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Electron Paramagnetic Resonance Study of Two Smectic A Liquid Crystals

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Abstract—We have studied the molecular ordering in two smectic A liquid crystals using vanadyl acetylacetonate as a paramagnetic probe. We have also measured the average hyperfine splitting of the spectrum in the smectic A mesophase as a function of orientation relative to the d.c. magnetic field of the spectrometer, after the molecules of the liquid crystal were aligned by cooling from the nematic mesophase in a magnetic field. Aligning fields of 3300 and 11 000 gauss were used. 4-butyloxybenzylidene-4-acetoaniline exhibited a monotonically increasing order with decreasing temperature throughout its nematic and smectic A mesophases. 4-octyloxybenzylidene-4′-ethylaniline displayed an abrupt change in molecular order at the nematic–smectic A transition. If aligned in a 3300 gauss field, the order apparently decreased. If aligned in an 11 000 gauss field, the order apparently increased. The different behavior of the two compounds may be explained on the basis of their different heats of transition. The orientation studies indicated that, if the molecules of the liquid crystal were aligned in the smectic A mesophase, they maintained this alignment upon rotation in the magnetic field of the spectrometer.

1. Introduction

In the past nematic liquid crystals have been used as orienting solvents in nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) studies. At first sight, smectic liquid

crystals should be even more advantageous in such studies. This arises from the belief that their preferred direction would remain fixed with respect to the sample tube even upon rotation in the d.c. magnetic field of the spectrometer. Generally, it has been found that the high viscosity of most smectic liquid crystals results in such broad resonance lines that meaningful results are unobtainable.[1] Recently, however, Yannoni[2] has shown that narrow NMR lines are obtainable for an organic solute dissolved in the smectic liquid crystal, *p*-(*p*-2-*n*-propoxyethoxybenzylideneamino) acetophenone, and Luckhurst[3] has obtained narrow EPR lines for an inorganic solute dissolved in another smectic liquid crystal 4-4′-di-*n*-heptyloxyazoxybenzene.

We have been determining the degree of order in several nematic liquid crystals[4,5] using an EPR technique in which the liquid crystal is doped with a nearly planar paramagnetic molecule, vanadyl acetylacetonate (VAAC). From the measurement of the average hyperfine splitting of the eight lines in the spectrum of the VAAC, it is possible to determine the ordering of the probe molecules. The degree of order of the molecules of the liquid crystal is inferred from this. We have been extending these studies to liquid crystals that have both nematic and smectic mesophases, and have also obtained usable EPR spectra in the smectic mesophases of several liquid crystals. In recent work[6] using a smectic C liquid crystal it was possible to infer the tilt angle of the liquid crystal. The tilt angle was determined from the variation of the average hyperfine splitting of the probe molecule upon rotation of the sample in the magnetic field.

In this article we describe some results of the application of the technique to two smectic A liquid crystals. For one of them we have determined the degree of order as a function of temperature. And for both of them we have measured the variation of the average hyperfine splitting of the probe molecule as a function of orientation relative to the magnetic field after the molecules of the liquid crystals were aligned in magnetic fields of 3300 and 11 000 gauss.

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2. Experimental

The two liquid crystals used were: 4-octyloxybenzylidene-4′-ethylaniline (OBEA), and 4-butyloxybenzylidene-4′-acetoaniline (BBAA). Both displayed a nematic mesophase at a temperature just above the smectic A phase. The nematic range of OBEA is from 72.5 to 71.0 °C, and its smectic A range is from 71.0 to 62.5 °C. The corresponding ranges for BBAA are 111 to 99 °C, and 99 to 84 °C. The transition temperatures were obtained from differential thermal analysis (DTA) measurements made with a Dupont Thermograph analyzer; this instrument employs precision-made chromel–alumel thermocouples directly immersed in the sample under investigation. Programmed heating was linear at 5° per minute; samples were 3–5 mg and were referenced to alumina which exhibits no thermal transitions over the temperature range of interest (25 to 200°). The method described by David[7] was used for determination of heats of transition; 20–30 mg samples were used for these measurements. Benzoic acid was employed to calibrate the thermocouple and sample compartment; measurements were reproducible to within ±20%.

