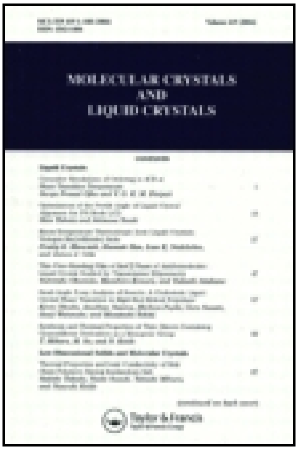

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Electron Paramagnetic Resonance Study of Alinement Induced by Magnetic Fields in Two Smectic *A* Liquid Crystals Not Exhibiting Nematic Phases

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Abstract—Using vanadyl acetylacetonate (VAAC) as a paramagnetic probe, we have studied the molecular ordering in two smectic *A* liquid crystals that do not display nematic phases. We have attained reproducible alinement by slow cooling through the isotropic–smectic *A* transition in dc magnetic fields of 11,000 G and 21,500 G. The degree of order attained is small for a smectic *A* liquid crystal, being $\sigma_z = -0.1$. Measurements have been made of the variation of the average hyperfine splitting of the alined samples as a function of orientation relative to the dc magnetic field of the spectrometer. This functional dependence is in agreement with the theoretical prediction except where the viscosity of the liquid crystal becomes large enough to slow the tumbling of the VAAC as indicated by asymmetry in the end lines of the spectrum.

1. Introduction

The technique of electron paramagnetic resonance (EPR) has previously been used to determine the ordering properties of both nematic liquid crystals(1,2) and smectic liquid crystals which have a nematic phase.(3,4) The technique consists of doping the liquid crystal with a small amount (10^{-3} M) of the nearly planar paramagnetic molecule, vanadyl acetylacetonate (VAAC). This molecule exhibits a broad, eight-line spectrum with axial *g* and hyperfine tensors. From the measurement of the average hyperfine splitting of the spectrum, it is possible to determine the orientation of the probe molecules, and from this the degree of order of the molecules of the liquid crystal is inferred.

The dc magnetic field of the EPR spectrometer is large enough to aline the molecules in a nematic liquid crystal; that is, the field makes the preferred direction of the liquid crystal molecules uniform throughout the sample. The degree of order can be determined as a function of temperature throughout the nematic phase. A magnetic field will not aline the molecules in the smectic phase of a liquid crystal. However, if the smectic liquid crystal displays a nematic phase, the molecules can be alined in this phase and then slowly cooled into the smectic phase while in the magnetic field.(3) Since the magnetic field will not realine the molecules in the smectic phase, it is possible to study the EPR spectra as a function of sample orientation relative to the field.(3,4)

In this study a dc magnetic field was used to aline two smectic *A* liquid crystals that do not display a nematic phase. Foex(5) has stated that an alined smectic phase could be obtained by cooling the isotropic melt in a magnetic field, though Luckhurst and Sanson,(6) more recently, were unable to duplicate this claim with fields up to 6,500 G. We have been able to obtain alinement in fields of 11,000 G and 21,000 G. We have also measured the effect on the hyperfine splitting of sample orientation relative to the magnetic field.

This investigation is part of a continuing cooperative research program between personnel of the NASA Lewis Research Center and Kent State University. The research in The Liquid Crystal Institute at Kent State University is partly supported by the Air Force Office of Scientific Research, Office of Aerospace Research Contract F 44620–69–C–0021.

2. Experimental

The two liquid crystals used were: 4-hexyloxybenzylidene-4′-aminobenzoate ethyl ester (HBABE) and 4-octylyoxybenzylidene-4′-aminobenzoate ethyl ester (OBABE). The HBABE displayed a smectic *A* phase from 69° to 96 °C, while the OBABE displayed a smectic *A* phase from 75° to 98 °C. The materials were synthesized and purified for us by Dr. D. L. Fishel of Kent State University.

The details of the sample preparation were described previously.⁽¹⁾ Briefly a small amount of VAAC (10^{-3} M) was added to each liquid crystal sample and dissolved oxygen was removed by evacuation during melting. EPR spectra were obtained using a modified Varian E-12 X-band spectrometer. Samples were heated using a modified 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 smectic *A* liquid crystals were ordered by slow cooling through the isotropic → smectic *A* transition while in a magnetic field. Fields of 3,300 G, 11,000 G, and 21,000 G were used. Cooling rates of $\frac{1}{8}$ °C per minute were employed. The EPR spectra of the alined smectic sample were recorded for every 10° of rotation relative to the magnetic field of the spectrometer (3,300 G).

