CHAPTER VII

DIELECTRIC INVESTIGATION OF LIQUID CRYSTALLINE SWALLOW-TAILED COMPOUNDS

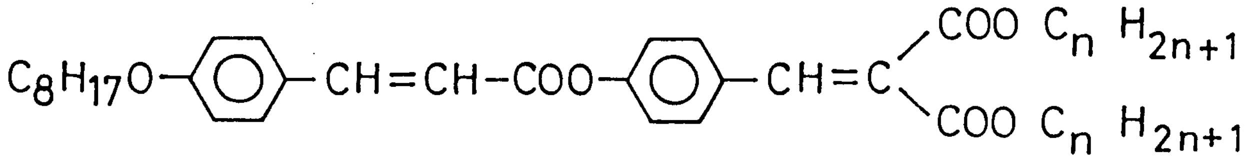
7.1 INTRODUCTION

Thermotropic liquid cr'ystals generally consist of molecules which are rod-like, i.e., which have an elongated shape. Initial studies on the effect of lateral branching on the stability of the liquid crystalline phase appeared to indicate that only systems with a relatively short lateral substituent showed liquid crystallinity, those with longer lateral substituents failed to show mesomorphism. However, recently Weissflog et al.[1] synthesised several homologous series of compounds which consist of two lateral chains at one end of the molecule. These materials, which are referred to as "swallow-tailed" compounds show not only nematic but also smectic A phases. Also, mixture of a swallow tailed compound and a rod-like terminalnon-polar compound showed reentrant nematic behaviour[2] although none of the constituent materials possessed a cyano or nitro end group. Preliminary Xray studies showed that the smectic A phases formed by these compounds are of the monolayer type and it was suggested that the molecules are perhaps arranged in an antiparallel configuration. It is known that dielectric studies offer direct evidence of near-neighbour antiparallel correlation~.~The more recent measurements carried out with greater precision[7-9] show even a pre-transition anomaly in the isotropic phase of strongly polar materials. We have undertaken measurements of the dielectric constants of two biaromatic swallow-tailed compounds, viz., the hexyl and nonyl homologs of di-n-alkyl 4-(4-n-octyloxy-cinnamoyloxy)-benzylidene-malonates or nOCBM for short. The results of these studies will be presented in the Section I of this chapter. In Section II, we present results of our studies on a 35 weight % eutectic mixture of 6OCBM/9OCBM, and ternary systems comprising of this eutectic mixture with 4-n-heptyloxy phenyl 4-n-decyloxybenzoate (7OPDOB). The latter studies were undertaken to investigate the effect of a rod-like molecules on the dipole-dipole correlations in swallow-tailed compounds.

SECTION I - STUDIES ON 6OCBM and 9OCBM

7.2 MATERIALS

The structural formulae of the materials studied is shown in Fig.7.1 while the transition temperatures are listed in Table 7.1. A plot of nematic-isotropic transition temperature (T_{NI}) versus the chain length is shown in. Fig.7.2a. It is seen that T_{NI} initially decreases with increasing n, passes through a minimum for n=6 and then increases as n is increased further. It has been reported[1]



di-n-alkyl 4-(4-n-octyloxy-cinnamoyloxy)-benzylidenemalonates

(nOCBM) n = 6 & 9

Figure 7.1

The structural formula and the abbreviation used for the compounds studied.

TABLE 7.1

The sequences and the temperatures of transitions

of the compounds studied

S. No.	Compound	Transition temperature (°C)
1	6OCBM	$I \xrightarrow{35.1} N$
2	9OCBM	$I \xrightarrow{41.2} N \xrightarrow{34} A$