Syntheses of Liquid Crystals

4-*Alkyloxybenzaldehydes.* Alkyloxybenzaldehydes were prepared by the Williamson method from 4-hydroxybenzaldehyde and either *n*-butyl or *n*-octyl bromide in absolute ethanol with sodium ethoxide. The crude products were stripped of ethanol, washed with water then dried over sodium sulfate and vacuum distilled.[8,9]

4-*Alkyloxybenzylidene-4′-substituted anilines.* Equimolar amounts of the appropriate 4-alkyloxybenzaldehyde and either 4-ethylaniline or 4-aminoacetophenone were mixed at room temperature in absolute ethanol (100 ml for 0.1 mole) then heated on a steam bath for 20 minutes. The product which crystallized from the cooled solution was collected, dried, and recrystallized from ethanol to give the pure mesomorphic compound.

Procedure

A small amount of VAAC (mole fraction $< 10^{-3}$) was added to each liquid crystal sample to act as a paramagnetic probe. EPR spectra were obtained using a Varian 4502 X-band spectrometer. The samples were heated using a Varian 4547 variable temperature accessory and temperatures were monitored with a 36 gauge copper - constantan thermocouple inserted in the nitrogen stream that heated the sample. The details of the sample preparation were described previously.[4,5]

We determined the degree of order as a function of temperature in the same manner as that reported previously,[4,5] by heating the liquid crystal into its isotropic phase, and recording the spectra at a series of descending temperatures throughout the nematic and smectic mesophases.

In the smectic A mesophase we also determined the average hyperfine splitting as a function of rotation of the sample relative to the d.c. magnetic field of the spectrometer. The molecules of the liquid crystal were aligned in the nematic phase by a magnetic field, and the sample was then slowly cooled into the smectic A phase. Aligning fields of 3300 and 11 000 gauss were used. The EPR spectra were recorded in the smectic mesophase in a magnetic field of 3300 gauss at every 10° rotation of the sample relative to the magnetic field.

3. Theory

VAAC has approximately axial "g" and hyperfine tensors, so that its spin Hamiltonian can be written as

$$\mathscr{H} = \beta[g_{\parallel} H_r S_r + g_{\perp}(H_p S_p + H_q S_q)] + A_{\parallel} I_r S_r + A_{\perp}(I_p S_p + I_q S_q) \tag{3.1}$$

where p, q, and r are a set of rectangular axes fixed with respect to the VAAC molecule, and r is parallel to the $V = 0$ bond direction (see Fig. 1). $A_{\perp}$, $A_{\parallel}$ and $g_{\perp}$, $g_{\parallel}$ are the perpendicular and parallel components of the hyperfine and "g" tensors, respectively, and S and I are components of the electronic and nuclear spin vectors. If $g\beta H$ is very large compared to the anisotropic part of the hyperfine

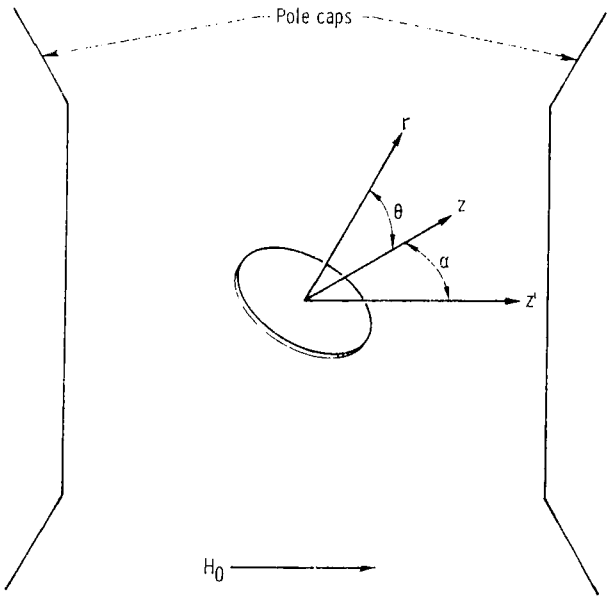


Figure 1. Coordinates, looking down on magnet; both z and z' are in the horizontal plane. The disk is representative of the plane of the VAAC molecule.

