CHAPTER V

ELECTRICAL CONDUCTIVITY MEASUREMENTS ON STRUCTURALLY RELATED SMECTOGENIC COMPOUNDS

5.9 Introduction

Svedberg,[1] as early as in 1914, noticed that for a nematic the electrical conductivity (due to ionic impurities) measured along the director ($\sigma_{\parallel}$) is greater than that measured normal to it ($\sigma_{\perp}$). For a nematic liquid crystal without any cybotactic structure, anisotropy ratio σ_R (= $\sigma_{\parallel}/\sigma_{\perp}$) is greater than one and is known to depend only on the orientational order parameter S, decreasing monotonically with temperature,[2,3] the rate of decrease increasing as T_{NI} is approached. But in a compound exhibiting both A and N phases, generally, the conductivity anisotropy (= $\sigma_{\parallel} - \sigma_{\perp}$) changes sign near the nematic-smectic A transition point, becoming negative at lower temperatures. On the basis of electric field studies on ethyl-p-(p'-methoxybenzylidene)aminocinnamate, Carr[4] originally suggested that the anisotropy ratio σ_R is less than one in the A phase. The measurements on the influence of smectic order were first made by Rondelez[5] who found a decrease of the ratio σ_R, with decreasing temperature in some nematic compounds exhibiting smectic like short range order. Similar observations were made by Mircea-Roussel and Rondeles[6] and Heppke and Schneider.[7] Mircea-Roussel et al[8] made measurements in the A phase as well. σ_R is also known to depend upon the nature and concentration of ionic species,[2,3] σ_R generally increasing with increasing conductivity or the medium.

Further, the principal conductivities are known to be frequency dependent. This arises from the low frequency dispersion of orientation polarization. Schadt and Von Planta[9] obtained the following expression for the frequency dependence of the conductivity of a dielectric

$$\sigma(\omega) = \sigma(dc) + \frac{\varepsilon_0(\varepsilon - 1)}{1 + \omega^2 \tau^2} \tau \omega^2 \qquad (5.1)$$

where τ is the relaxation time of the orientation polarization. For $\omega\tau \ll 1$, eqn.(5.1) takes the form

$$\sigma(\omega) = \sigma(dc) + \varepsilon_0(\varepsilon - 1) \tau \omega^2 \qquad (5.2)$$

which shows that $\sigma(\omega)$ is a quadratic function of frequency.

Conductivity studies carried out by Mircea-Roussel et al.[8] in the smectic and nematic phases of several compounds have shown that the behaviour of transport properties in bilayer structures is different from that in monolayer smectics. The compounds studied by them are the following: some compounds belonging to the alkoxy benzylidene alkyl aniline series (nO.m series), 4,4'-diheptylazoxybenzene (HAB), N-p-cyanobenzylidene-p-n-octyloxyaniline (CBOOA), 4'-n-octyl-4-cyanobiphenyl (8CB) and 4'-n-octyloxy-4-cyanobiphenyl (8 OCB). Though all these compounds show pretransitional effects in the N phase near T_{AN}, they fall into two distinct groups as regards their electrical conductivity in the A phase. In the first group consisting of the compounds of the nO.m series and HAB, $\sigma_{\parallel}$ decreases continuously as the temperature is decreased close to T_{AN} both in the A and N phases and then levels off at lower temperatures in the A phase. On the other hand, as the temperature is lowered, $\sigma_{\perp}$ decreases in the N phase and then starts to increase near T_{AN}. The increase of $\sigma_{\perp}$ is so large that it becomes at least five times greater than $\sigma_{\parallel}$. Thus, these compounds have a very low value of σ_R in the A phase.

In the second group of compounds consisting of CBOOA, 8CB and 8 OCB, both $\sigma_{\parallel}$ and $\sigma_{\perp}$ decrease with decrease of temperature. The ratio σ_R initially rises as the sample is cooled from T_{NI} and then decreases slowly with further lowering of temperature. In 8 OCB and 8CB, σ_R reaches the value unity in the A phase indicating that there is no preferential direction for the flow of charges. In CBOOA, σ_R becomes just less than unity (0.85) in the A phase. Hence the strong anisotropy observed in the first group of compounds is not seen here.

It is interesting to note that all the compounds belonging to the second group are strongly polar and possess partially bilayer structures in the smectic A[10,11] while the compounds belonging to the first group have monolayer smectics. Therefore, this difference in the behaviour of the transport properties is associated with the different structures of the smectic A layers.

As we saw earlier in chapter III, strongly polar cyano and nitro compounds studied by us have large bilayer spacings which are extremely sensitive to temperature. The spacings increase enormously as the temperature is lowered in the A phase. This has a strong influence on the dielectric behaviour also as we have seen in chapter IV. To study the influence of such structural changes on the transport properties, we have measured the temperature variations of the principal electrical conductivities of the compounds. The results are presented in this chapter.

5.2 Experimental

The compounds studied are 12 PMCBB, 10 PMeOOBB, 11 PMeOOBB, 9 PMNBB, 10 PMNBB, 12 PMNBB, 11 CPMeOBB, 12 CPMeOBB and 11 PMeOBrBB. Structural formulae, names of the compounds and the heats of transitions are given in fig.3.1 and table 3.1 of chapter III.

The conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ were determined at 1592 Hz using a Wayne Kerr (B642) autobalance bridge using the experimental set up described in the previous chapter. $\sigma_{\parallel}$ and $\sigma_{\perp}$ were also measured for a few compounds at 300 Hz by using the Wayne Kerr bridge in conjunction with an external AC source (Systronics Sf oscillator) and a PAR 186 lock-in-amplifier as the detector. As mentioned in chapter IV, the sample taken between two tin oxide coated glass plates was aligned by a magnetic field of strength ~ 14 KGauss. A good alignment in the A phase was obtained by a slow cooling of the sample from the N phase in the presence of the magnetic field.

5.3 Results and discussion

The principal electrical conductivities of 12 PMCBB measured at 1592 Hz are shown in fig.5.1. The conductivity anisotropy which is positive in the N phase changes sign and becomes negative in the A phase, as in other smectogenic compounds. As the temperature is lowered in the A phase, the ratio σ_R ($= \sigma_\parallel/\sigma_\perp$) decreases. Further, both $\sigma_\parallel$ and $\sigma_\perp$ decreasing initially. However, at $T_{NI} - T \simeq 80°C$, $\sigma_\parallel$ attains a broad minimum, and starts increasing slightly as the temperature is further lowered. This is caused by the effect of the relaxation of $\epsilon_\parallel$ on $\sigma_\parallel$. With decreasing temperature, the relaxation time corresponding to $\epsilon_\parallel$ dispersion increases rapidly and, as can be seen from the eqn.(5.2), it enhances the measured value of $\sigma_\parallel$. The relaxation of $\epsilon_\parallel$ thus causes $\Delta\sigma$ at 1592 Hz to reverse sign again, becoming positive at very low temperatures. The variation of σ_R is also shown in the figure. If we reduce the frequency of measurement to 300 Hz, however, $\sigma_\parallel$ monotonically decreases with decreasing temperature (fig. 5.2) and there is no reversal of the sign of $\Delta\sigma$ which remains negative.