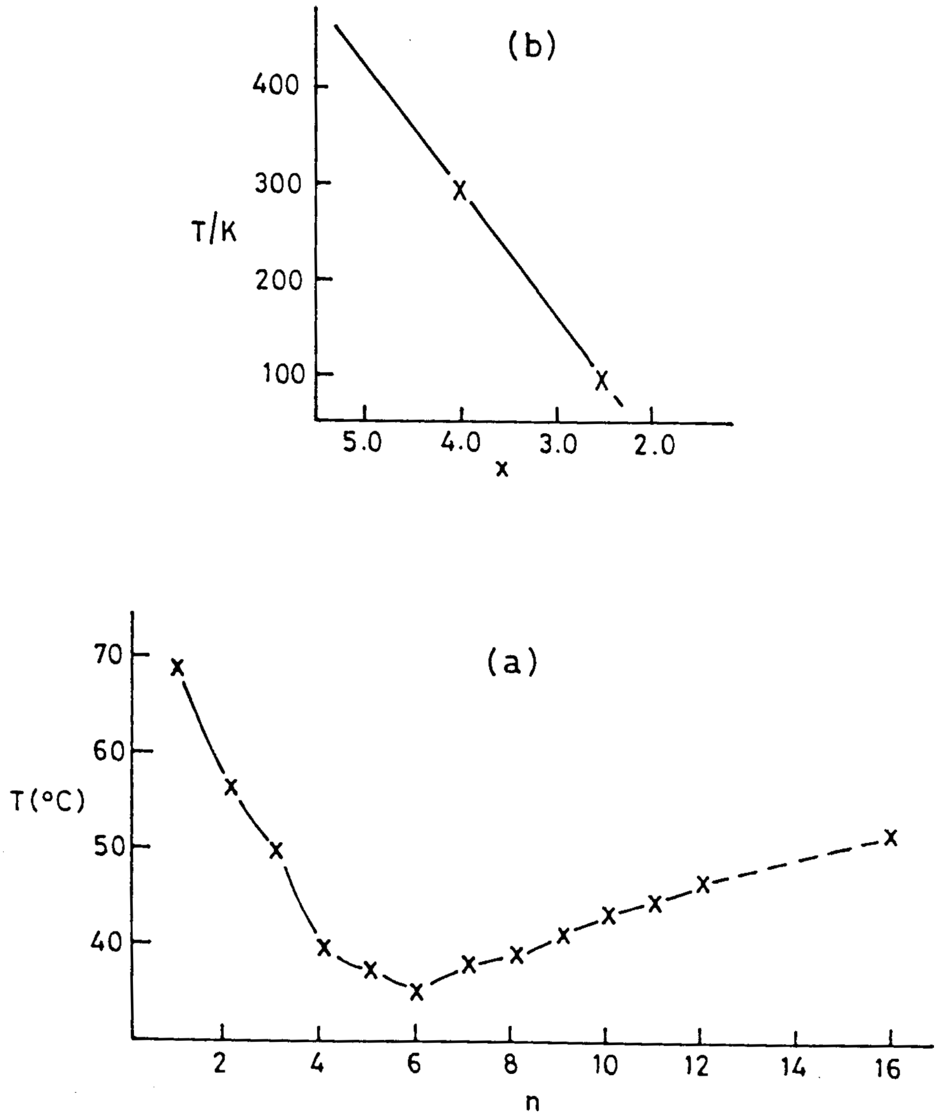


Figure 7.2

(a) Experimental nematic-isotropic transition temperatures of the homologous series di-n-alkyl-4-(4-n-octyloxy-cinnamoyloxy)-benzylidene-malonates (nOCBM). n represents the number of carbon atoms in the alkyl chain.

(b) Nematic-isotropic transition temperature vs. length to breadth ratio X = L/B according to theoretical results of Baron and Gelbart[11] (Ref. 1).

that this is the first instance wherein T_{NI} is found to initially decrease with increasing n, but for higher n values it reverses its trend and shows an increase. The following explanation for this unusual behaviour was given. In the lower members of the series the lengthening of the swallow tails diminishes the length to breadth ratio of the molecules and therefore, according to hard rod theories[10] or van der Waals approaches[11] of the nematic state, the transition temperatures decrease (Fig. 7.2b). For higher chain lengths the alkyl chains of the swallow tails can become more rigid and become nearly parallel to one another, thereby the length to breadth ratio can increrase for higher n. This will in turn lead to an increase in transition temperatures.

7.3 EXPERIMENTAL

The details of the experimental set up used for the Xray and dielectric studies have already been described in Chapters 111 and II respectively and will not be repeated here.

7.4 **RESULTS** AND **DISCUSSIONS**

7.4.1. Xray

As mentioned earlier we have studied two compounds, viz., 6OCBM and 9OCBM. 9OCBM exhibits a monotropic smectic

A phase. However owing to its metastability, it was possible to measure the layer spacing (d) only at one temperature in this phase. This data gave a d/ℓ value of –0.9 showing thereby that the A phase is of the monolayer type.

7.4.2 Dielectric

The measurements of static dielectric constants $\varepsilon_\parallel$ and $\varepsilon_\perp$ in the nematic phase and the permittivity in the isotropic phase (ε_{is}) have been carried out for the compounds. (No measurements were possible in A phase). The temperature variation of $\varepsilon_\parallel$, $\varepsilon_\perp$, and the isotropic value ε_{is} for 6OCBM and 9OCBM are shown in Figures 7.3 and 7.4 respectively. The variations of the mean dielectric constant $\bar{\varepsilon}$ and ε_{is} in the vicinity of T_{NI} are shown on an enlarged scale in Fig.7.5. For both the compounds essentially the same behaviour is seen. It is seen that $\bar{\varepsilon}$ is, throughout the nematic phase, lower than the extrapolated ε_{is} value, this difference increasing with decreasing temperature. At T_{NI}, $\bar{\varepsilon}$ shows a jump. In the isotropic phase, ε_{is} initially increases with decrease of temperature in the usual way, but, on approaching T_{NI}, ε_{is} shows an anomalous decrease. These results, which are similar to those seen in terminally cyano compounds,[7,8] demonstrate clearly the existence of antiparallel correlations in the nematic and isotropic phases of both the swallow-tailed compounds. The