3. Theory and Results

The theory required for interpreting the results of this study has been described previously.⁽³⁾ The variation of the average hyperfine splitting of the spectra, $\langle a \rangle$, with the angle of rotation relative to the dc magnetic field, α, is given by the expression

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

where a is the isotropic hyperfine splitting⁽⁷⁾ (-107 G) and b is the anisotropic splitting (-121.5 G). The ordering parameter, σ_z, for $\alpha = 0$ is obtained from the expression

$$\sigma_z = \frac{\langle a \rangle_0 - a}{2(a - A_\perp)} \qquad (2)$$

where $A_\perp$ is the perpendicular component of the axial hyperfine tensor⁽⁷⁾ (-66.5 G) and $\langle a \rangle_0$ is the experimentally determined average hyperfine splitting after cooling through the isotropic to smectic *A* transition. It should be noted that the pseudo-secular terms have been neglected in deriving Eq. (1). This results in a maximum difference from the exact equation⁽⁸⁾ of less than 1% at $\alpha = 45°$. At $\alpha = 0°$ and 90° the two equations are equivalent.

Preliminary experiments with these two liquid crystals indicated that cooling through the isotropic → smectic $A(i \rightarrow S_A)$ transition in a 3,300 G field resulted either in no ordering or, sometimes, in a very small degree of ordering ($\sigma_z < -0.05$). The degree of ordering was not reproducible even though slow cooling rates were used. However, with 11,000 G and 21,000 G fields, reproducible ordering was obtained with slow cooling. The degree of order attained was the same for both the 11,000 G and the 21,000 G fields. With rapid cooling, no order was effected. Frequently, the spectra obtained after cooling in the 21,000 G field displayed small extra lines. This effect became progressively greater with sample use, and when the effect became pronounced, the sample was discarded.

Slow cooling of HBABE in an 11,000 G (or 21,000 G) field resulted in a small degree of order: $\sigma_z = -0.087$. The EPR spectra indicated that the viscosity of the liquid crystal was exerting only a moderate influence; that is, the lines were broadened but they were not asymmetric. In Fig. 1 we show the results of the rotation of the alined sample in the 3,300 G dc field of the spectrometer. We have plotted the average splitting, $\langle a \rangle$, as a function of the angle of rotation relative to the magnetic field, α. At 0° and 180° the average splitting is characteristic of the order for the given temperature ($T = 91.5$ °C); namely, $\sigma_z = -0.087$. The curve is representative

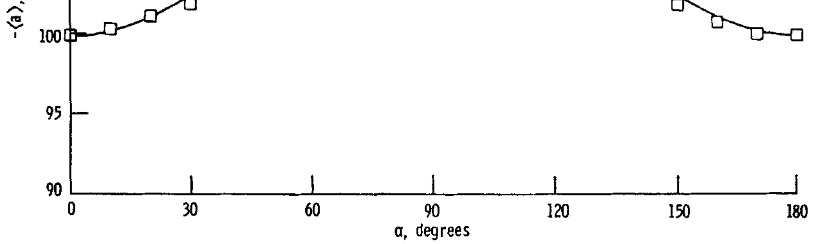

Figure 1. Average hyperfine splitting, $\langle a \rangle$, as a function of angle of rotation, α, for 4-hexyloxybenzylidene-4′-aminobenzoate ethyl ester at 91.5 °C.

of the theoretical function obtained from Eq. (1) by substituting the experimental value of σ_z and the reported hyperfine parameters.$^{(7)}$ The agreement between the experimental points and the theoretical curve is within experimental error.

Slow cooling of OBABE in an 11,000 G or 21,000 G field gave results very similar to those obtained with HBABE. The degree of order was a little higher, $\sigma_z = -0.115$. Spectra were taken at three different temperatures within the smectic *A* phase; namely 96 °C, 84 °C, and 75 °C. Spectra obtained at 96 °C show little viscous effects other than some line broadening, and are similar to those obtained with HBABE. However, spectra obtained at 84 °C show slight asymmetry in the shape of the two end lines. This asymmetry indicates that the viscosity is significantly affecting the tumbling time of the VAAC molecules.$^{(2)}$ This effect is even more pronounced in the spectra obtained at 75 °C. Rotation experiments were performed at these same three temperatures. The results are presented in Fig. 2. The degree of order was the same at all temperatures; $\sigma_z = -0.115$. Again, the curve is representative of the theoretical function obtained by substituting this value of σ_z along with the reported hyperfine parameters into Eq. (1). The data taken at 96 °C agrees with the theoretical curve within experimental

