Molecular Ordering in Nematic MBCA and EPAPU

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By EPR, two nematic liquid crystals (MBCA and EPAPU) were investigated using a steroidal nitroxide spin probe. In both liquid crystals the isotropic-nematic phase transition is of first order. The observed variation of the order parameter with temperature is compared with predictions from the Maier-Saupe and Humphries-James-Luckhurst models and with results obtained by several other experimental techniques.

Introduction

The lowest orientational order parameter ($\bar{P}_2$) [1] in the mesophase of a nematic liquid crystal having rod-like molecules is defined as

$$\bar{P}_2 = \overline{(3\cos^2\theta - 1)/2},$$

where θ is the angle between the rod-axis and the nematic director. $\bar{P}_2$ is known [2] to decrease steadily with increasing temperature in the mesophase and then to decrease discontinuously at the nematic-isotropic transition temperature. There are several techniques for measuring $\bar{P}_2$, but the results are rarely compared [3, 4]. In this communication, we report on the variation of the order parameter with temperature obtained with the EPR technique in two nematic liquid crystals: p-(p'-methoxybenzylidene)-cyanoaniline (MBCA), which because of the cyano group has a specific significance in liquid crystal research [5] and application, and p-p'(ethoxyphenylazo)-phenyl undecylenate (EPAPU). Using the results from EPR, the temperature dependence of the orientational order parameter $\bar{P}_2$ and the next higher order parameter

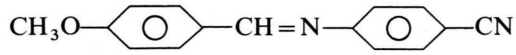
$$\bar{P}_4 = \overline{(35\cos^4\theta - 30\cos^2\theta + 3)/8}$$

have been predicted by the Humphries-James-Luckhurst (HJL) theory.

Experimental

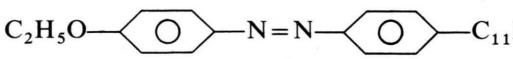
MBCA was synthesized in our laboratoy and EPAPU was procured from Eastman Organic Company (USA). Both materials were recrystallized from absolute alcohol before use. The transition temperatures and phases of the pure compounds were determined with a polarizing microscope and differential scanning calorimetry. The phase transitions and molecular structures are as follows:

(I) MBCA



Solid $\overset{379\ K}{\rightleftharpoons}$ Nematic $\overset{391\ K}{\rightleftharpoons}$ Isotropic

(II) EPAPU



Solid $\overset{341\ K}{\rightleftharpoons}$ Nematic $\overset{383\ K}{\rightleftharpoons}$ Isotropic

A speck of the nitroxide spin probe (3-spiro-[2'N-oxyl-3,3'-dimethyloxazolidine]) 5 α-cholestane [6] and, the liquid crystals were filled in a quartz tube, heated to the corresponding isotropic temperatures and stirred continuously until the spin probe was homogeneously mixed ($\sim 10^{-3}$ M) with the liquid crystals. EPR spectra of both MBCA and EPAPU were recorded with an E-112 X-Q band Varian spectrometer with a Varian temperature accessory, using a copper-constantan thermocouple inside the quartz tube.

The EPR spectrum of the spin probe (electron spin $S = 1/2$) consists of three well resolved hyperfine lines around $g = 2$ due to the coupling with the nitrogen

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spin (I = 1). When the spin probe is aligned in a nematic host matrix and is tumbling freely, the alignment is measured by an order parameter $\bar{P}_2$ given by

$$\bar{P}_2 = 2(a - A)/A',$$

where a is the isotropic coupling constant and A' is the parallel component of the anisotropic nitrogen hyperfine tensor. When the nematic director is parallel to the magnetic field, the spacing between the hyperfine lines is $2mA$, where m is the nuclear magnetic quantum number of the nitrogen state. In our measurements, a and A' are taken to be 14.76 gauss and 18.31 gauss, respectively. The hyperfine splitting was used to determine the order parameter.