tensor it can be shown[4,5] that the Hamiltonian may be rewritten as

$$\mathscr{H} = g\beta H_z S_z + a\mathbf{I}\cdot\mathbf{S} + \frac{b}{3}(3\cos^2\theta - 1)I_z S_z \tag{3.2}$$

where x, y, and z are a set of rectangular coordinates fixed in the laboratory frame, with z parallel to the preferred direction of the molecules of the liquid crystal. For nematic materials this direction coincides with the magnetic field direction. Also $a = (1/3)(A_\parallel + 2A_\perp)$ and $b = (A_\parallel - A_\perp)$ are the isotropic and anisotropic parts of the hyperfine tensor. We have assumed $\Delta g = g_\parallel - g_\perp = 0$. This leads to an error of less than 1%. If the material is in the nematic phase and the VAAC molecules can tumble freely we can rewrite the Hamiltonian (Eq. (3.2)) by temporal averaging as

$$\mathscr{H} = g\beta H_z S_z + a\mathbf{I}\cdot\mathbf{S} + \frac{2b}{3}\sigma_z S_z I_z \tag{3.3}$$

where $\sigma_z \equiv \langle 3\cos^2\theta - 1\rangle/2$ is the order parameter. If $\langle a\rangle$ is the

average hyperfine splitting of the eight vanadium lines ($I = 7/2$, $S = 1/2$), then the order is given[4,5] by $(\langle a \rangle - a)/2(a - A_\perp)$ in which we have used[10] $a = -107$ gauss and $A_\perp = -68.5$ gauss. Complete order corresponds to a value for σ_z of -0.5. The negative sign arises because the VAAC is aligned with its plane parallel to the direction of the magnetic field and with the $V = 0$ bond direction perpendicular to the field.

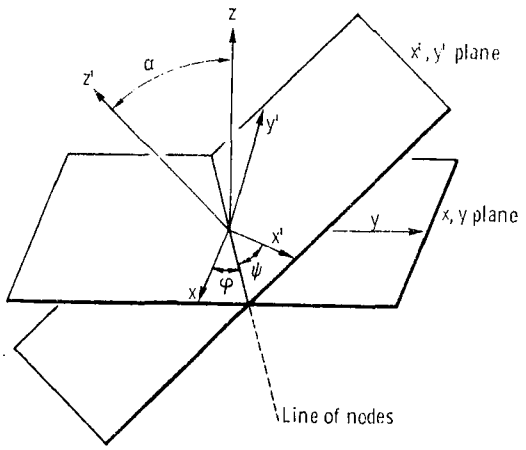


Figure 2. The Euler angles, after Goldstein.[11]

Let us now consider what happens when the material is in a smectic A mesophase, and let us recall that the z axis was defined to be parallel to the preferred molecular direction. Suppose the magnetic field has been rotated an angle α away from the z axis (see Fig. 1). Unlike nematic liquid crystals, the molecular direction does not remain parallel to the magnetic field. If x', y', and z' represent a rectangular coordinate system with z' parallel to the magnetic field, and if the Euler[11,12] angles of x', y', and z' relative to x, y, and z are given by φ, α, and ψ (see Fig. 2), then we can write Eq. (3.2) in the primed system as:

$$\begin{aligned}\mathscr{H} = g\beta H_{z'} S_{z'} + a\mathbf{I}\cdot\mathbf{S} + \frac{b}{3} I_{z'} S_{z'} \Big[& \frac{1}{2}(3\cos^2\alpha - 1)(3\cos^2\theta - 1) \\ & + 3i \sin\alpha \cos\alpha \, e^{i\psi} \sin\theta \cos\theta \, e^{i\varphi} + \text{complex conjugate} \\ & + \frac{3}{4} \sin^2\alpha \, e^{2i\psi} \sin^2\theta \, e^{2i\varphi} + \text{complex conjugate} \Big] \end{aligned} \tag{3.4}$$

If we now take the temporal average remembering that the averages over φ go to zero, then Eq. (3.4) simplifies to

$$\mathcal{H} = g\beta H_{z'}S_{z'} + a\mathbf{I}\cdot\mathbf{S} + \frac{b}{3}I_{z'}S_{z'}\frac{1}{2}(3\cos^2\alpha - 1)\langle 3\cos^2\theta - 1\rangle \quad (3.5)$$

If $\alpha = 0$, Eq. (3.5) reduces to Eq. (3.3) and the order parameter can be obtained as before.

