
conductivity (at a common temperature = 42°C)
$\bar{K} = \frac{l'}{A} \bar{\sigma}$, where ($l'$/A) is the geometric parameter of the
measuring cell which is calculated using the measured
value of the capacitance of the empty cell. $\bar{\sigma}$ is the
measured value of the conductivity if the sample is in
the isotropic phase or $\bar{\sigma} = (a_{,,} + 2\sigma_{\perp})/3$ if the sample
is in the nematic phase. It is clear that our 7CB sample
has a much higher impurity content than 7P(2CN)5BC
sample, the mixtures having some intermediate values.
In view of these differences in $\bar{K}$ values of different
systems, we can only discuss the temperature variations
of σ_R values, rather than their absolute values. For a
nematic liquid crystal without any cybotactic structure,
σ_R depends only on the orientational order parameter S,
and should monotonically decrease with temperature,[12,13]
the rate of decrease increasing as T_{NI} is approached.
745 has a cybotactic structure of the smectic A type,

ZPIQ.7.17: Temperature variations of the ratio of conductivities (at 1592 Hz) in the nematic phase of the systems studied. The numbers appearing immediately after the symbols are the mole percentages of 7P(2CN)5BC and the next number is the mean specific conductivity $\bar{K} \times 10^9$ (ohm cm)$^{-1}$ at 42°C.

which is made up of bilayers[14] which arise due to
the antiparallel correlations between the highly
polar neighbouring molecules.[5] The cybotactic order
becomes somewhat stronger (i.e., its correlation
length increases) with decrease of temperature, though
7CB does not exhibit the smectic A phase. As such σ_R
of 7CB which is relatively high tends to level off and
even decrease slightly at lower temperatures (fig.7.17).
(we have already discussed in chapters V and VI that
smectic A layering increases $\sigma_\perp$ and lowers $\sigma_{\shortparallel}$ leading
to a decrease in the ratio $\sigma_R = \sigma_{\shortparallel}/\sigma_\perp$.) On the other
hand, as we have discussed earlier, 7P(2CN)5BC has a
very strong skew cybotactic order whose strength as
well as tilt angle decrease with increase of tempe-
rature. Both of these parameters determine σ_R, assuming
that ions can flow more easily in the plane of the
layers than in the perpendicular direction. At tempe-
ratures close to T_{NI}, the tilt angle is small, and
$\sigma_R < 4$ (fig.7.17), i.e., the compound has negative @oR-
ductivity anisotropy $\%@ ^{*} @_,- #\&$). As the temperature
is lowered, there is a very rapid increase of σ_R, the
rate of increase becoming larger at lower temperatures,
mainly because both the strength and tilt angle of the
cybotactic groups increase. This can be understood from
eqn.(7.7) for $\sigma_{\shortparallel}$ and $\sigma_\perp$. ($\sigma_n - \sigma_p$) must be negative,

since $(\sigma_{\parallel} - \sigma_{\perp})$ is negative even at the highest
temperature. As Ma temperature is lowered, δ increases
or $(3\cos^2 \delta - 1)/2$ decreases rapidly. This decrease
is stronger than the increase of both δ and the magni-
tude of σ_p/σ_n at lower temperatures, and $\sigma_{\parallel}/\delta_{\perp}$ increases
at lower temperatures. The lowering of the relaxation
frequency of $\varepsilon_{\parallel}$ might also contribute to this trend
in the σ_R values.[11]

Even for the mixture with 15% 7CB, as we discu-
ssed in connection with the dielectric properties, the
structure should retain the skew cybotactic nature, but
its strength is reduced (as evidenced from Xray studies)
(fig.7.12) so that σ_R values go up compared to those of
7P(2CN)5BC. The temperature variation of σ_R is similar
to that of the pure compound. With 40% 7CB (or 60%
7P(2CN)5BC) in the mixture, σ_R value shows a broad
maximum and then a minimum before it starts to increase
again close to T_{NI}, the strength of the cybotactic order
should be so small that the temperature variation of σ_R
is determined by that of the orientational order para-
meter. As the temperature is lowered, the cybotactic
order starts building up and σ_R decreases. With further
decrease of temperature, the increase in tilt angle
finally leads to an increasing trend of σ_R. With higher

concentrations of 7CB, the peak in σ_R is shifted towards T_{NI}, probably because the cybotactic groups are more and more smectic A like for these concentrations. In any case, the nematic range is also reduced and we see a general levelling off of σ_R at the lowest temperatures (fig. 7.17).

In conclusion, we have found that the temperature variation of the tilt angle of skewed cybotactic structure has an observable effect on both the dielectric constants and conductivities of the systems studied.

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