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Experimental Studies on the Electrical Conductivity of Two Re-entrant Nematogens†

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The principal electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$ have been studied as functions of temperature in the nematic, smectic *A* and re-entrant nematic phases of a pure compound, 4-cyanophenyl-3′-methyl-4(4′-*n*-dodecylbenzoyloxy)benzoate, and a 35.8/64.2 weight mixture of 6 OCB and 8 OCB. In both cases, the ratio $R(=\sigma_{\parallel}/\sigma_{\perp})$ in the smectic phase exhibits a marked pretransitional increase on approaching the re-entrant nematic phase.

1 INTRODUCTION

Since the first observation of re-entrant behavior[1] in liquid crystals there have been several experimental reports on this phenomenon in pure compounds as well as in mixtures.[2-10] In an earlier paper on the dielectric properties of some re-entrant nematogens[7] we showed that the molecular associations are significantly different in the normal nematic and re-entrant nematic phases, the activation energy in the latter phase being nearly 80% higher. To find out if this difference is reflected in the transport properties also, we have studied the temperature dependence of the principal electrical conductivities.

2 EXPERIMENTAL

The compounds studied were 4-cyanophenyl-3′-methyl-4(4′-*n*-dodecylbenzoyloxy)benzoate[10,11] (12 CPMBB)

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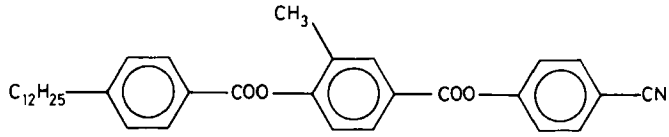
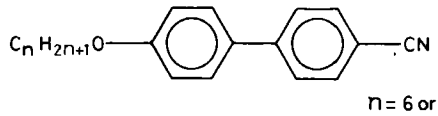


and a 35.8% weight mixture of 4'-*n*-hexyloxy-4-cyanobiphenyl (6 OCB) in 4'-*n*-octyloxy-4-cyanobiphenyl (8 OCB)[3]



12 CPMBB was synthesized in our chemistry laboratory by Dr. B. K. Sadashiva while the 6 OCB/8 OCB mixture was kindly given to us by Dr. P. E. Cladis. The transition temperatures (on cooling) are given in Table I.

The conductivities along ($\sigma_{\|}$) and perpendicular ($\sigma_{\perp}$) to the optic axis were determined at 1592 Hz using a Wayne Kerr B642 autobalance universal bridge. The samples were sandwiched between two tin oxide coated glass plates (thickness of the sample $\sim$ 125 to 250 μm). A 15 kG magnetic field was used to obtain the aligned samples in both configurations. The aligned smectic phase was easily obtained by cooling a well aligned nematic in the presence of the magnetic field. The accuracy of the relative variation of $\sigma_{\|}$ and $\sigma_{\perp}$ was $\pm 0.2\%$ while the absolute accuracy was estimated to be about 3 to 4%. During each measurement the temperature of the sample was stable to within $\pm 0.025°$ C, which was also the accuracy in the determination of temperature.

3 RESULTS

The variation of $\sigma_{\|}$, $\sigma_{\perp}$ as well as their ratio $R(= \sigma_{\|}/\sigma_{\perp})$ with temperature for 12 CPMBB and the 6 OCB/8 OCB mixture are shown in Figures 1 and 2 respectively.