Eq. (3.5) predicts absorption lines at magnetic fields given by

$$H = (2/g)H_0 - am_I - \frac{b}{3}\sigma_z(3\cos^2\alpha - 1)m_I + \text{terms in } m_I^2 \quad (3.6)$$

where H_0 is the field corresponding to $g = 2$ at our spectrometer frequency, and a and b are now in units of gauss. The average line splitting for the eight line spectrum, i.e., the total separation divided by seven, is then given by

$$\langle a\rangle = a + \frac{b}{3}\sigma_z(3\cos^2\alpha - 1) \quad (3.7)$$

Our results, presented below, show that $\langle a\rangle$ varies with α approximately as predicted by this equation.

4. Results

Liquid Crystal BBAA

Typical spectra of VAAC in BBAA are shown in Fig. 3. Curve (a) was obtained in the nematic mesophase of the liquid crystal (T = 100 °C), and displays the contracted spectrum indicative of ordering ($\sigma_z = -0.21$). Curve (b) was obtained in the smectic A mesophase (T = 90 °C) after cooling from the nematic mesophase while in a magnetic field of 3300 gauss. Curve (b) also displays a contracted spectrum indicative of ordering ($\sigma_z = -0.26$). The line widths are larger than in the nematic mesophase and some overlapping of both pairs of end lines is evident. In addition, the end lines are slightly asymmetric. These two features indicate that the VAAC molecules are undergoing some restriction of their free tumbling due to the higher viscosity of the smectic mesophase. The effect of high viscosity is to cause a decrease in the average splitting,[13] resulting in an " apparent " increase in the degree of order; i.e., an increase in the absolute magnitude of σ_z. In the extreme, this effect leads to a

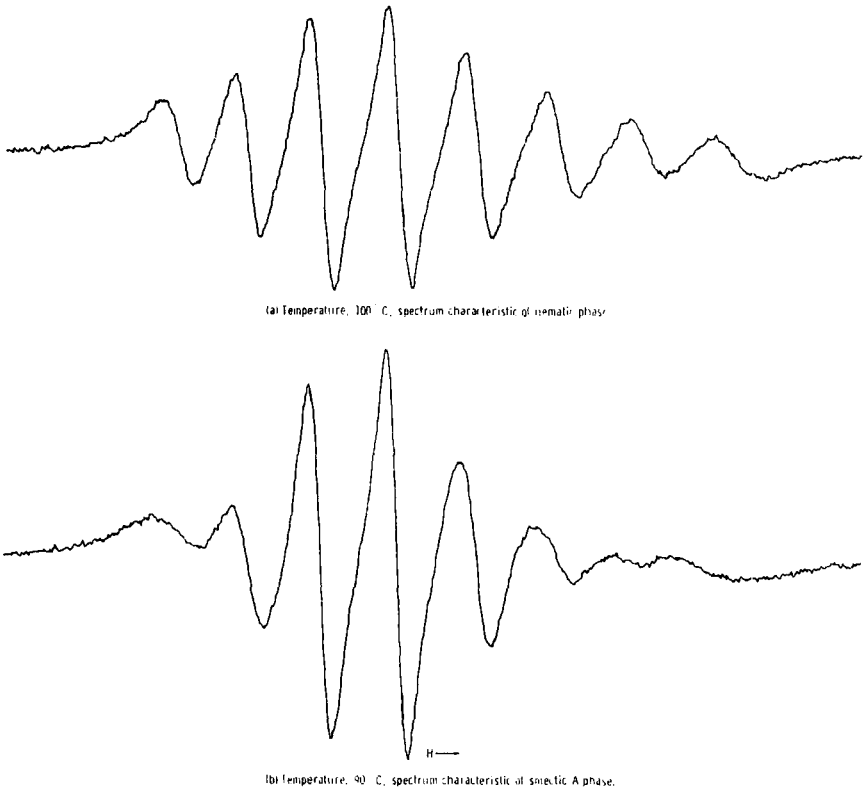


Figure 3. Derivative spectra of vanadyl acetyacetonate in 4-butyloxy benzal-4′-acetoaniline.

" glassy type " spectrum with apparently complete ordering in the liquid crystal.[5] The spectrum shown here indicates that while there is some restriction on the free tumbling of the VAAC molecules, it should still be of value to investigate σ_z in the smectic A mesophase. It must be kept in mind, however, that the absolute values of the σ_z may be high due to viscosity effects.

