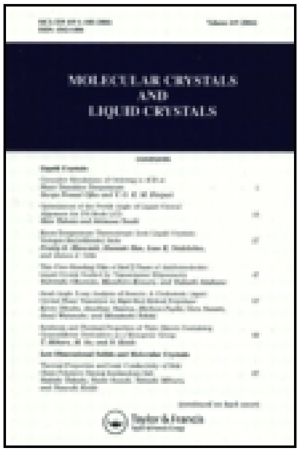

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On the Orientational Order and Molecular Dynamics of N-(4-butoxybenzylidene)-4'-butylaniline (4o.4) by ESR

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On the Orientational Order and Molecular Dynamics of *N*-(4-butoxybenzylidene)-4′-butylaniline (4o.4) by ESR

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The orientational order parameters $\overline{P}_2$ and $\overline{P}_4$, and the correlation times τ_0 and τ_2 of the androstane nitroxide spin probe dissolved in *N*-(4-butoxybenzylidene)-4′-butylaniline (4o.4), determined from the angular dependence of the nitrogen coupling constant and the linewidth in ESR spectra, have been reported as a function of temperature. For high ordered smectic G phase, $\overline{P}_2$ and $\overline{P}_4$ are in a very good approximation, assuming the molecular field theory. The activation energies in smectic G phase are found to be 16.4 kJ/mol for τ_0 and 29.6 kJ/mol for τ_2, respectively.

Keywords: ESR, order parameters, smectic G, correlation times

INTRODUCTION

Spin probes have proved to be extremely valuable for studies on the long range orientational order and rates of molecular reorientations in a wide variety of liquid crystals. Luckhurst et al.[1,2] proposed a theoretical treatment for analyzing the angular dependent ESR spectra to determine orientational order parameters $\overline{P}_2$ and $\overline{P}_4$, and the two correlation times τ_0 and τ_2 associated with the reorientations of a molecule and applied it to the smectic A phase. An important characteristic of this procedure is to be able to determine the $\overline{P}_4$ which is difficult to determine in any other way. A similar study was done by Pusnik and Schara[3] for various temperatures in the smectic A and B phases. The rotational diffusion of liquid crystals was studied by a number of methods, including neutron quasi-elastic scattering,[4] NMR,[5] and ESR.[6,7] However, no other detailed study has been reported on the molecular order and the molecular motion in smectic G phase.

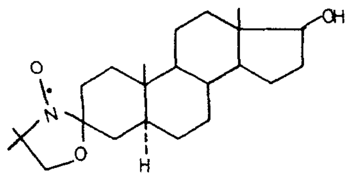
The present study reports the temperature dependence of $\overline{P}_2$ and $\overline{P}_4$, and of the motional parameters obtained from the ESR spectra of the spin probe in smectic G and B phases of *N*-(4-butoxybenzylidene)-4′-butylaniline (4o.4).

EXPERIMENTAL

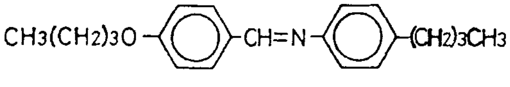
The *N*-(4-butoxybenzylidene)-4′-butylaniline (4o.4) used was purchased from Fuji Shikiso Co. Ltd., and was purified by vacuum distillation. This compound exhibits nematic, smectic mesophases A, B and G, and the sequence of phase transition temperature on heating is shown in

$$\mathrm{C}\ \underset{8.0}{\rule{2em}{0.4pt}}\ \mathrm{S_G}\ \underset{41.0}{\rule{2em}{0.4pt}}\ \mathrm{S_B}\ \underset{45.2}{\rule{2em}{0.4pt}}\ \mathrm{S_A}\ \underset{45.7}{\rule{2em}{0.4pt}}\ \mathrm{N}\ \underset{74.7}{\rule{2em}{0.4pt}}\ \mathrm{I}\quad (^\circ\mathrm{C}).$$