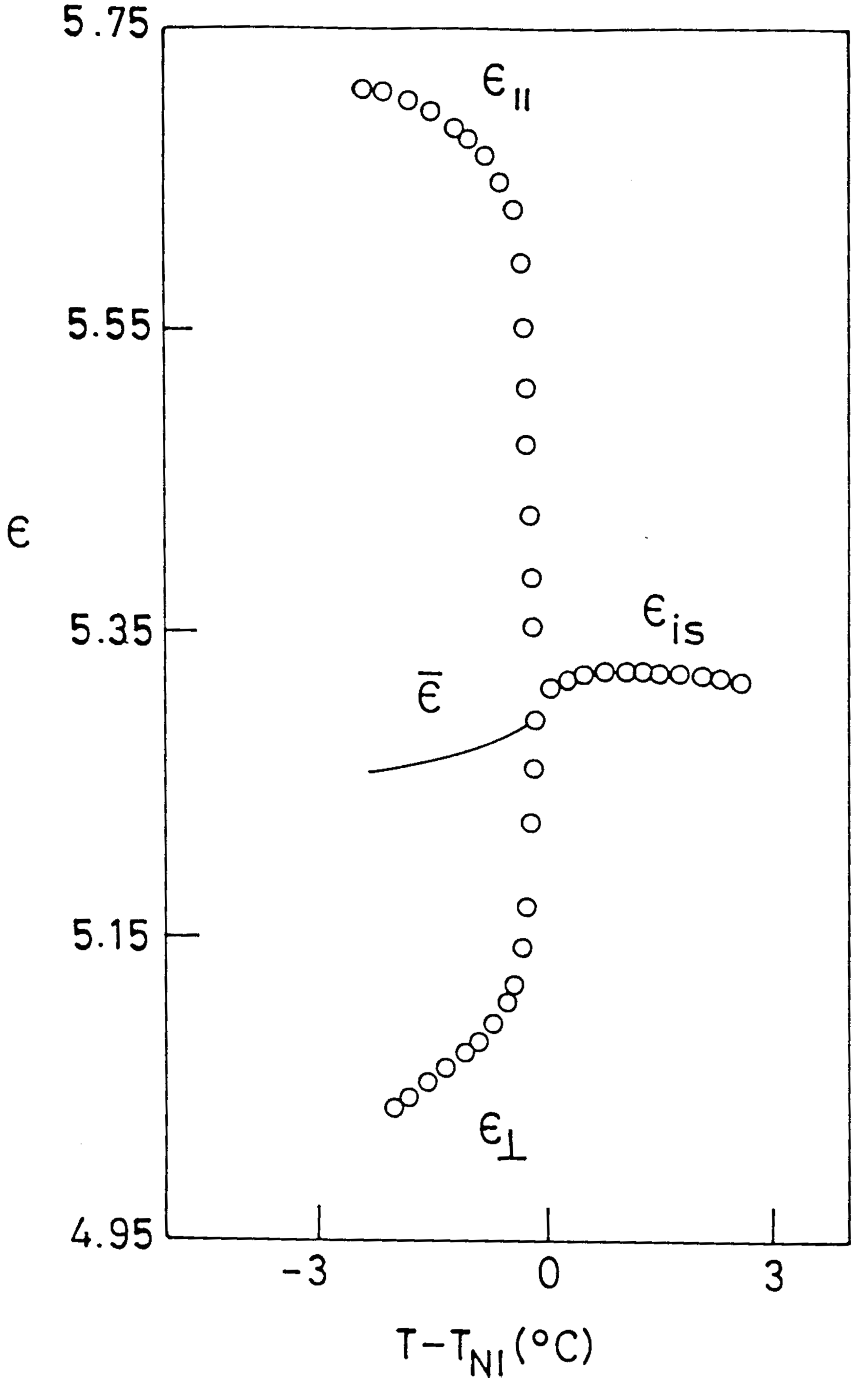


Figure 7.3

The temperature variation of the dielectric constants $\epsilon_{\parallel}$, $\epsilon_{\perp}$, ϵ_{is} and of the mean dielectric constant $\bar{\epsilon}$ of 6OCBM.

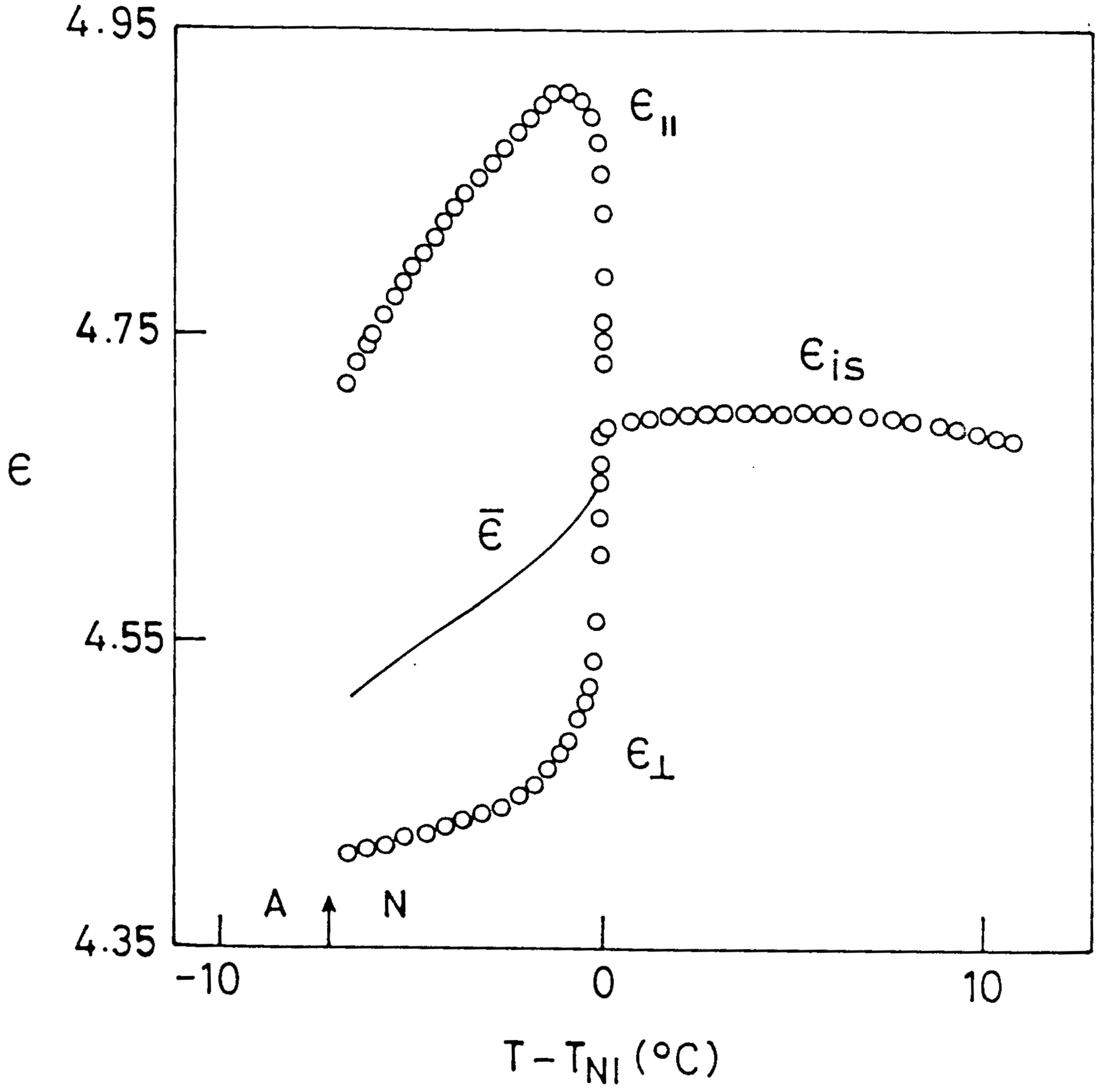


Figure 7.4

The temperature variation of the dielectric constants of 9OCBM.