Results and Discussion

(I) MBCA: A graph of the order parameter ($\bar{P}_2$) vs. the reduced temperature ($= T/T_{NI}$, where T_{NI} is the nematic-isotropic transition temperature) is given in Figure 1. $\bar{P}_2$ varied from 0.65 at 379 K to 0.45 at 391 K in the nematic phase. The value 0.45 is in good agreement with the theoretical value of 0.43 predicted for the nematic-isotropic transition of any liquid crystal [1, 7]. In the present case, the sudden fall at 391 K of the order parameter from 0.45 in the nematic phase to zero in the isotropic phase indicates the expected first order phase transition.

The variation of the order parameter with reduced temperature found by other methods, such as EPR [3], NMR [8], specific volume and ultrasonic measurements [9] is also given in Figure 1. Further, the variations of $\bar{P}_2$ and $\bar{P}_4$ predicted from the HJL theory [7] using our experimental data and the Maier-Saupe (MS) theory [1] are incorporated in Figure 1. From the graph, it is seen that the behaviour of the curves is similar except for the ultrasonic measurements [9]. The graphs from EPR [3] and NMR [8] compare well

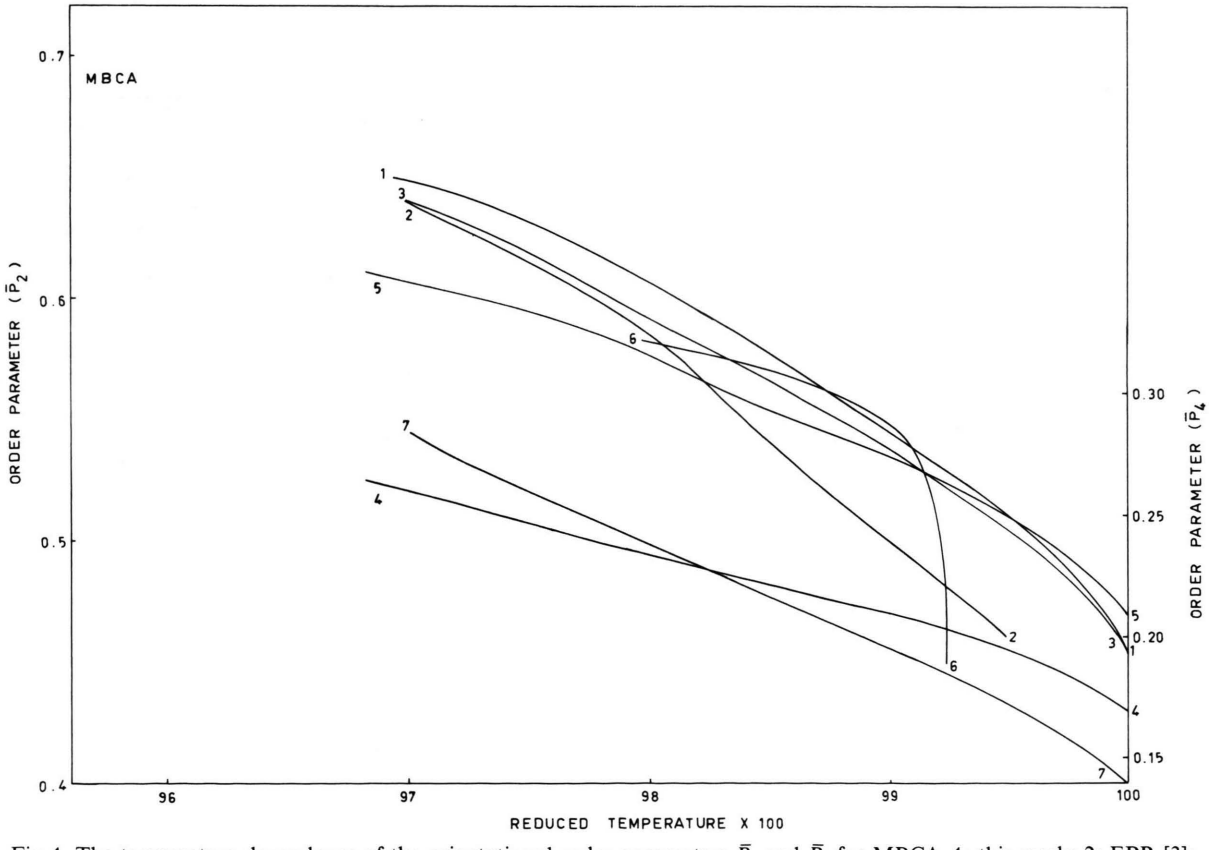
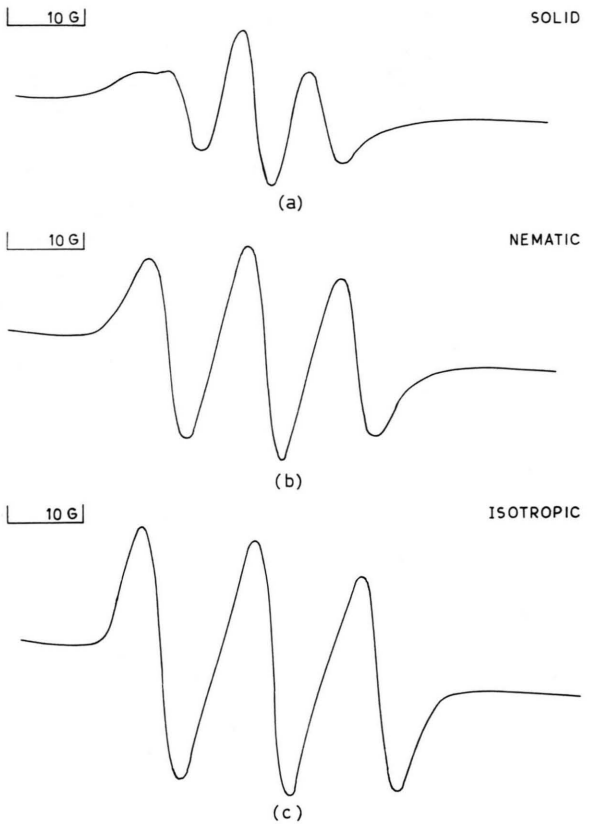