The transition temperatures of 4o.4 were confirmed by DSC measurement. The paramagnetic spin probe, 17β-hydroxy-4′-4′-dimethylspiro-[5α-androstane-3,2′-oxazolidin]-3′-ylocyl was purchased from Kanto Chemical Co. Ltd. The molecular structures of this probe and of 4o.4 are shown in Figure 1. The spin probe was introduced into 4o.4 in the nematic phase by dissolving it in ethanol as a solvent, and the solvent was taken off by a pump. The transition temperatures of the



spin probe



4o.4

FIGURE 1 Molecular structures of 4o.4 and of the probe molecule.

doped liquid crystal were about 0.1–1.0°C lower than those of a pure liquid crystal. The sample was prepared in a 5 mm o.d. quartz tube, and was degassed by several repetitions of a freezing and melting cycle under vacuum. The sample was heated in a strong magnetic field (23 kG) until the nematic phase was formed, and then the temperature was lowered slowly until the smectic G phase was formed.

The electron spin resonance spectra were taken on a JEOL JES-FE3X spectrometer with a JEOL-NM7700 temperature controller. ESR measurements were performed at 10, 20, 30, 40 and 43°C, and at each temperature the spectra were obtained as a function of the angle between the director of the liquid crystal and the magnetic field. In the nematic phase, ESR spectra were measured at 5°C intervals from 50°C to 75°C.

The order parameters and the correlation times were evaluated by using the non-linear least square program, SALS[8] for simulations.

RESULTS AND DISCUSSION

The line shape of ESR spectra in the smectic phases was dependent on the angle, γ, between the director of the smectic liquid crystal and the magnetic field. When γ is 0°, the director is parallel to the magnetic field. As shown in Figure 2, the typical ESR spectra demonstrate clearly not only the angular dependence of the nitrogen coupling constant but also that of the linewidth.

Figure 3 shows the plots of the hyperfine splitting versus γ at 20°C in the smectic G phase. The hyperfine splitting, **A**, has a maximum value near $\gamma = 90°$. The relationship between **A** and γ is given by

$$\mathbf{A}(\gamma) = [\overline{A}_r^2 + (\overline{A}_l^2 - \overline{A}_r^2)\cos^2(\gamma + \alpha)]^{1/2} \qquad (1)$$

where $\overline{A}_r$ and $\overline{A}_l$ are the partially averaged components of the hyperfine tensor, and α is the error of the angle for setting the sample tube.[9] These can be written in terms of hyperfine tensor as

$$\overline{A}_l = a + 2(A_l - A_r)\overline{P}_2/3$$

and

$$\overline{A}_r = a - (A_l - A_r)\overline{P}_2/3$$

where $\overline{P}_2$ is order parameter, and a, A_l and A_r in this case are 14.6G, 5.86G and 19.1G, respectively.

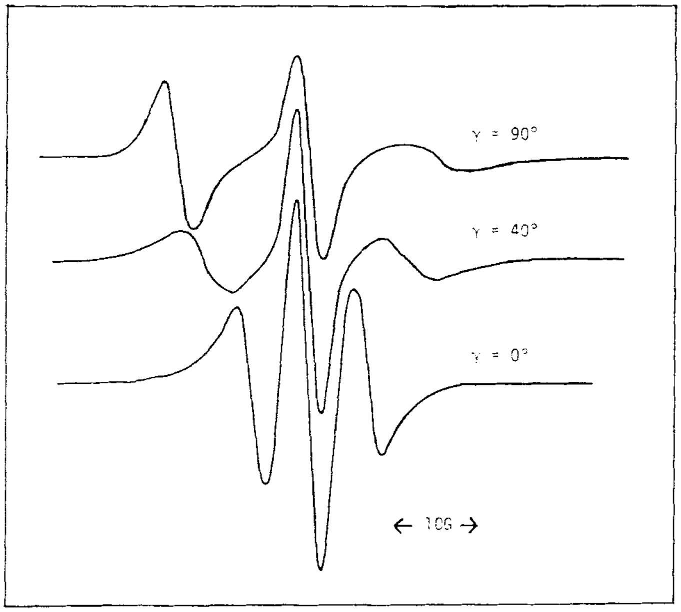


FIGURE 2 ESR spectra of the spin probe in the smectic G phase of 4o.4 at 20°C.