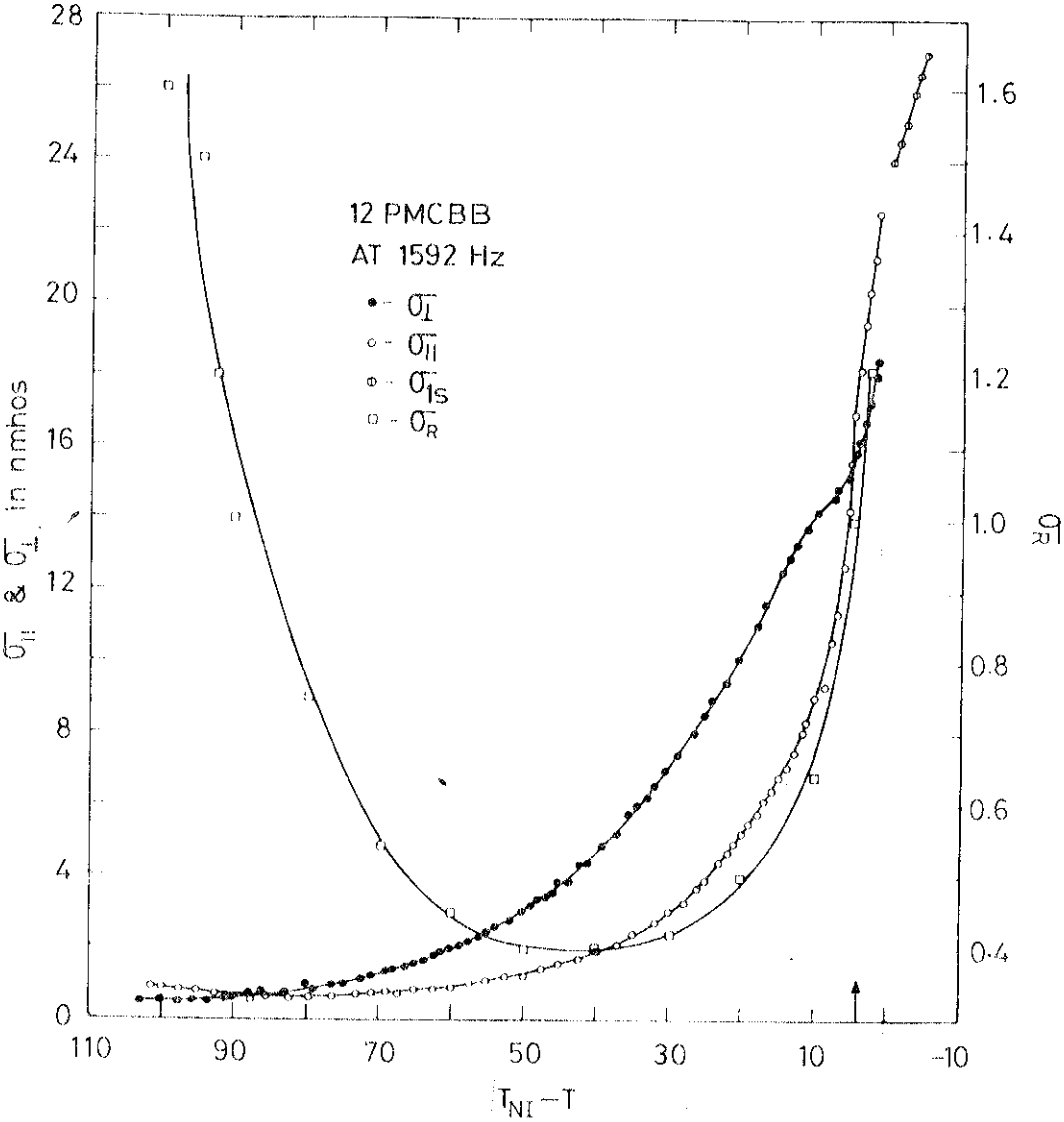


FIGURE 5.1

Temperature variations of $\sigma_\parallel$, $\sigma_\perp$, σ_{Is} and σ_R of 12 PMCBB at 1592 Hz. (T_{NI} - T) is the relative temperature, T_{NI} being the nematic-isotropic transition temperature. The arrow mark on the temperature axis indicates the smectic A - nematic transition point (T_{AN}).