(i) *12 CPMBB*: Starting from T_{NI}, where $R = 1$, R increases with decrease of temperature throughout the (normal) nematic range reaching a maximum

TABLE I

Transition temperatures in °C (on cooling)

Transition	12 CPMBB	6 OCB/8 OCB mixture
isotropic—nematic (T_{NI})	147.8	78.5
nematic—smectic *A* (T_{AN})	138.5	45.5
smectic *A*—re-entrant nematic ($T_{RN\text{-}A}$)	59.8	30.0
re-entrant nematic—solid ($T_{S\text{-}RN}$)	~57	~25

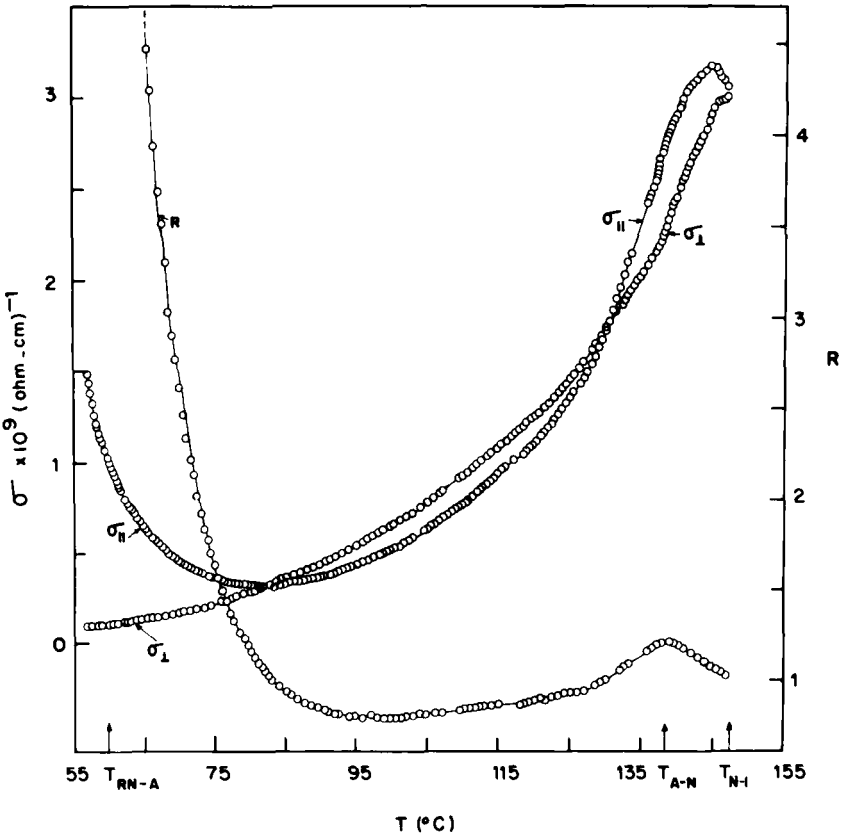


FIGURE 1 The principal electrical conductivities $\sigma_{\parallel}$ and $\sigma_{\perp}$, and the ratio $R = \sigma_{\parallel}/\sigma_{\perp}$ of 12 CPMBB as functions of temperature in the nematic, smectic A and re-entrant nematic phases.

value of 1.3 very close to T_{AN}, below which it starts decreasing with decreasing temperature (Figure 1). Similar decreasing trends of R in the smectic A phase have been observed for several bilayer smectics.[12] As the temperature is decreased below T_{AN}, the decreasing trend of R continues till about the midpoint of the smectic range, where $R \approx 0.8$. Below this point R *increases* with decrease of temperature, the increase becoming very pronounced as $T_{RN\text{-}A}$ is approached. The increasing trend in R continues below $T_{RN\text{-}A}$, the value in the re-entrant nematic at the lowest temperature studied ($T_{RN\text{-}A} - T = 1.2°\,C$) being about 16 (not shown in the figure).

(ii) *6 OCB/8 OCB mixture*: An exactly similar behavior is seen for the mixture also (Figure 2) except that in this case the increase of R near $T_{RN\text{-}A}$ is less steep and the maximum value of R in the re-entrant nematic phase is only 1.8 (at $T_{RN\text{-}A} - T = 2.1°\,C$).

