ESR Study of Molecular Ordering in PEBAB and PMBAB

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An ESR study of the nematic liquid crystals PEBAB and PMBAB has been carried out using a nitroxide radical as paramagnetic probe. The order parameter (S) determined this way are in close agreement with those determined by NMR. For EBAB our S values differ from those determined by ESR with a different probe (VAAC).

Introduction

Cyano substituted organic compounds exhibiting mesomorphic properties are of particular importance in liquid crystal research [1] and application [2]. The orientational order parameter [3] in the mesophase of a nematic liquid crystal composed of rod like molecules may be defined as

$$S = \langle (3\cos^2\theta - 1)/2 \rangle ,$$

where θ is the angle between the rod-axis and the nematic director. S is found [4] to decrease with increasing temperature with in the mesophase and to vanish suddenly at the nematic-isotropic transition temperature T_{NI}. Though several techniques are used for measuring S, comparison of the values obtained with different methods is meagre. Previous studies using Vanadyl Acetyl Acetonate (VAAC)-probe in nematics [5] met some problems, viz. solubility [6], incompletely averaged ESR spectra of highly viscous nematic liquids leading to wrong S values, etc. [6]. The present work reports on ESR measurements using (3 spiro [2′-N-*Oxyl*-3′,3′-dimethyloxazolidine])-5α-cholestane (N → O Probe, kindly supplied to us by Dr. S. K. Ghosh, Italy) in N-(p-ethoxy benzylidene)-p-amino benzonitrile (PEBAB) and N-(p-methoxy benzylidene)-p-amino benzonitrile (PMBAB).

Experimental

The N → O probe (10^{-3} M) is easily dissolved in PEBAB and PMBAB in their isotropic phases in a quartz tube. The ESR spectra were recorded with a varian E-4-x-band 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_{NI} of all the samples is decreased by ~0.5 °C after dissolving the nitroxide probe in them.

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The transition temperatures of the pure compounds, as observed with a polarizing microscope, are:

PEBAB Solid $\overset{105\,^\circ C}{\longleftrightarrow}$ Nematic $\overset{125.5\,^\circ C}{\longleftrightarrow}$ Isotropic

PMBAB Solid $\overset{106\,^\circ C}{\longleftrightarrow}$ Nematic $\overset{118\,^\circ C}{\longleftrightarrow}$ Isotropic.

Results and Discussion

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

$$S = [(\langle a \rangle - a)/(A_\parallel - a)] .$$

Maximum order corresponds to $S = -0.5$, i.e. the order parameter obtained by ESR should be double the S value obtained by NMR.

$\langle a \rangle$ = coupling constant obtained from the experimental motionally averaged spectrum in the nematic phase;
a = $(1/3)(A_\parallel + 2A_\perp)$ = isotropic hyperfine parameter measured in the isotropic phase;
$A_\parallel, A_\perp$ = parallel and perpendicular components of the hyperfine tensor;
$A_\parallel$ = 30.8 Gauss is taken from literature [8].

PEBAB

ESR spectra of PEBAB are shown in Figure 1. At 124.5 °C coexistence of the two phases (for about 0.2 °C) is

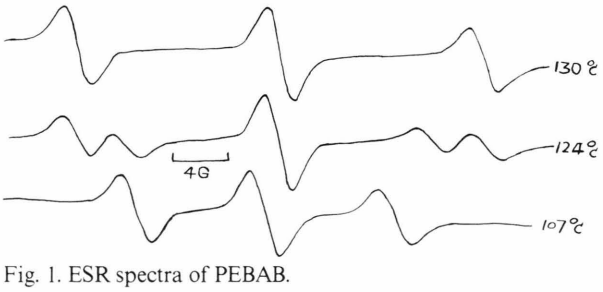

Fig. 1. ESR spectra of PEBAB.

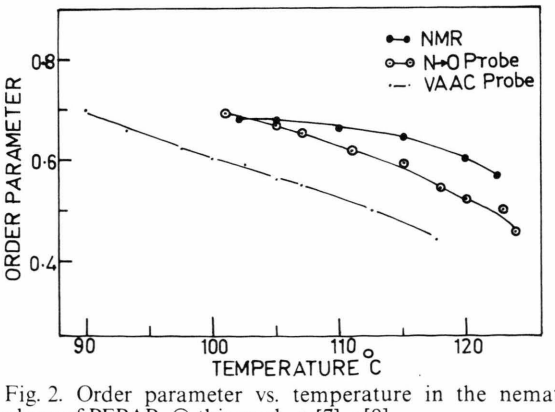

Fig. 2. Order parameter vs. temperature in the nematic phase of PEBAB. ⊙ this work, ● [7], · [9].

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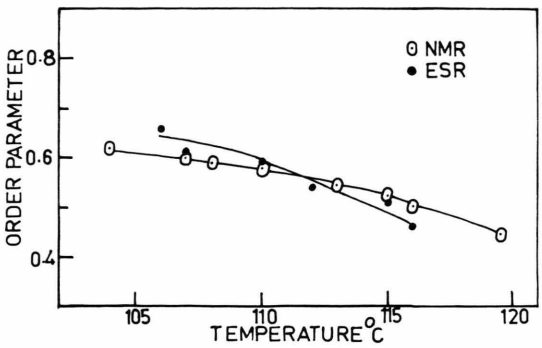

Fig. 3. Order parameter vs. temperature in the nematic phase of PMBAB. ● this work, ⊙ [7].

indicated by the five line spectrum. Below 124 °C the order parameter rises sharply, indicating the transition to be of first order. S increases further with decreasing temperature as shown in Figure 2. Our results are found to be in close agreement with the NMR data [7] while those obtained by ESR using VAAC probe [9] are low at all temperatures. The present work does not support the idea of A. S. N. Rao et al. [9] that higher order terms for the molecular potential are necessary to explain the discrepancy of experimental and theoretical order parameters. The lower values of S obtained in [9] may be due to the use of VAAC probe in PEBAB since highly viscous nematics with VAAC probe cannot give correct values of S [6].

PMBAB

Our S values again agree well with those obtained with NMR [7] (Fig. 3), indicating that the use of N → O probe in a nematic phase gives correct order parameters. The S values varied from 0.46 at 116 °C to 0.66 at 105 °C in the nematic phase.

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