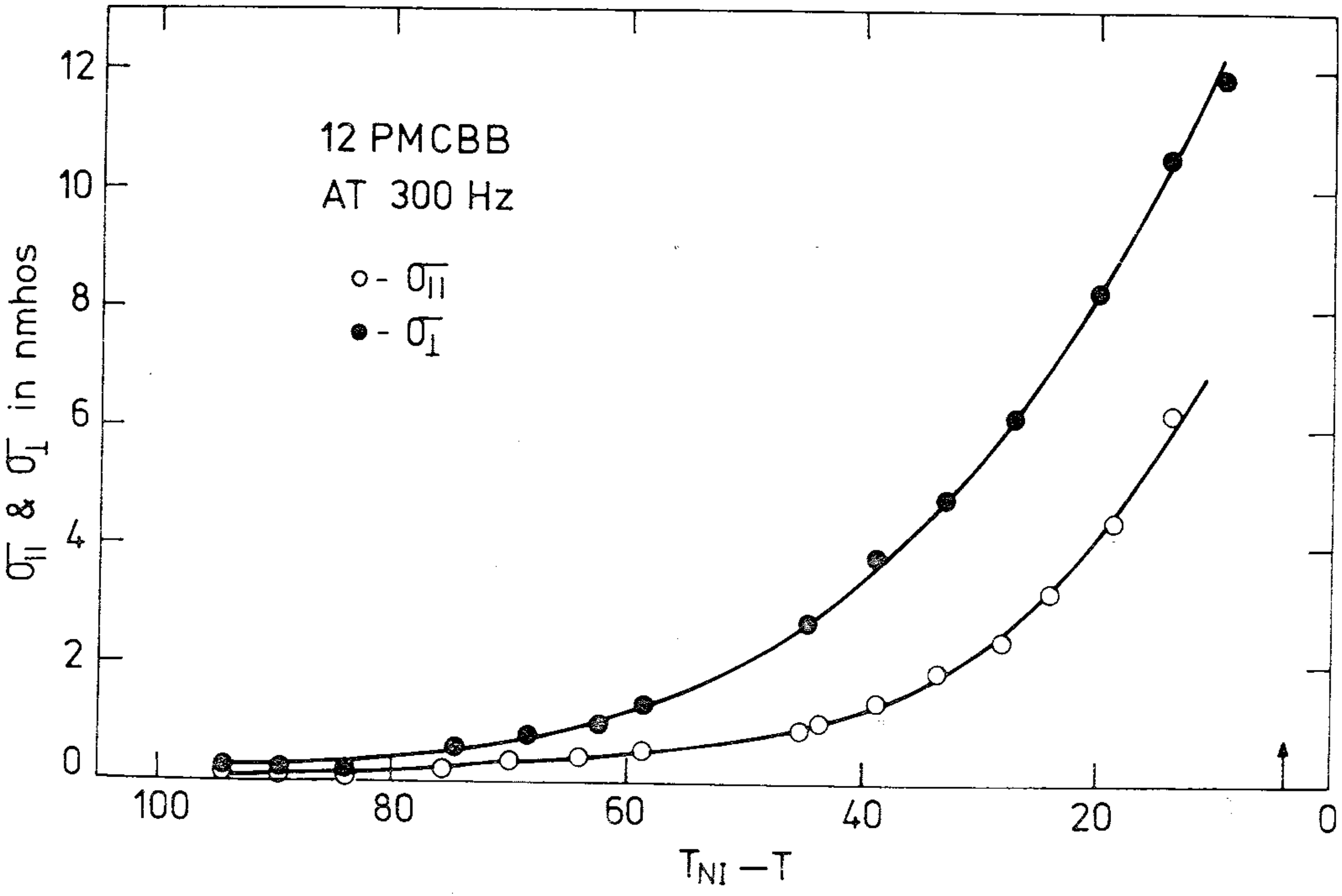


FIG.5.2: Temperature variations of the principal conductivities of 12 PMCBB measured at 300 Hz. The arrow mark indicates T_{AN}

The temperature variations of the principal conductivities of 10 PMeOCBB and 11 PMeOCBB are shown in figs.5.3 and 5.4 respectively. In 10 PMeOCBB, σ_R does not become < 1, but tends to increase at low temperatures because of the relaxation effect of $\varepsilon_{\parallel}$ as discussed above. The anisotropy $\Delta\sigma$ does not change sign in the A phase as it is monotropic occurring at $\sim 40°C$ below T_{NI} and at such low temperatures the relaxation effect can be expected to dominate. In the case of 11 PMeOCBB, the anisotropy changes sign at temperatures very close to T_{AN}, becoming negative in the A phase. As the temperature is lowered, σ_R decreases first, reaches a value of ~ 0.9 and then increases due to $\varepsilon_{\parallel}$ relaxation leading to positive anisotropy at very low temperatures.

The trends in the conductivities of 9PMNBB (fig. 5.5) are similar to those of 10 PMeOCBB. In the case of 10 PMNBB, as the temperature is lowered, the conductivity ratio at 1592 Hz becomes less than unity $\sim 15°$ above T_{AN}, but does not go to very low values. It starts increasing as the temperature is lowered below $\sim T_{AN} - 15°$ (fig.5.6). In 12 PMNBB (fig.5.7), the conductivity ratio at 1592 Hz takes a value considerably less than unity before it starts increasing as the sample

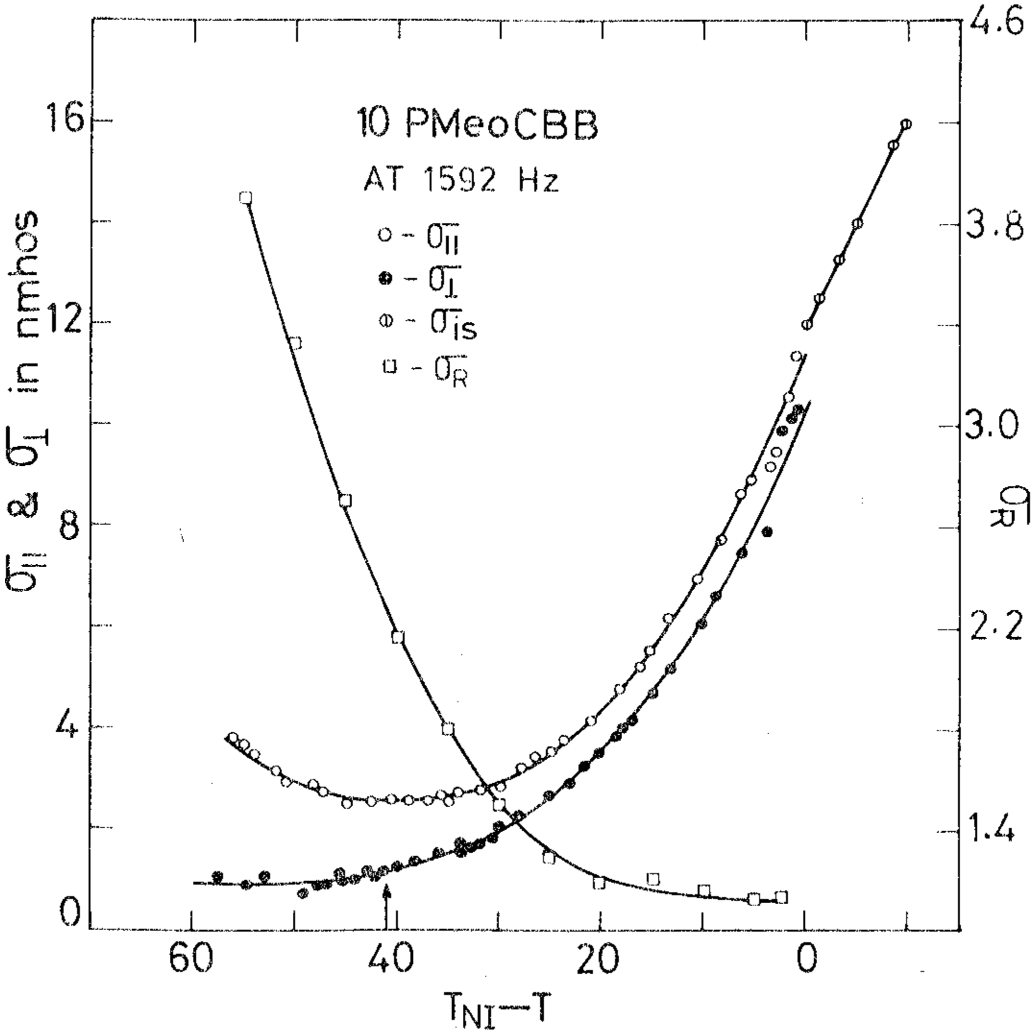


FIGURE 53

Temperature variation of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{is} and σ_R 04 10 PMeOCBB at 1592 Hz. The arrow mark indicates T_{AN}.