The variation of the order parameter as a function of temperature throughout the nematic and smectic A ranges is shown in Fig. 4 where we have plotted $-\sigma_z$ against the reduced temperature, T^*. Here $T^* = T/T_K$ where T_K is the nematic–isotropic ($n \rightarrow i$) transition temperature in Kelvins. The behavior is typical for nematic liquid crystals.[4,14] There appears to be no discontinuity at the nematic–

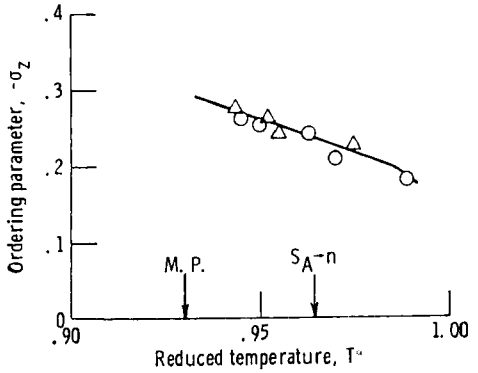


Figure 4. Ordering parameter $-\sigma_z$ as a function of reduced temperature T^* for 4-butyloxybenzal-4′-acetoaniline. Different symbols denote different samples.

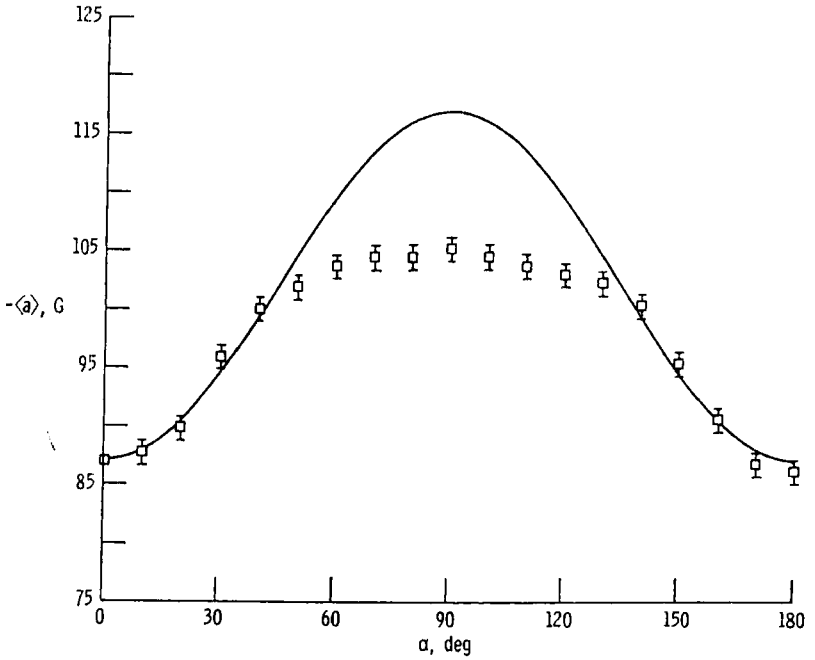


Figure 5. Average splitting constant $\langle a \rangle$ as a function of the angle of rotation α for 4-butyloxybenzal-4′-acetoaniline (T = 90 °C). Sample previously aligned by cooling through the nematic phase in a magnetic field of 3300 gauss.

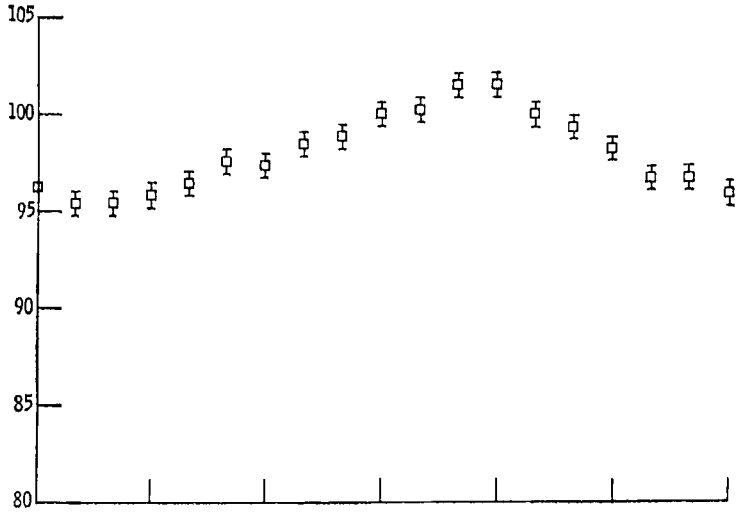
smectic A ($n \rightarrow S_A$) transition indicating that the order is maintained through the transition and that it is determined by a similar parameter in both mesophases.