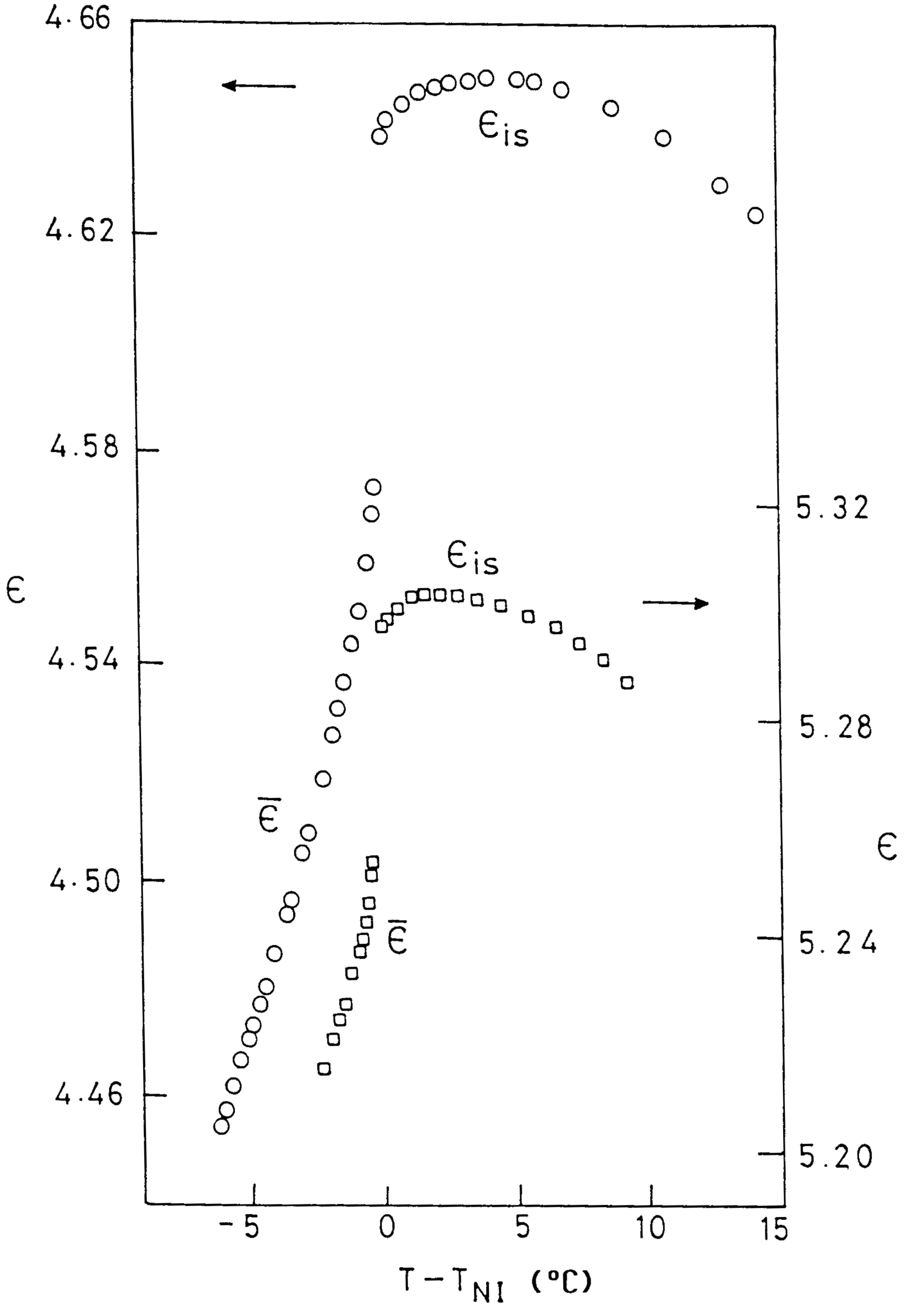


Figure 7.5

Variation of the mean dielectric constant ($\bar{\varepsilon}$) as well as the permittivity in the isotropic phase (ε_{is}) in the vicinity of the nematic-isotropic transition in 6OCBM (□) and 9OCBM (○).

diple-dipole interactions are essentially due to the geometrical factors related with the shape of the molecule. Following Bradshaw and Raynes,[7] the extent of antiparallel correlation can be expressed by the quantity, $\Delta\varepsilon_{is}$, which is given by

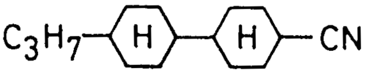
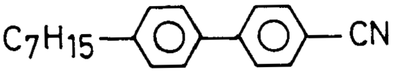
$$[\varepsilon_{is}]_{max} - [\varepsilon_{is}]_{T_{NI}}$$

where $[\varepsilon_{is}]_{max}$ is the maximum value of ε_{is} and $[\varepsilon_{is}]_{T_{NI}}$ is ε_{is} value at the nematic-isotropic transition temperature. This quantity evaluated for 6OCBM and 9OCBM are shown in Table 7.2 along with the values for several strongly polar mesogens[7] for the sake of comparison. It is interesting to see that $\Delta\varepsilon_{is}$ for the swallow-tailed compound is about the same as that seen in a bicyclohexane compound with a cyano end group while it is an order of magnitude less than that seen in a biaromatic compound with a terminally cyano group. Thus it is clear that though less pronounced than in cyanobiphenyl compounds, pronounced antiparallel dipole-dipole correlations exist in the isotropic phase of both the swallow-tailed compounds.