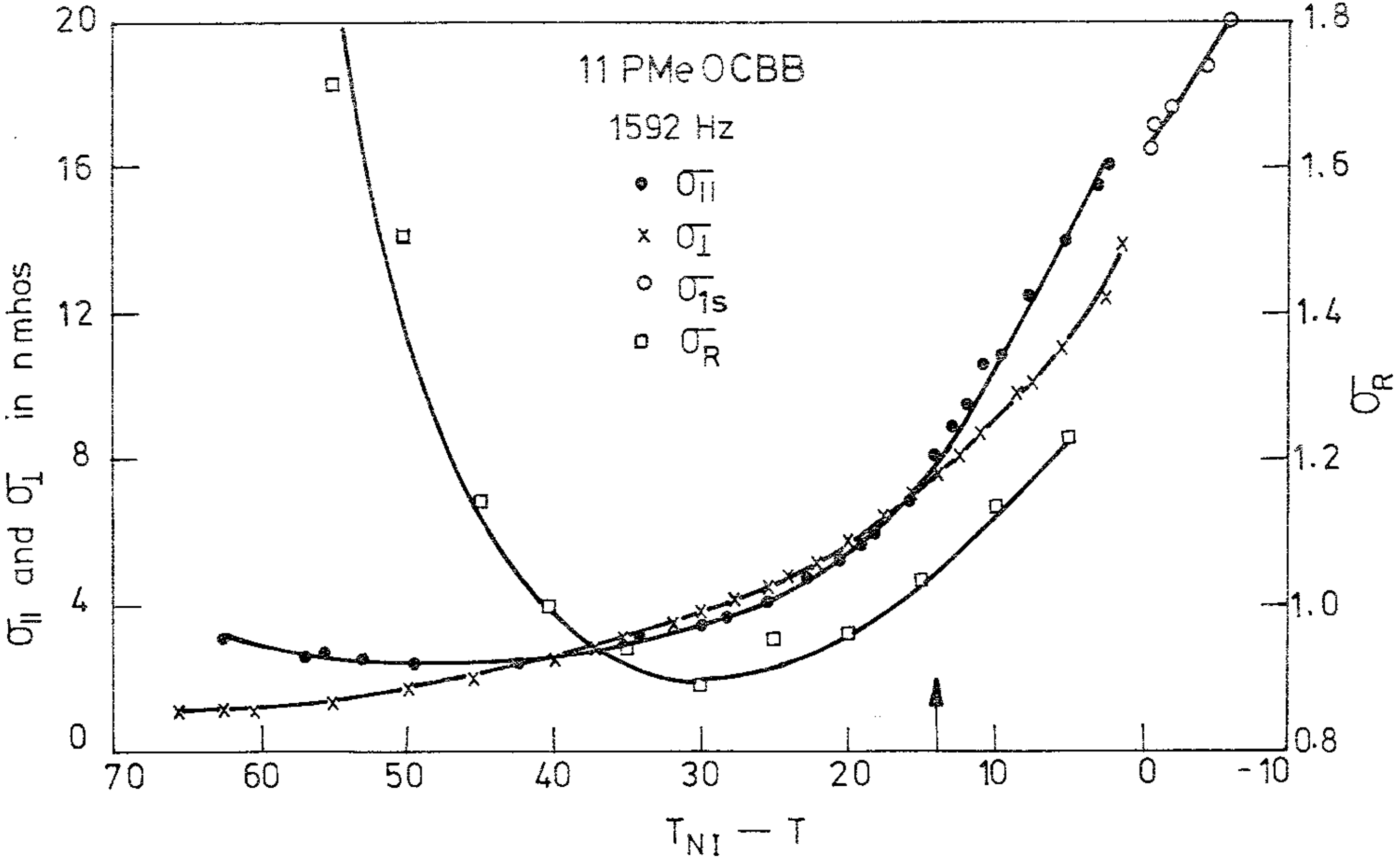


FIGURE 5.4: Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{is} and σ_R of 11 PMeOCBB at 1592 Hz. The arrow mark indicates T_{AN}.