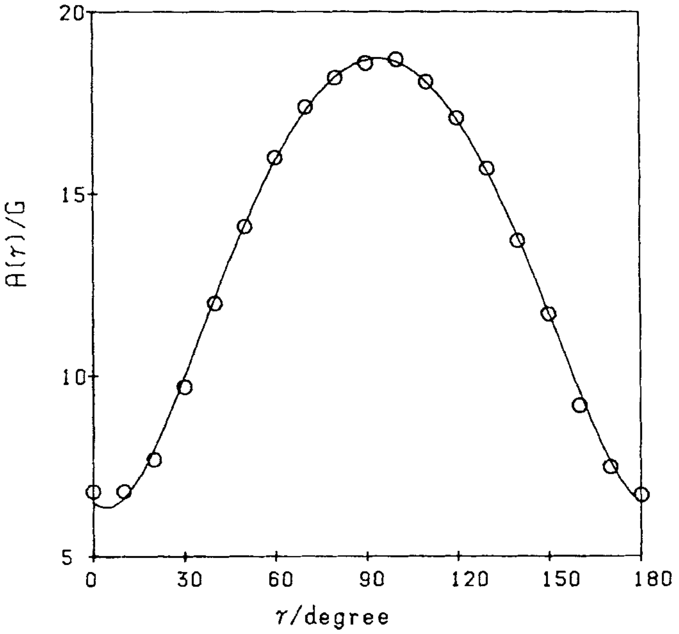


FIGURE 3 The angular dependence of hyperfine splitting at 20°C. Open circles are the observed values and the solid line is the simulated curve in Eq. (1). $\alpha = -4.1°$.

The order parameter $\overline{P}_2$ was determined by fitting the above equation to experimental values of A using the least square method. The curve calculated from this procedure is in fair agreement with the experimental values as shown in Figure 3. The order parameter $\overline{P}_2$ obtained at 20°C is 0.93, from which the smectic G phase is found to be a high order phase with crystalline nature. As the angle α in the measurement is less than 5 degrees and γ is close to zero, the molecules are oriented to the magnetic field, whereas the layer plane is considered to be tilted.

The widths $T_2^{-1}(m)$ of the three hyperfine lines were determined from the width of the central line and the heights of the outer two peaks relative to the central peak, where m is a nuclear quantum number. These linewidths were then used to determine the line width coefficients, A, B and C in the expression,

$$T_2^{-1}(m) = A + Bm + Cm^2. \tag{2}$$

The angular dependence of B is given by the following form assuming that the nuclear spin is quantized along the magnetic field,

$$B(\gamma) = B_0 + B_2P_2(\cos\gamma) + B_4P_4(\cos\gamma), \tag{3}$$

where $P_L(\cos\gamma)$ is Lth Legendre polynomial,

$$P_2(\cos\gamma) = (3\cos^2(\gamma + \alpha) - 1)/2 \tag{4}$$

and

$$P_4(\cos\gamma) = (35\cos^4(\gamma + \alpha) - 30\cos^2(\gamma + \alpha) + 3)/8. \tag{5}$$

The other two linewidth coefficients, A and C, are also given by the same expression. The experimental values of the line width coefficients A, B and C were obtained from the simultaneous linear equation (2). These values at 20°C are plotted as a function of the angle γ, as shown in Figure 4. The parameters in equation (3) were adjusted in order to fit them to the data using the non-linear least square routine called SALS. Good agreement is shown as solid curves in Figure 4. The A linewidth coefficient contains a contribution from the unresolved proton hyperfine structure while the coefficient C is most affected by imperfect alignment of the director.[10,11,12]