We shall now discuss the data in the nematic phase. It is seen that $\varepsilon_{\parallel}$ shows a steep decrease with decrease of temperature in the nematic phase while no such decrease is seen for 6OCBM (Fig.7.3). This is perhaps attributable due to the fact

TABLE 72

Comparison of the extent of antiparallel correlation in 6OCBM and 9OCBM with other materials

S.No.	Compound	$\Delta\epsilon_{is} = [\epsilon_{is}]_{max} - [\epsilon_{is}]_{T_{NI}}$ (in percentage)
1	6OCBM	0.1
2	9OCBM	0.2
3	 trans-4-n-propyl-4'-cyanobicyclohexane (CCH_3)	0.24
	 4'-n-heptyl-4-cyanobiphenyl (7CB)	1.0

that the former compound exhibits the smectic A phase at lower temperatures while the latter does not. Consequently as the temperature is decreased in the nematic phase of 9OCBM there would be an increase in the cybotactic smectic-like ordering leading to an increase in antiparallel correlations which in turn could lead to a decrease of $\varepsilon_{\parallel}$.

Thus our dielectric studies show clearly the existence of pronounced antiparallel correlations in the nematic as well as isotropic phases of the swallow-tailed compounds. It is interesting that such correlations should be present even when the A phase formed by these molecules is of the monolayer type.

SECTION II

7.5 DIELECTRIC STUDIES ON SWALLAW-TAILED LIQUID CRYSTALLINE MIXTURES

In the previous section it was shown that the swallow-tailed liquid crystalline compounds which have a very strong geometrical anisotropy of the shape of the molecule, exhibit pronounced antiparallel correlations. Recently Kresse et al.[12] demonstrated that these dipole-dipole correlations will be destroyed by the addition of compounds with lateral chain substituents. They carried out the measurements of the static dielectric constants on (i) a swallow-tailed compound, viz., di-n-decyl-4-[4-(4 n-octyloxy- benzoyloxy)-benzoyloxy] benzylidenemalonate (Compound A), (ii) a compound with lateral chain substituent, viz., 1,4-bis-4-n-octyloxy-benzoyloxy-2-heptylbenzene (compound B) and (iii) their mixture with a composition 40% A/B. It was found the antiparallel correlations present in the swallow-tailed compound were suppressed by the addition of a compound with the lateral chain substituent.

It is therefore of interest to investigate as to how the dipole-dipole interactions are influenced by adding a compound whose molecules have the usual rod-like geometry. For this purpose, we have studied the dielectric behaviour of (1) an eutectic mixture (hereafter referred to as Mixture I) of two swallow-tailed compounds, viz., (35 weight % of 6OCBM in 9OCBM), (2) a three component system (referred to as Mixture II) containing 80% of mixture I and 20% 4-n-heptyloxyphenyl-4-n-decyloxybenzoate (7OPDOB), a molecule with rod-like geometry and (3) a three component system (Mixture III) containing 70% of mixture I and 30% 7OPDOB. (For molecular formulae of the materials see Fig. 7.1 and Fig. 3.2 of Chapters VII and III.) The transition temperatures of the mixtures studied are given in the Table 7.3.

TABLE 7.3

The sequences and temperatures of transitions of the swallow-tailed liquid crystalline mixtures I, II and III

S.No.	Mixture	Transition temperatures (in °C)
I	I	$\mathrm{I} \overset{39.4}{\text{———}} \mathrm{N} \overset{29.7}{\text{———}} \mathrm{A}$ (metastable)
2	II	$\mathrm{I} \overset{55.2}{\text{——}} \mathrm{N} \overset{45.2}{\text{——}} \mathrm{A}$
3	III	$\mathrm{I} \overset{55.6}{\text{——}} \mathrm{N} \overset{49.6}{\text{——}} \mathrm{A}$

7.5.1 Eutectic mixture (Mixture I)

35 weight % 6OCBM/9OCBM

The temperature variation of static dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and of mean dielectric constant $\bar{\varepsilon}$ of the eutectic mixture which has an extended nematic range is shown in Fig. 7.6a. The crystallisation prevented us from taking measurements in smectic A phase. A strong decrease in $\varepsilon_{\parallel}$ can be seen indicating. dipole-dipole correlations only along the uniaxial direction. A step in $\bar{\varepsilon}$ at the isotropic-nematic transition indicates the strong dipole-dipole correlation in the nematic phase. $\bar{\varepsilon}$ value continues to decrease with decrease in temperature, indicating an increase of these correlations at lower temperature. $\varepsilon_{\perp}$ on the other hand shows the usual behaviour which is expected from the Maier-Meier theory.[13]

7.5.2 A three component mixture (Mixture II) containing 80% eutectic mixture and 20% 7OPDOB

The temperature variation of the dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$ and also of $\bar{\varepsilon}$ is shown in the Fig. 7.6b. It is clear that even here a strong decrease of $\varepsilon_{\parallel}$ is observed with decreasing temperature. Also the addition of 7OPDOB stabilizes the smectic A phase and we could take measurements in the A phase. In A phase,