Fig. 1. The temperature dependence of the orientational order parameters $\bar{P}_2$ and $\bar{P}_4$ for MBCA. 1: this work; 2: EPR [3]; 5: NMR [8]; 6: specific volume and ultrasonic [9] results. 3: HJL theory with $\lambda = 0.05$ and $\alpha = 4.52$; 4: MS theory, 7: $\bar{P}_4$ according to HJL.



with our results, particularly at the beginning and the end of the nematic phase, respectively.

The variation of $\bar{P}_2$ with reduced temperature predicted by the HJL theory incorporating volume correction agrees quite well with the experimental graph. The order parameter $\bar{P}_4$, which contains further information about the orientational order, has a similar temperature dependence as $\bar{P}_2$.

(II) EPAPU: A representative plot of the hyperfine spectra of this liquid crystal is shown in Figure 2. At 334 K, the spectrum shown in Fig. 2 resembles that of a solid phase having a three line hyperfine pattern. The variations of the order parameter with the reduced temperature obtained by the present method, NMR [10], specific volume and ultrasonic measurements [9], refractive index measurements at 5893 Å [11] using the Neugebauer method, and refractive index measurements at 6328 Å [12] using the Vuks and Neugebauer methods are represented in Figure 3. It also showns $\bar{P}_2$ and $\bar{P}_4$ graphs predicted from the HJL theory with volume correction and the universal MS graph.

Fig. 2. EPR spectra of the EPAPU: (a) in the solid phase at 334 K, (b) in the nematic phase at 383 K, (c) in the isotropic phase at 385 K.