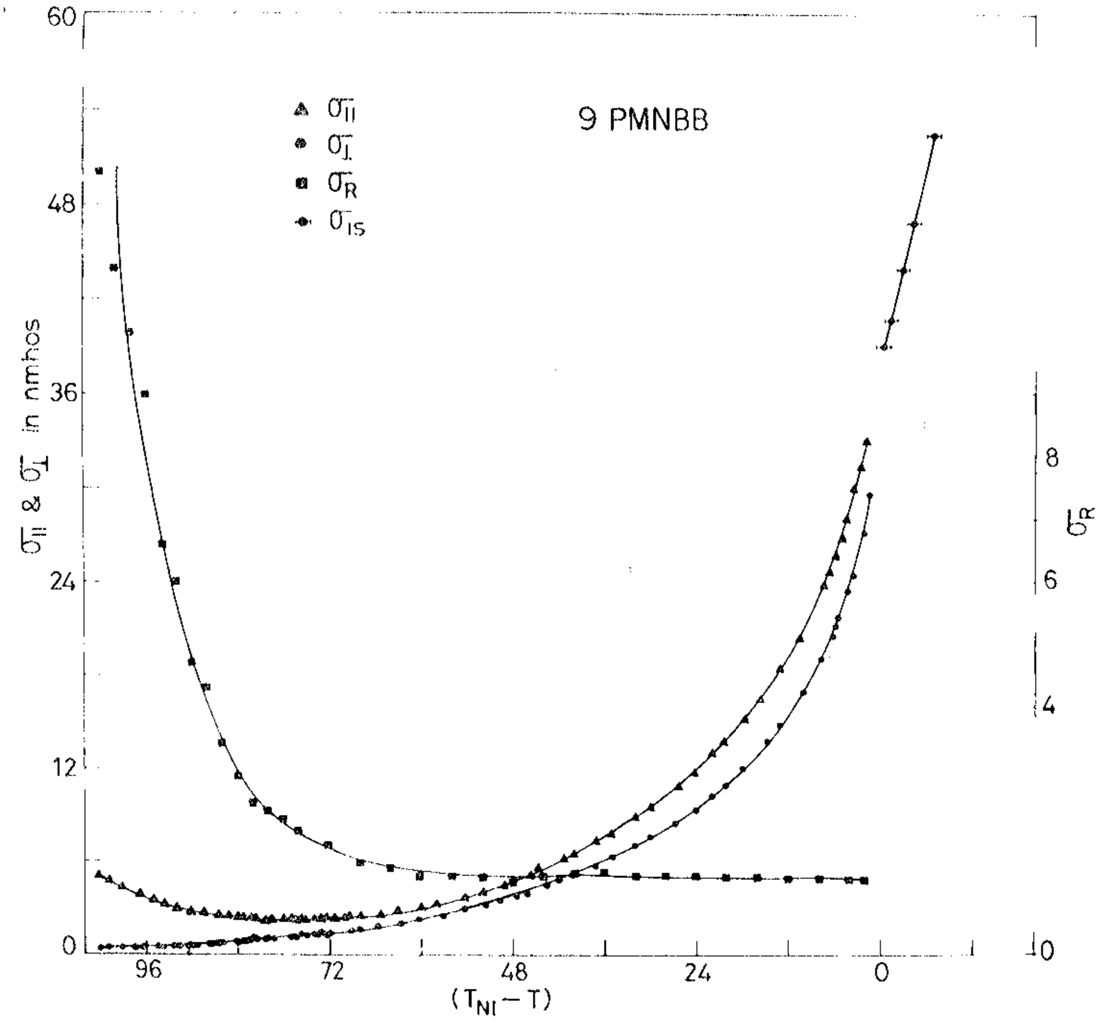


FIGURE 5.5

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{is} and σ_R of 9 PMNBB at 1592 Hz. The arrow mark indicates T_{AN}.

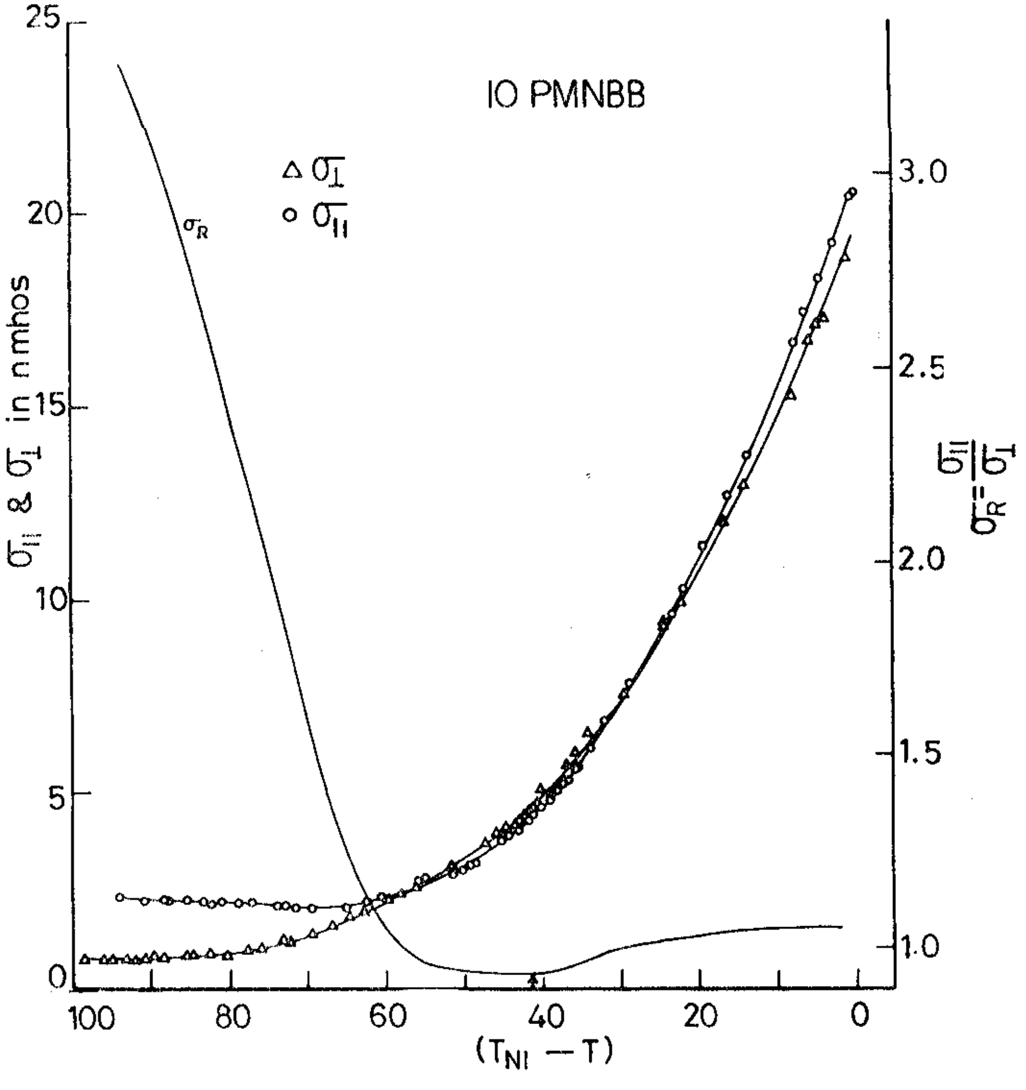


FIGURE 5.6

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{is} and σ_R of 10 PMNBB at 1592 Hz. The arrow mark indicates T_{AN} .