The coefficient B was then used to determine the parameters $\overline{P}_4$, τ_0 and τ_2. The correlation time τ_0 is associated with fluctuations in the orientation of the long axis of the spin probe and τ_2 with rotations about this axis. Figure 5 shows the temperature dependence of $\overline{P}_2$

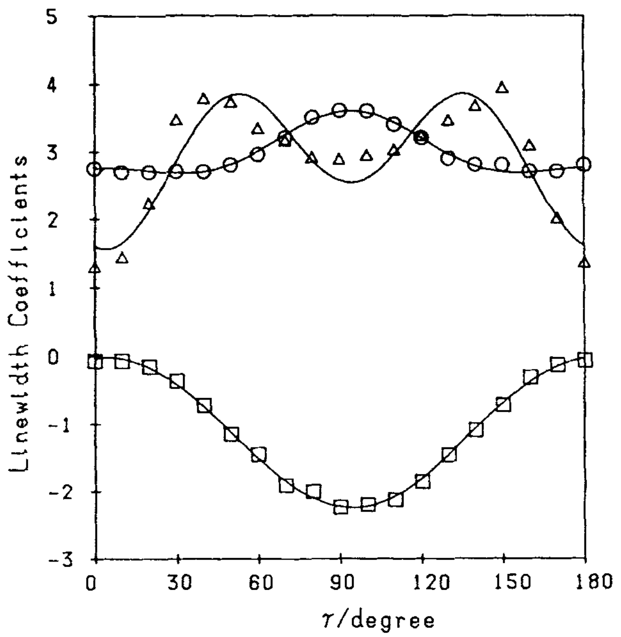


FIGURE 4 The angular dependence of the linewidth coefficients A(○), B(□) and C(△). Three solid lines are the simulated curves in Eq. (3). $B_0 = -26.16$, $B_2 = 26.48$, $B_4 = -0.65$, and $\alpha = -4.1°$.

and $\overline{P}_4$ and that the smectic B to G phase transition is evident from discontinuities in both the $\overline{P}_2$ and $\overline{P}_4$. However, for 5o.7—d_4 the discontinuity in a quadrupolar splitting corresponding to the order parameter was not observed at this phase transition temperature by ^{2}D-NMR.[13] A knowledge of $\overline{P}_4$ is important since it provides a test of the statistical theory of liquid crystals. As the orientational order in the smectic G phase is high at each temperature, $\overline{P}_2$ and $\overline{P}_4$ are in a very good approximation related by

$$\overline{P}_4 = 1 - 10(1 - \overline{P}_2)/3, \tag{6}$$

assuming the molecular field approximation.[2] In the smectic B phase, however, $\overline{P}_4$ calculated from $\overline{P}_2$ using the above equation is in disagreement with the measured value. The order parameter $\overline{P}_2$ is almost independent of the temperature in the smectic G phase, but $\overline{P}_4$ is decreased with temperature. It is apparently true that $\overline{P}_4$ should be more sensitive to molecular fluctuations because of the higher powers of the deviation angle. The molecular fluctuations increase evidently with temperature even in the high ordered smectic G phase. It will