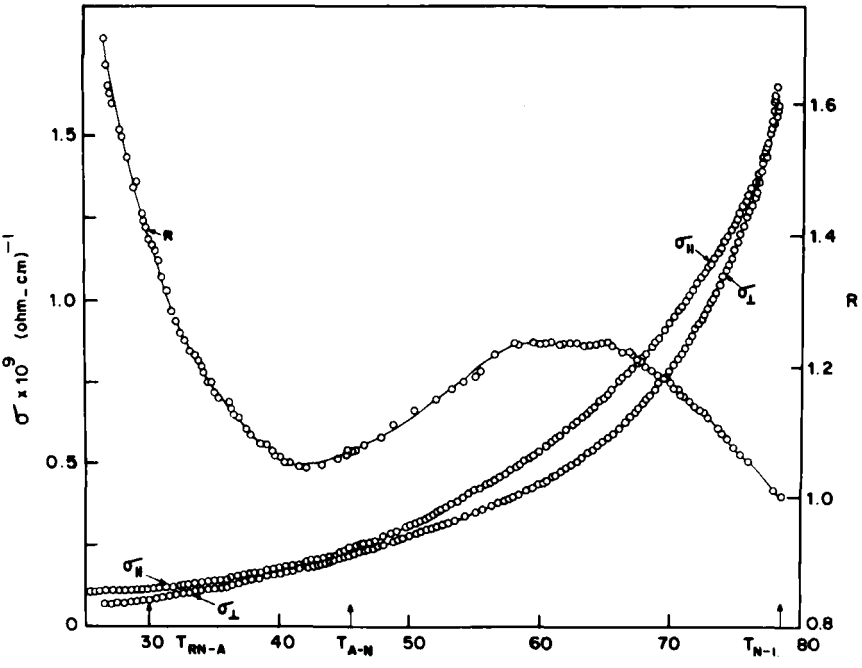


FIGURE 2 The principal electrical conductivities $\sigma_\parallel$ and $\sigma_\perp$, and the ratio $R = \sigma_\parallel/\sigma_\perp$ of a 35.8/64.2 weight mixture of 6 OCB/8 OCB as functions of temperature in the nematic, smectic *A* and re-entrant nematic phases.

4 DISCUSSION OF RESULTS

It is worth noting that the variation of R with temperature appears to be mainly due to the variation of $\sigma_\parallel$ and not due to $\sigma_\perp$; the latter exhibits a continuously decreasing trend over the entire temperature range. In other words, only the ionic mobility parallel to the director axis is affected. The marked increase in R on approaching $T_{RN\text{-}A}$ clearly indicates that a nematic-like behavior is manifested as a pretransitional effect even in the smectic phase. This effect is more pronounced in the pure compound than in the mixture.

Three other relevant observations on the same compound may be mentioned here. (i) The average dielectric constant $\bar{\epsilon} = 1/3(\epsilon_\parallel + 2\epsilon_\perp)$ which is less than the extrapolated isotropic value because of the antiparallel ordering of the molecules,[13] decreases with decrease of temperature throughout the normal nematic and over a part of the smectic range. On further decrease of temperature, $\bar{\epsilon}$ starts to *increase*, the increasing trend continuing right through up to the lowest temperature of the re-entrant nematic, where it practically merges with ϵ_{is}.[7] (ii) The activation energy W, as determined by the dielectric

relaxation measurements of $\epsilon_{\|}$, is nearly 80% higher in the re-entrant nematic phase than in the normal nematic phase. In the smectic phase, the plot of the relaxation frequency versus $1/T$ consists of two distinct straight lines with different slopes (or different W).[7] (iii) Precise X-ray determinations of the temperature variation of the layer spacing in the smectic A phase have shown[5] that, on cooling from T_{AN}, the layer spacing decreases at first over a part of the smectic range and then *increases* with further decrease of temperature. In other words there is a thermal expansion of the smectic A layer spacing on approaching $T_{RN\text{-}A}$.

All these observations are evidently very closely related and reflect the structural rearrangement taking place as a precursor to the appearance of the re-entrant nematic phase.

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