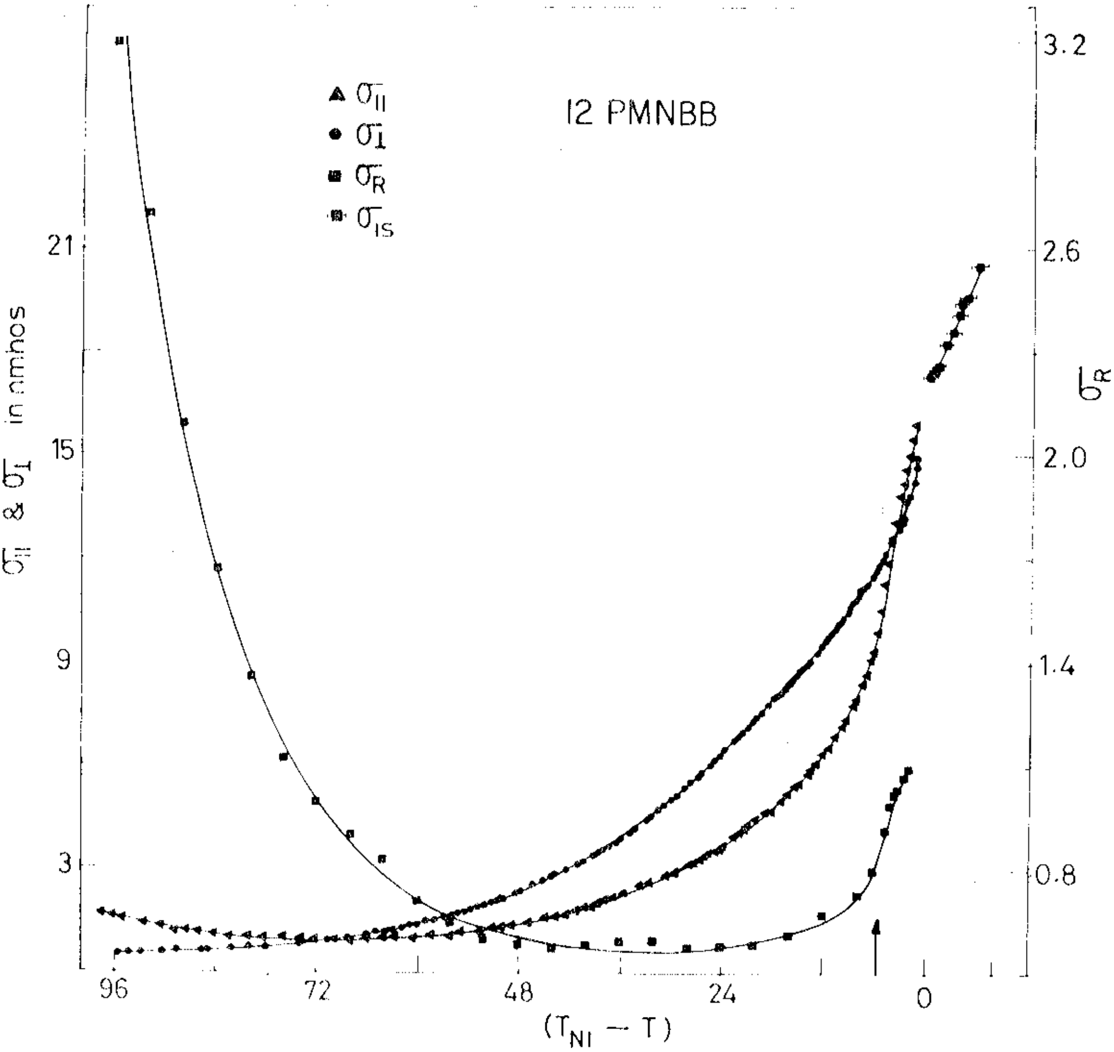


FIGURE 5.7

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{is} and σ_R of 12 PMNDB at 1592 Hz. The arrow mark indicates T_{AN}.

is cooled in the A phase. At 300 Hz (fig.5.8), the conductivity ratio takes lower values as can be expected, but the relaxation effect is felt even at this frequency at low temperatures. The progressive reduction in the minimum value of σ_R at 1592 Hz, as we increase n from 9 to 12 in nPMNBB, is connected with the progressively increasing smectic order of the higher homologues.

The results (at 1592 Hz) on 11 CPMeOBB, 12 CPMeOBB and 11 PMeOBrBB are shown in figs.5.9–5.11 respectively. In all the cases, the conductivity anisotropy is negative in the A phase. In 11 CPMeOBB and 11 PMeOBrBB, as the temperature is lowered, σ_R decreases first, reaches a minimum and then increases.

It is generally observed, as la area in our studies also, that $\sigma_{\parallel}$ decreases faster than $\sigma_{\perp}$ near the nematic-smectic A transition point. This can be most probably attributed to the permeation process,[12] which dominates flow along the layer normal, due to the layering. The increase in viscosity due to the permeation process is enormous when compared to the increase in the normal viscosity due to the lowering of temperature. This can lead to the faster variation of $\sigma_{\parallel}$.