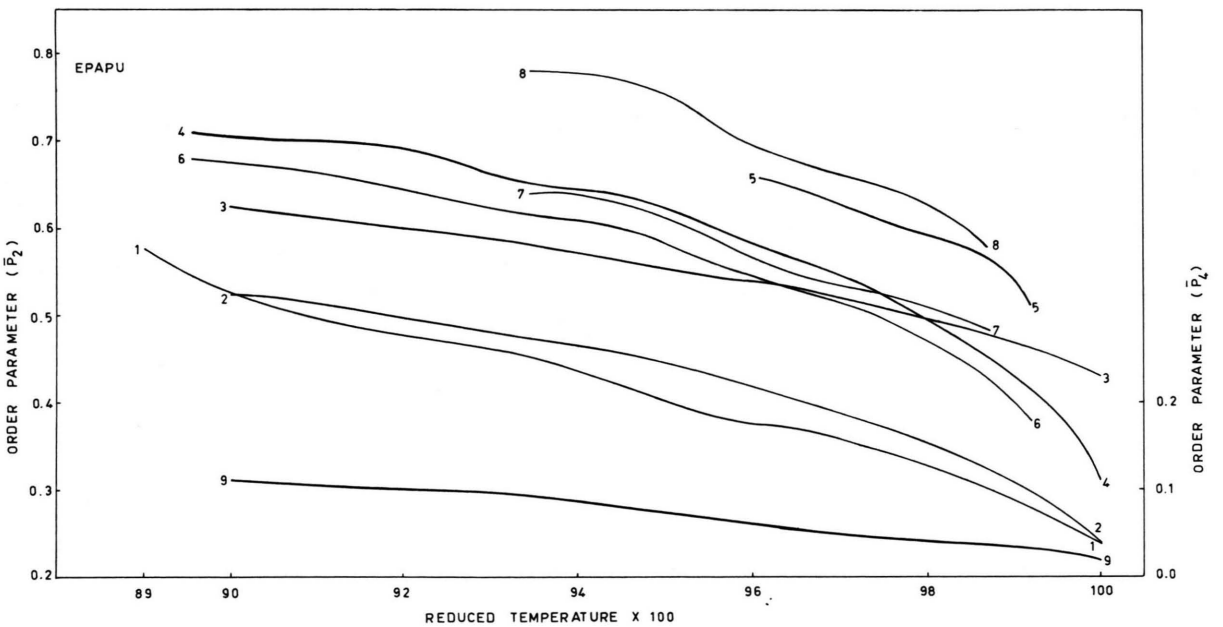


Fig. 3. The temperature dependence of the orientational order parameters $\bar{P}_2$ and $\bar{P}_4$ for EPAPU. 1: this work; 4: NMR [10]; 5: specific volume and ultrasonic [9] results. 6: refractive index [11]; 7: refractive index, Neugebauer method [12]; 8: refractive index, Vuks method [12]. 2: HJL theory with $\lambda = -1.01$ and $\alpha = -4.71$; 3: MS theory; 9: $\bar{P}_4$ according to HJL.

The $\bar{P}_2$ value 0.25 obtained at the isotropic-nematic transition is well below the theoretical order parameter of 0.43. This might be due to pre-transitional effects in the nematic phase which occur in many liquid crystals. However, the total increase of the order parameter from 0.25 to 0.57 with increasing reduced temperature in the nematic phase is in qualitative agreement with other studies [6, 7, 13, 14]. The diagram shows that the nematic-isotopic transition is of first order as expected.

The disagreement of the results obtained with different methods may be due to the different theoretical assumptions related to these methods. One should note that the HJL theory predicts variations of $\bar{P}_2$ consistent with our experimental data. However, the theoretical temperature dependence of $\bar{P}_4$ evidently is quite different from that of $\bar{P}_2$.

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