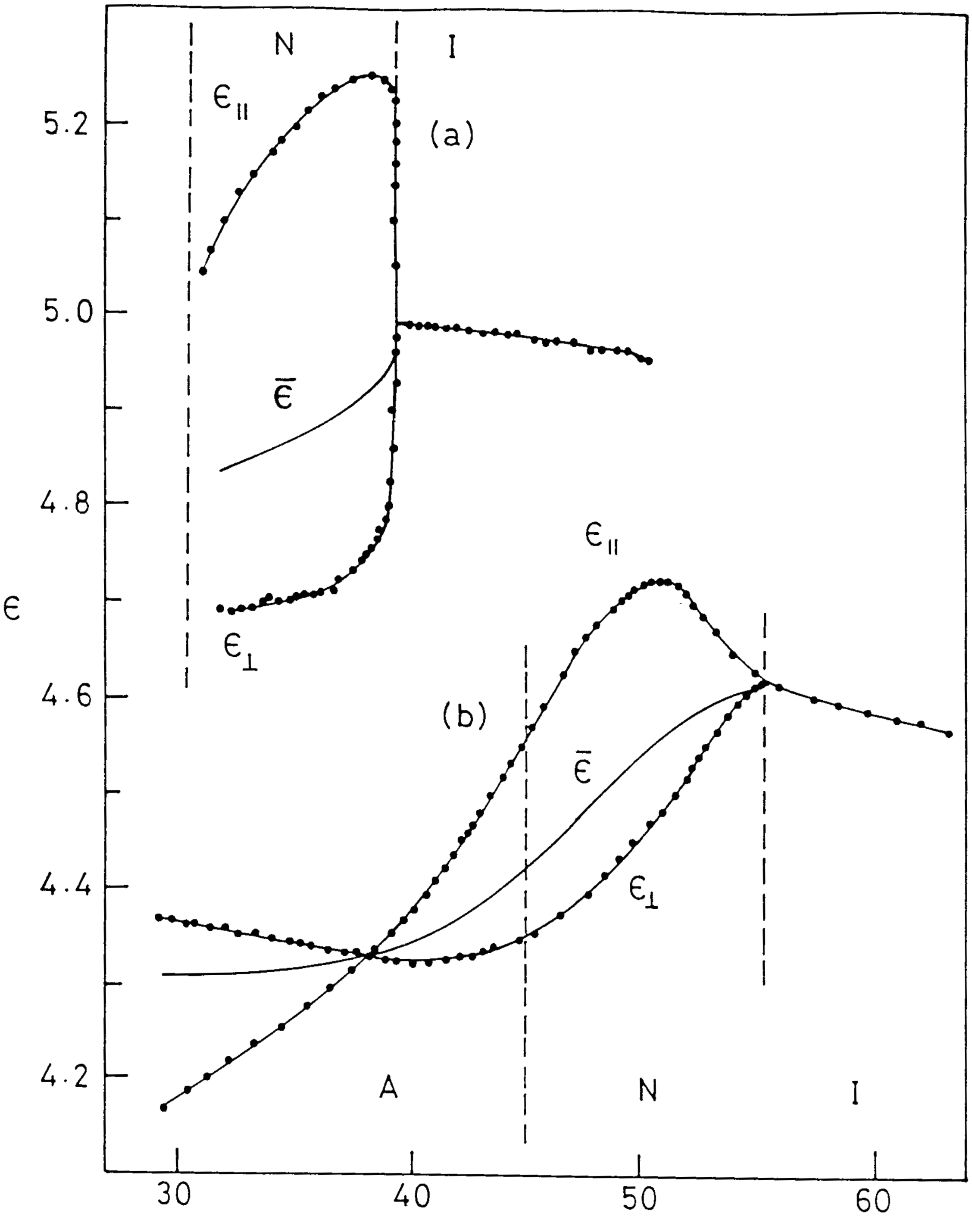


Figure 7.6

The temperature variation of the dielectric constants $\varepsilon_{\parallel}$, $\varepsilon_{\perp}$, ε_{is} and of $\bar{\varepsilon}$ for the (a) Mixture I, and (b) Mixture II.

we could observe the cross over of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ around 38°C. This results in a reversal of the dielectric anisotropy $\Delta\varepsilon$ (see Fig.7.7).

The important feature of these results is that the decrease in $\varepsilon_{\parallel}$ with decrease of temperature is really of the same magnitude in both mixtures I and II (−0.21 for the range of 7°C).

7.5.3. A three component mixture (Mixture III) containing 70% eutectic mixture and 30% 7OPDOB

The temperature variation of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for Mixture III is shown in the Fig.7.8. The behaviour of these constants is almost similar to those of the Mixture II. The temperature variation of $\Delta\varepsilon$ is shown in Fig. 7.9. Even in this mixture, the decrease in $\varepsilon_{\parallel}$ with decrease of temperature is equally pronounced as in mixtures I and II. These results therefore show that the antiparallel correlations in the swallow-tailed compounds is very strong and is not effected easily by the addition of a compound with rod-like molecules.