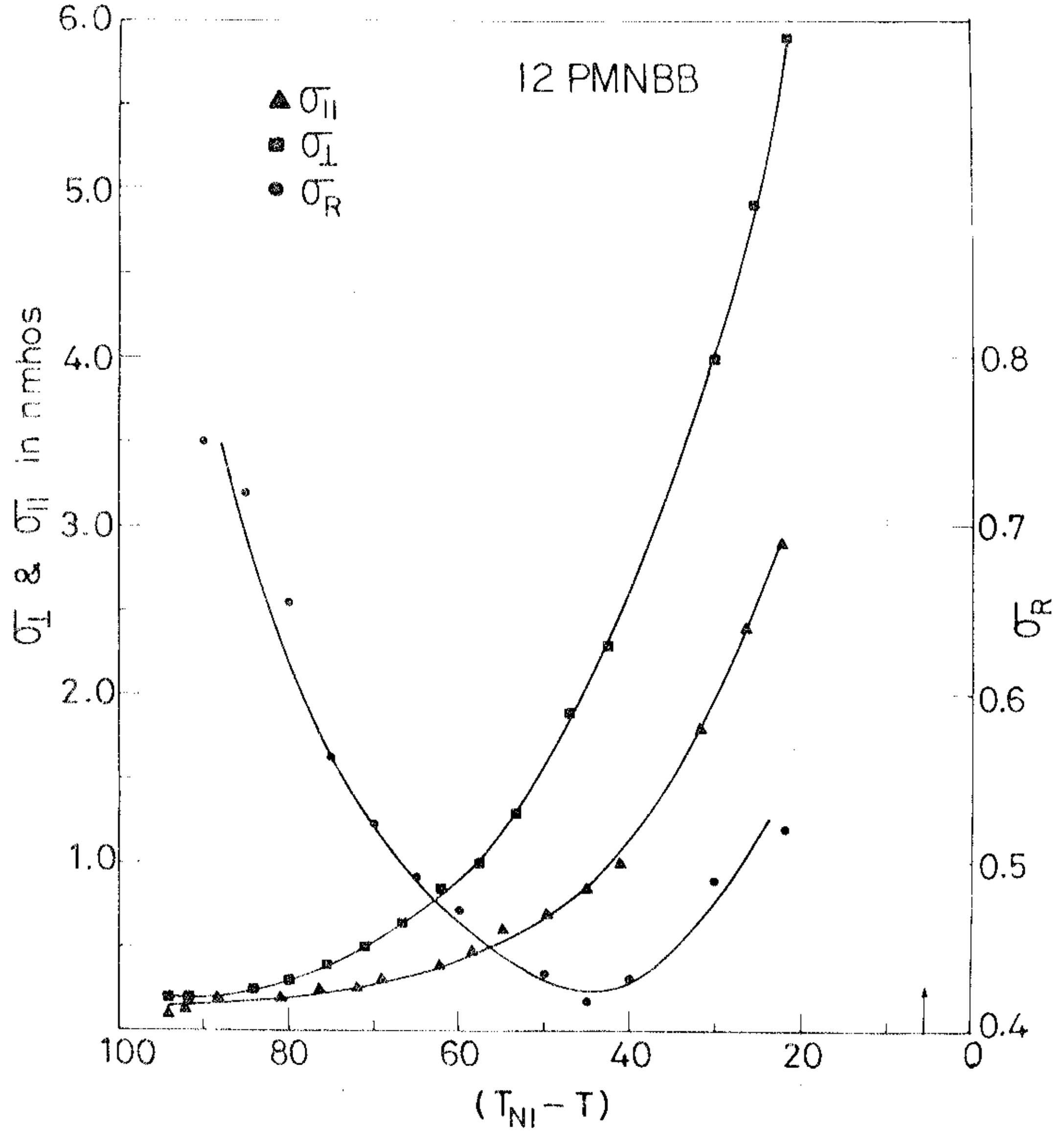
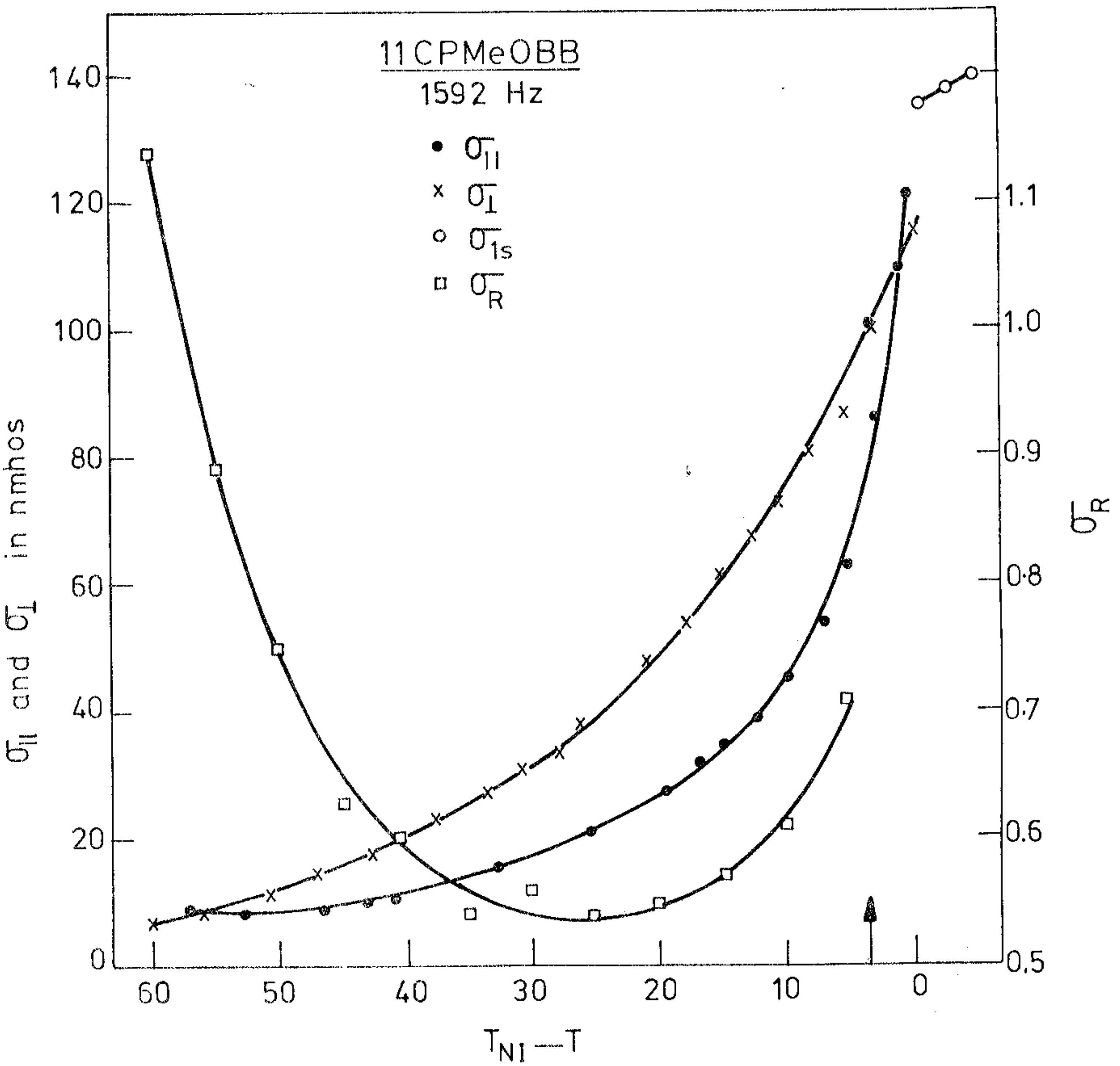


FIGURE 5.8

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, and σ_R of 12 PMNBB at 300 Hz. The arrow mark indicates T_{AN}.



~~FIGURE 5.9~~

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, c_{is} and σ_R of 11CPMeOBB at 1592 Hz. The arrow mark indicates T_{AN}.