The average splitting in the ordered smectic A mesophase as a function of the orientation relative to the magnetic field is plotted in Fig. 5. As shown by the error bars the measurements are not of good precision. This is caused by the overlap of the end lines due to line broadening. At 0 and 180° the average splitting is characteristic of the order for the given temperature ($T = 90\,°C$). The curve is representative of the function $-107 + 10(3\cos^2\alpha - 1)$, which was obtained from Eq. (3.7) taking $a = -107$ gauss, $A_\parallel = -185$ gauss, and $A_\perp = -68.5$ gauss, and using our experimental value $\sigma_z = -0.26$ obtained at this temperature. The average splitting varies with α as predicted by the theoretical curve except for values of α between 45 and 135°. In this region the results fall below the predicted values. The discrepancy may result from restriction of the free tumbling of the VAAC molecules discussed above. In spite of the discrepancy, the agreement with the theoretical equation allows us to conclude that the molecules of the liquid crystal indeed maintain their orientation with respect to the sample tube upon rotation in the magnetic field. It should be noted that the results were the same whether the sample was aligned in a 3300 or 11 000 gauss field.

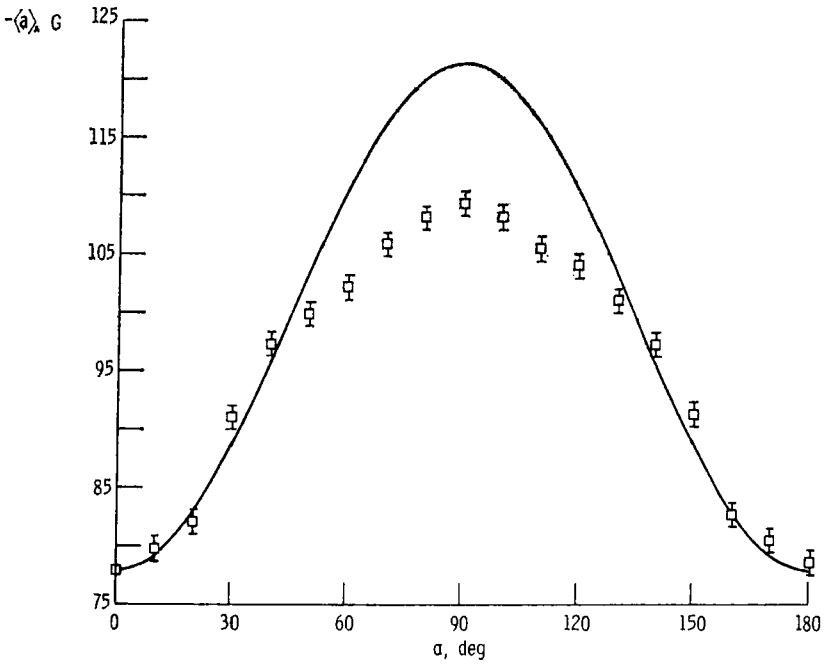
Liquid Crystal OBEA

The spectra of VAAC in OBEA were similar in appearance to those in BBAA, though in some cases the viscosity effects were even more pronounced. The nematic range in OBEA is only 1.7 °C, so it was not possible to measure σ_z as a function of temperature in this phase. Selected values obtained in the nematic mesophase were around $\sigma_z = -0.2$. The order parameter displayed a sharp discontinuity at the $n \rightarrow S_A$ transition when cooled in the 3300 gauss field. The value of σ_z changed from -0.2 to -0.15 indicating an apparent decrease in the order.

The average splittings as a function of orientation relative to the magnetic field are plotted in Fig. 6(a) ($T = 67.5\,°C$). These results are for alignment in the 3300 gauss field. The data show that orientation relative to the field has little effect on the average line splitting.



(a) Sample previously aligned by cooling through the nematic phase in a magnetic field of 3300 gauss.



(b) Sample previously aligned by cooling through the nematic phase in a magnetic field of 11 000 gauss.

Figure 6. Average splitting constant $\langle a \rangle$ as a function of the angle of rotation α for 4-Octyloxybenzal-4′-ethylaniline ($T = 67.5$ °C).