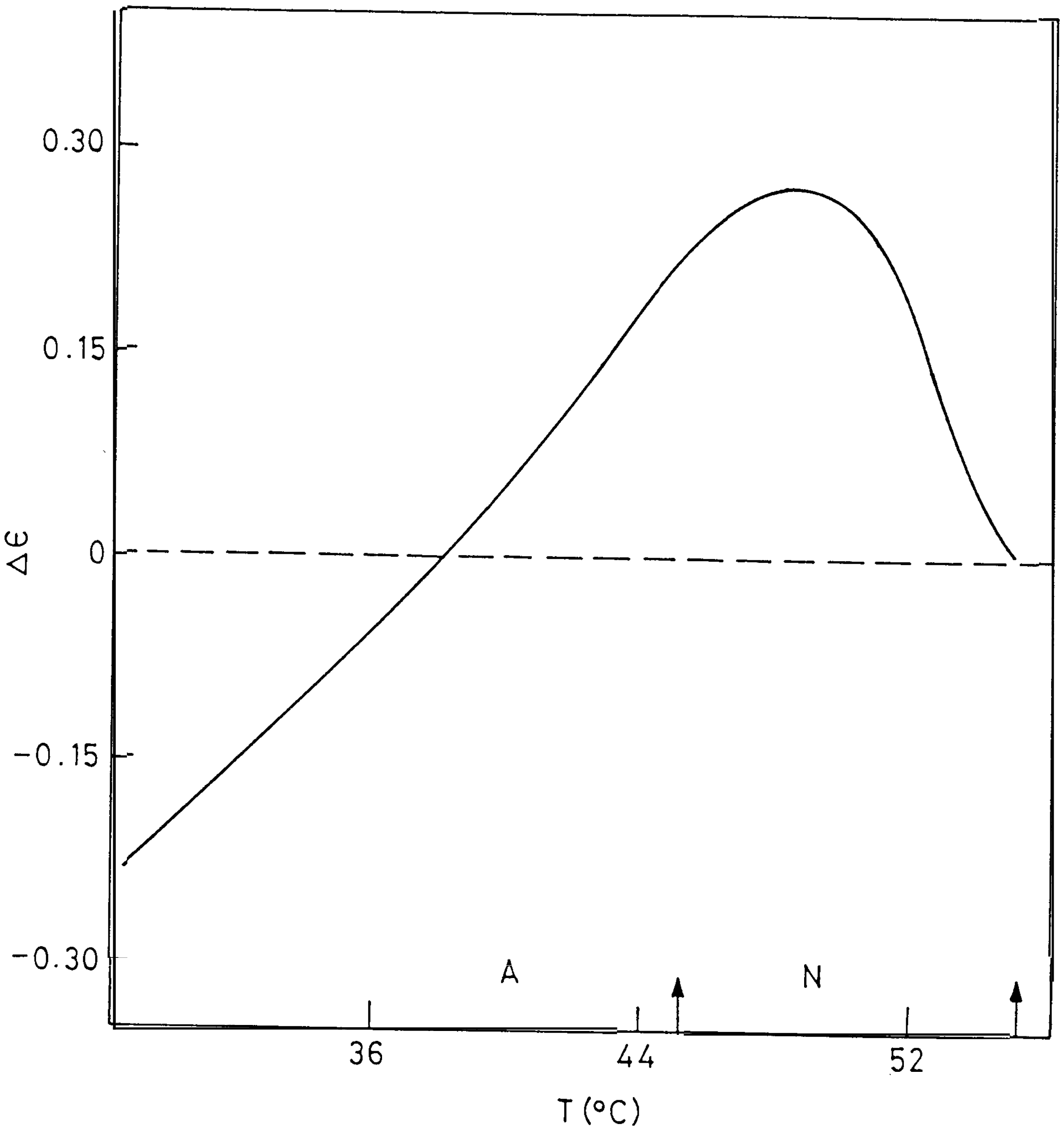


Figure 7.7

The temperature variation of the dielectric anisotropy Δε in the nematic and smectic A phases of the mixture II.