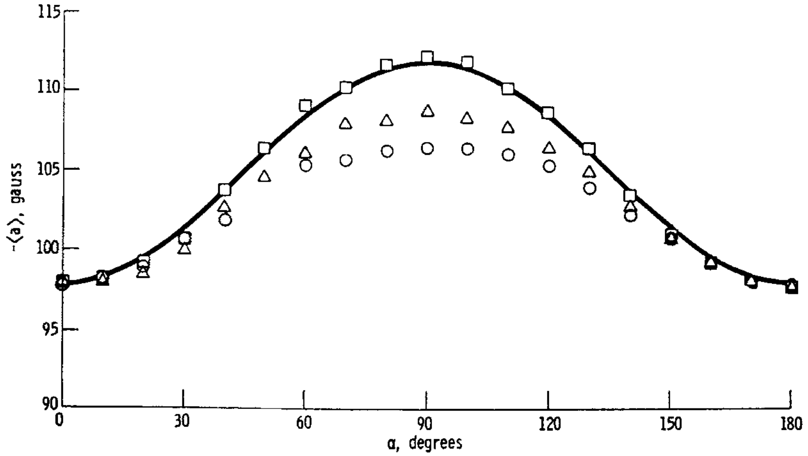

Figure 2. Average hyperfine splitting, $\langle a \rangle$, as a function of angle of rotation, α, for 4-octyloxybenzylidene-4′-aminobenzoate ethyl ester at 96 °C (squares), 84 °C (triangles) and 75 °C (circles).

error. However, the data taken at 84 °C and 75 °C fall below the theoretical curve at angles between 45° and 135°.

Some visual observations of the liquid crystals were made during their cooling through the $i \rightarrow S_A$ transition. The experiments were conducted in an auxiliary magnet capable of producing fields up to 21,500 G. For fields greater than 10,000 G and with slow cooling the first visual indication that the $i \rightarrow S_A$ transition has been reached was the appearance throughout the clear isotropic liquid of horizontal needles growing in from the inside surface of the quartz sample tube. This was followed by a gradual clearing until the entire sample was again quite clear. However, careful examination in oblique light revealed the presence of very fine horizontal rings visible at the tubing wall. Warming this sample up through the transition indicated that the process was reversible, though the needle-like phase was more pronounced and more opaque than during the cooling. For fields around 3,300 G or with fast cooling through the transition, the sample did not appear to be uniform throughout. There were several planes visible across the quartz tube, and they were not always horizontal. In addition, the samples did not become as clear, and different regions displayed different variations of clearing.

4. Discussion

Alignment of two smectic *A* liquid crystals not displaying nematic phases has been attained in the experiments described above. However, the degree of order attained is quite small for a smectic *A* liquid crystal. In addition, the spectral lines were quite broad, possibly indicating that the direction is not uniform throughout the entire sample. That this is the case is especially evident from our visual observations for the fast-cooling experiments and for the experiments in the 3,300 G field. The appearance of small extra lines in the spectra obtained in some of the slow-cooling, high-field experiments may also arise from the nonuniformity of the director throughout the entire sample.

In our orientation studies the agreement between the experimental values and the theoretical curve is good except in the case of OBABE at the lower temperatures (Fig. 2). The asymmetry in the end lines of the spectra obtained at these temperatures indicates that the tumbling of the VAAC molecule is being slowed by the higher viscosity of the liquid crystal. The effect becomes greater as the temperature is decreased. We feel the discrepancy between experiment and theory is associated with this viscous effect. This conclusion is in agreement with that postulated in one of our recent studies$^{(3)}$ involving two other smectic A liquid crystals: 4-butyloxybenzylidene-4′-acetoaniline (BBAA) and 4-octyloxybenzylidene-4′ethylaniline. For these liquid crystals the viscous effects were much more pronounced and the discrepancy between experiment and theory was larger. Recently, Luckhurst and Setaka$^{(9)}$ have repeated our experiments with BBAA, but using a nitroxide probe. The nitroxide probe tumbles rapidly ($\tau_c = 10^{-10}$ sec), and the effects associated with the viscosity are absent. They found very close agreement between their experimental points and their fitted equation. This result corroborates our contention that the discrepancy between experimental points and the theoretical curve in these orientation experiments arises from a viscous effect of the liquid crystal on the probe molecule, VAAC.

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