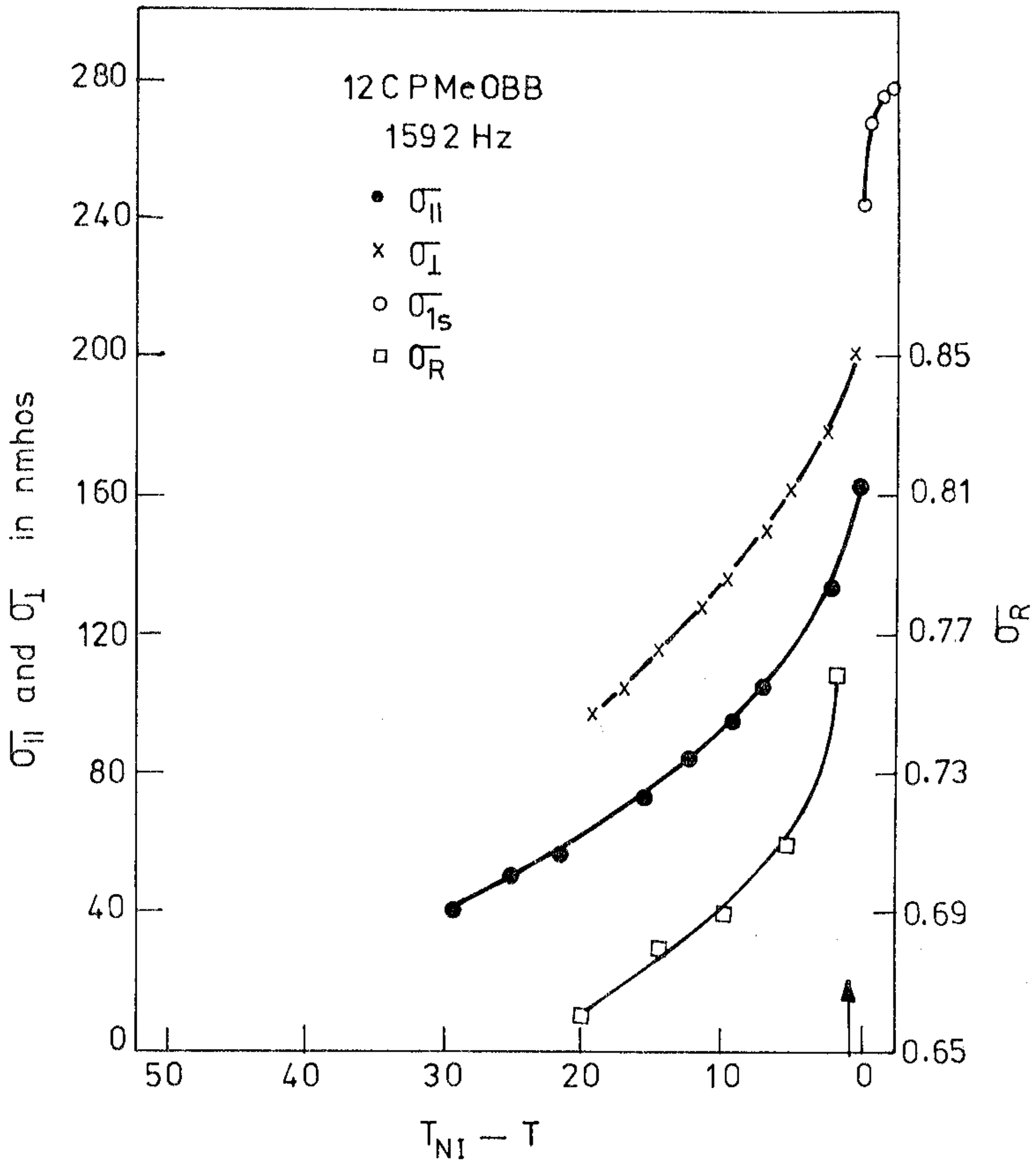


FIGURE 5.10

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{1s} and σ_R of 12 CPMeOBB at 1592 Hz. The arrow mark indicates T_{AN}.

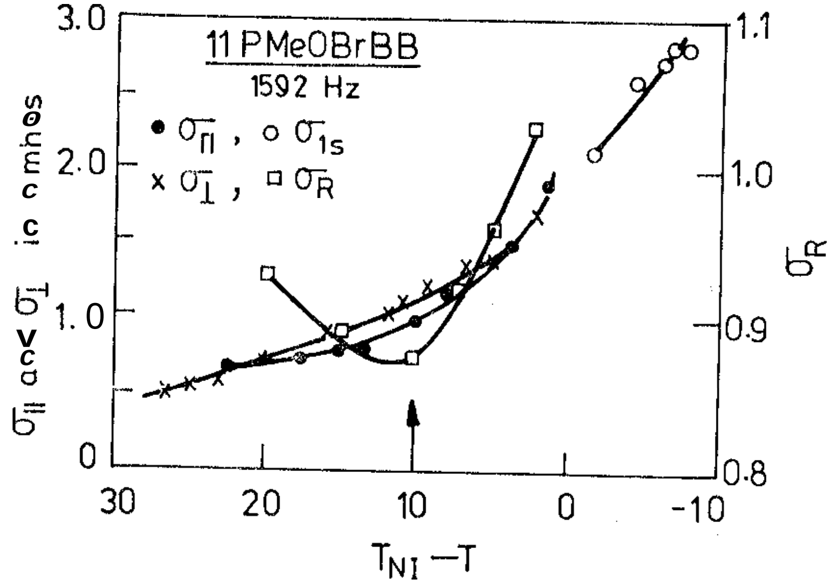


FIGURE 5.11

Temperature variations of $\sigma_{\parallel}$, $\sigma_{\perp}$, σ_{is} and σ_R of 11 PMeOBrBB at 1592 Hz. The arrow mark indicates T_{AN}.

It is instructive to compare the cross over temperatures in the sign of conductivity anisotropy in the three compounds, viz., 11 PMeOCBB, 11 CPMeOBB and 11 PMeOBrBB. The respective cross over temperatures are $T_{AN} - T \simeq 2^\circ$ (in the A phase), $T_{AN} - T \simeq -3^\circ$ (in the N phase) and $T_{AN} - T \simeq -7^\circ$ (in the N phase).

The heats of smectic A-nematic transition (ΔH_{AN}) of these compounds are 0.035 KJ/mole in 11 PMeOCBB, 0.17 KJ/mole in 11 CPMeOBB and 0.26 KJ/mole in 11 PMeOBrBB. If ΔH_{NA} is small, one would expect the smectic like short range order to build up far above T_{AN} and hence the cross over should occur at a relatively higher temperature (relative to T_{AN}) in the N phase. But experimental results indicate exactly the reverse trend. We attribute this reverse trend in the cross over temperatures to the difference in the layer structures of the A phase of the compounds. The layer spacings in the A phase are $\geqslant 1.5\ell$ in 11 PMeOCBB, $\sim 1.3\ell$ in 11 CPMeOBB and $\sim \ell$ in 11 PMeOBrBB, where ℓ is the molecular length which is practically the same in all the three compounds (see chapter III). As mentioned earlier, the permeation process due to layering has a profound influence on the ionic mobilities. It is well known that the permeation parameter is given by

λ_p $(\bar{\eta}\, q_0^2)^{-1}$ where $\bar{\eta}$ is the average viscosity coefficient and q_0 (= 21/64 where d is the layer thickness) Is the wave vector along the layer normal.[12] Further, λ_p is a measure of ionic mobility. Since $\lambda_p \propto d^2$, the ionic mobility along the director and hence $\sigma_{\parallel}$ should be higher in the bilayer structures than in monolayer smectics leading to a higher value of σ_R in the former. Hence, σ_R becomes less than unity at lower temperatures relative to T_{AN} la bilayer smectics than in monolayer smectics as is indeed observed in our systems as well as in other systems described in We introduction to this chapter.

Thus, our results clearly demonstrate the influence of the short range order in the medium on the conductivity anisotropy.

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