ESR Study of Molecular Ordering in PEBAB and PMBAB

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Z. Naturforsch. **39a**, 700–701 (1984);
received March 21, 1984

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

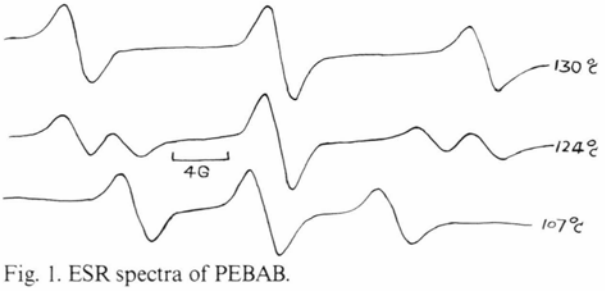

Fig. 1. ESR spectra of PEBAB.

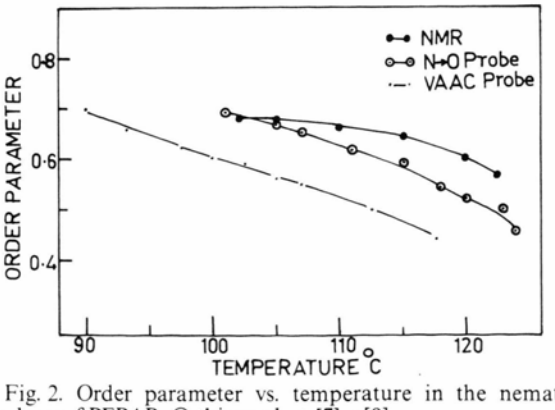

Fig. 2. Order parameter vs. temperature in the nematic phase of PEBAB. ⊙ this work, ● [7], · [9].

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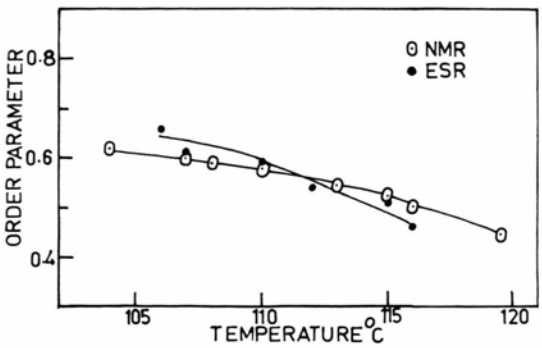

Fig. 3. Order parameter vs. temperature in the nematic phase of PMBAB. ● this work, ⊙ [7].

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.

Acknowledgements

Financial assistance was provided by UGC., New Delhi. The authors are thankful to Dr. G. C. Upreti and Dr. Premchand for extending the laboratory facilities to record ESR spectra.

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