Cooling through the $n \rightarrow S_A$ transition in an 11 000 gauss field had a very different effect. For this case σ_z was found to be -0.38, indicating an apparent marked increase in order compared with the nematic mesophase. However, the end lines of the spectra in the smectic mesophase now exhibited greater asymmetry. The orientation relative to the magnetic field had a large effect on the average splitting. The results are shown in Fig. 6(b). The curve is representative of the function $-107 + 14.5(3\cos^2\alpha - 1)$, where we have used the values for the splitting constants as before along with our experimental value of $\sigma_z = -0.38$. As with BBAA, the average splitting varies with α as predicted except for values of α from 45 to 135°, and as before the discrepancy in this region may result from restriction on the tumbling of the VAAC molecules.

5. Discussion

The appearance of the spectra obtained in the smectic A mesophase of these two liquid crystals indicates that the high viscosity of the mesophase may be a contributing factor in determining the average splitting. Nevertheless, certain conclusions may be deduced from consideration of the results presented above.

The two liquid crystals exhibited markedly different behavior in cooling through the $n \rightarrow S_A$ transition in the two different aligning fields. The BBAA maintained its degree of order in either field and the values of σ_z were essentially the same in both cases. It should be noted that σ_z was only -0.25 in the smectic A mesophase. In addition, rotation of the sample in the magnetic field of the spectrometer, showed that the molecules of the liquid crystal maintained their original alignment with respect to the sample tube. We may conclude, therefore, that the smectic A mesophase of 4-butyloxybenzylidene-4′-acetoaniline could be a useful solvent for NMR studies though a solvent with a higher degree of order might be preferable. It should be pointed out that the viscosity effect would be much less of a factor in NMR where the frequency of the exciting radio waves is smaller by a factor of 100. This relaxes the restrictions on the correlation time by a similar factor.

The OBEA, in contrast, exhibited a decrease in the absolute magnitude of σ_z in the 3300 gauss aligning field but a large increase,

in the 11 000 gauss field. In the low field case, the interaction between the field and the molecules is apparently not strong enough to maintain the alignment attained in the nematic mesophase. The liquid crystal probably " recrystallizes " into a domain structure in which different domains have preferred directions slightly different from the field direction. The variation in preferred direction is not enough to give a completely randomized sample, but it is enough to result in a decrease in the absolute magnitude of the order parameter from -0.2 to -0.15. Some of the domains may constitute a large fraction of the sample. This could account for the shift in the maximum in Fig. 6(a) from the theoretical angle of 90° to the experimentally observed angle of 115°, assuming a large domain was formed with its preferred direction tilted 25° to the field direction. In the high field case the interaction between the molecules of the liquid crystal and the magnetic field appears to be large enough to maintain the alignment attained in the nematic mesophase. The large increase in the absolute magnitude of σ_z, in part, probably arises from the viscosity effect, as the end lines in the spectra exhibit definite asymmetry. However, there may be some real increase in the order arising from the stronger lateral attractions between the molecules of the liquid crystal that are extant in the smectic mesophase. In any case, the rotation of the sample in the field of the spectrometer (see Fig. 6(b)) indicated that the molecules of the liquid crystal maintained their original alignment with respect to the sample tube once they were aligned in the smectic mesophase. Hence, 4-octylaxybenzylidene-4′-ethylaniline might also be a useful solvent for NMR studies provided a large enough field is used for alignment, especially if the degree of order is as high as indicated by the order parameter.

It is difficult to assess why the two liquid crystals behave so differently upon cooling from the nematic to the smectic A mesophase in the magnetic fields. There is a paucity of physical information pertinent to these $n \rightarrow S_A$ transitions. However, our DTA's of these two compounds indicate that the enthalpy change for the $n \rightarrow S_A$ transition is roughly three times greater for OBEA than for the BBAA. Since the $n \rightarrow S_A$ transition temperature of the OBEA is only 30 °C lower than that of the BBAA, the entropy change for the OBEA must be over three times greater in absolute magnitude than

for the BBAA. This indicates that much more ordering takes place during the $n \rightarrow S_A$ transition of the OBEA than during that of the BBAA, probably as a result of stronger lateral attractions between the molecules of this liquid crystal. Our experimental results are in agreement with these hypotheses, and it may be anticipated that the ordering behavior of a liquid crystal cooling through its $n \rightarrow S_A$ transition will be determined by the magnitude of the entropy change of the transition.

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