ESR Study of Molecular Ordering in 50.1, 50.2 and 50.4

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An ESR study of the liquid crystals N(p-n-pentyloxy benzylidene) p-n-alkylanilines [alkyl = methyl, 50.1; ethyl, 50.2; butyl, 50.4] has been carried out using a nitroxide radical as paramagnetic probe. The order parameters determined in this way are in close agreement with those determined from refractive indices by the Neugebauer method.

Introduction

ESR studies of molecular order and motion in liquid crystals are well established. Liquid crystals being diamagnetic, it is necessary to dope the liquid crystal with a small amount of a paramagnetic probe whose structure is such that the probe molecules follow the ordering of the liquid crystal to a great extent [1–3]. (3-Spiro[2′-N-Oxyl-3′,3′-dimethyl

oxazolidine]-5α-cholestane is chosen as the ESR probe because its hyperfine tensor A can be considered as approximately cylindrical around a Z axis lying along the direction of the p_2 orbitals of the nitrogen atom and perpendicular to the long axis of the molecule [4, 5]. The g anisotropy is \( \approx 7 \times 10^{-3} \) and can be neglected in first approximation. The probe, a rigid rod shaped molecule, is easily soluble, is oriented by the anisotropically ordered molecules of the solvent, and reflects local molecular orientation and mobility. We report here the temperature dependence of the orientational order of a spin probe in the mesophases of three N(p-n-pentyloxy benzylidene) p-n-alkylanilines.

Experimental

The transition temperatures are determined using a polarizing microscope combined with a hot stage. The molecular formulae and transition temperatures are as follows.

\[
\begin{align*}
R = CH_3 - 50.1 & \quad Solid \quad 57^\circ C \rightarrow \text{Nematic} \quad 62.4^\circ C \rightarrow \text{Isotropic} \\
& \quad 45^\circ C \rightarrow \text{Smectic G} \\
R = C_2H_5 - 50.2 & \quad Solid \quad 49^\circ C \rightarrow \text{Smectic G} \quad 53.7^\circ C \rightarrow \text{Nematic} \quad 59^\circ C \rightarrow \text{Isotropic} \\
R = C_4H_9 - 50.4 & \quad Solid \quad 8^\circ C \rightarrow \text{Smectic G} \quad 51^\circ C \rightarrow \text{Smectic A} \quad 52^\circ C \rightarrow \text{Nematic} \quad 69.4^\circ C \rightarrow \text{Isotropic}
\end{align*}
\]

The nitroxide probe molecule \((10^{-3} \text{ M})\) is easily dissolved in the corresponding liquid crystal in its isotropic phase in a quartz tube. The ESR spectra of the three compounds (50.1, 50.2, and 50.4) were recorded with a Varian E-4 spectrometer. The temperature of the sample was controlled with a Varian variable temperature accessory and measured with a copper-constantan thermocouple inside the quartz tube. \( T_{N-1} \) of all the samples is decreased by 0.5 °C after dissolving the nitroxide probe in them.

Results and Discussion

In a nematic phase the order parameter \( S \) is related to the ESR spectrum of the N → O probe by

\[
S = \frac{\langle a \rangle - a}{A_1 - a}
\]
Maximum order corresponds to $S = -0.5$, i.e. the order parameter obtained by ESR should be double the value of $S$ obtained by NMR.

$$\langle a \rangle = \text{coupling constant obtained from the experimental motionally averaged spectrum in the nematic phase;}$$

$$a = (1/3)(A_1 + 2A_\perp) = \text{Isotropic hyperfine parameter measured in the isotropic phase;}$$

$$A_1, A_\perp = \text{parallel and perpendicular components of the hyperfine tensor;}$$

$$A = 30.8 \text{ Gauss is taken from [6].}$$

The ESR spectra of 50.1, 50.2, and 50.4 in their nematic phases at $(T_{N-I} - 1.4)^{\circ}C$ are shown in Figure 1. At the N–I transition temperature all the three samples exhibited an order parameter $S = 0.44$, which is in agreement with Maier-Saupe's theoretical value at $T_{N-I}$. It is observed that the order parameter increases with increasing chain length at any temperature $(T_{N-I} - T)^{\circ}C$ in the nematic phases (Figure 2). The odd-even effect cannot be ascertained because of limited number of compounds. Furthermore we have calculated order parameters for 50.1 from refractive index data [7] via the methods of Vuk and Neugebauer, as given in Table 1. It is found that the order parameters from ESR are in close agreement with the Neugebauer values. This feature is also found for 50.2 and 50.4. The temperature dependence of the order parameter $S$ calculated from the Maier-Saupe theory [8] is shown in Fig. 2 as solid line. The experimental $S$ values obtained from ESR are found to be higher than the values predicted from Maier and Saupe's theory in all the compounds.

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