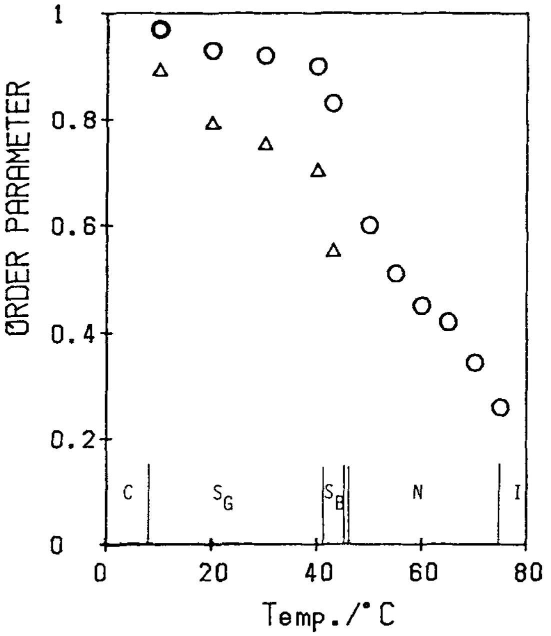


FIGURE 5 The temperature dependence of $\overline{P}_2$(○) and $\overline{P}_4$(△).

be noted that $\overline{P}_2$ in smectic B phase has a relatively high value, but the difference between $\overline{P}_2$ and $\overline{P}_4$ becomes larger than that in the smectic G phase. At the temperature of the nematic–isotropic phase transition, $\overline{P}_2$ is about 0.35 which is a reasonable value as compared to the values for liquid crystals obtained from other techniques, so it is found that the spin probe in the liquid crystal reflects exactly the ordering of the liquid crystal.

Figure 6 shows that the Arrhenius plots of τ_2 give a straight line in both the smectic phases G and B. The correlation time τ_2 is dependent merely on the temperature in spite of the smectic phases. The activation energy in these phases is found to be $Ea = 29.6$ kJ/mol. This value is slightly larger than 24.8 kJ/mol in the smectic B phase of *N*-(4-butoxybenzylidene)-4′-octylaniline.[3] The Arrhenius plots for τ_0 give a straight line from 40 to 20°C in the smectic phase G, and the activation energy obtained for τ_0 is 16.4 kJ/mol. It is apparent in the figure that τ_0 at 10°C is deviated from an extrapolated point of the line to the longer correlation time. These results indicate that the mobility about the rotation does not change in this temperature range, but the fluctuation begins to be restricted in the vicinity of the Smectic G–Crystal transition point. Upon passing into the smectic

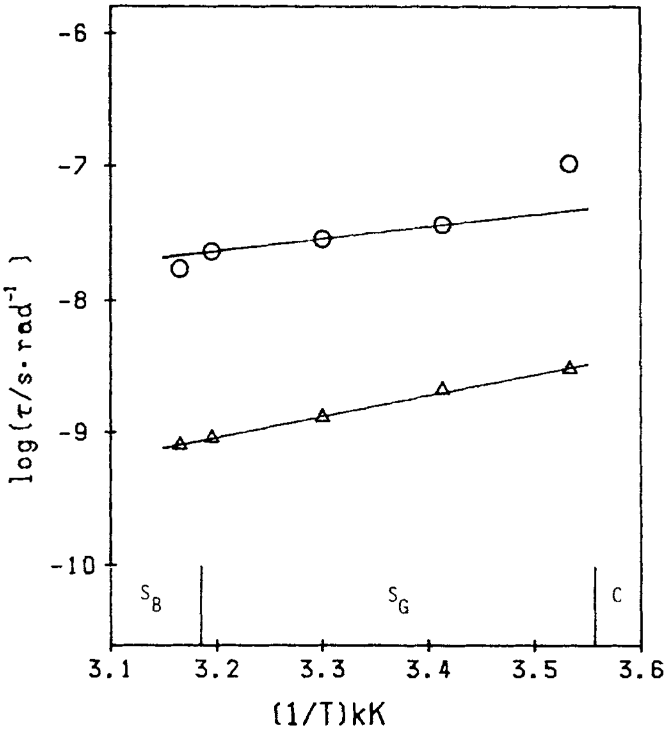


FIGURE 6 The temperature dependence of the correlation times τ_0(○) and τ_2(△).

B, τ_0 shows a shorter correlation time deviated from the straight line in the smectic G. It should be noted that the fluctuational motion is affected substantially compared to the rotational motion by the subtle change of the structure.

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