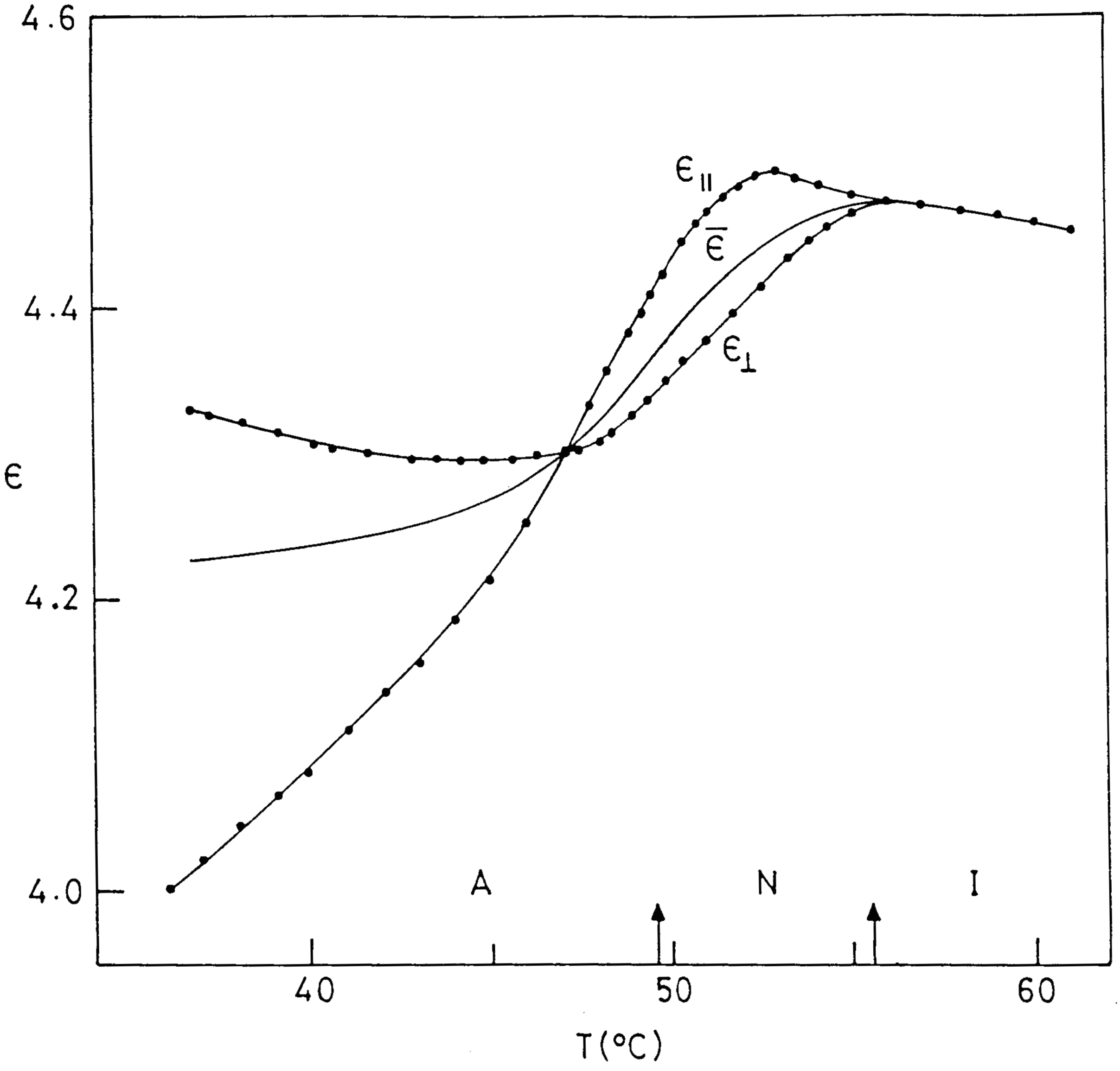


Figure 7.8

The temperature variation of the dielectric constants $\varepsilon_{\parallel}$ $\varepsilon_{\perp}$, E_{is} and of $\bar{\varepsilon}$ for the mixture III.

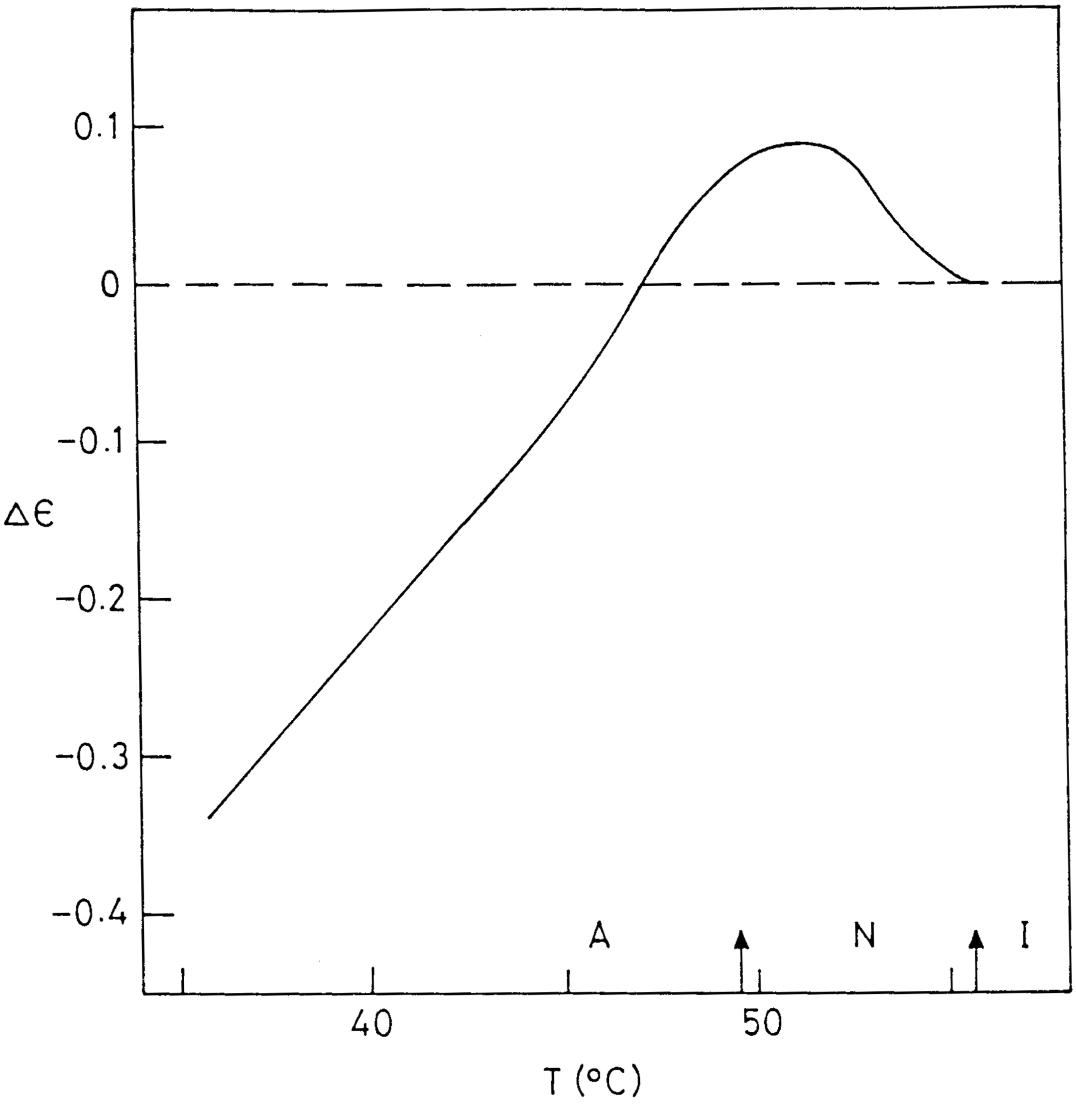


Figure 7.9

The temperature variation of Δε in the N and A phases of the mixture III.

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