



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/gmcl16>

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Version of record first published: 28 Mar 2007.

To cite this article: G. R. Luckhurst & M. Setaka (1972): Molecular Organization in the Nematic and Smectic A Mesophases of 4-n-butyloxybenzylidene-4'-acetoaniline, *Molecular Crystals and Liquid Crystals*, 19:2, 179-187

To link to this article: <http://dx.doi.org/10.1080/15421407208083862>

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Molecular Organization in the Nematic and Smectic A Mesophases of 4-*n*-butyloxybenzylidene-4'-acetoaniline

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Received May 15, 1972

Fryburg, Gelerinter and Fishel have studied the structure of two smectic A phases using electron resonance spectroscopy with vanadyl acetylacetonate as the spin probe.⁽¹⁾ Their analysis of the electron resonance spectra shows that in 4-*n*-butyloxybenzylidene-4'-acetoaniline the orientational order of the probe does not change at the nematic-smectic transition and that the temperature dependence of the order is the same in both phases. In addition the angular dependence of the vanadium coupling constant, in the smectic A phase, was found to be in poor agreement with theory. These findings are unexpected for the orientational order of spin probes dissolved in smectic A mesophases has been found^(2,3) to be essentially temperature independent in contrast to the behaviour in a nematic mesophase. Further the angular dependence of the hyperfine coupling was found to be in excellent agreement with theory.^(2,3) Finally earlier results indicate that there should be a discontinuity in the orientational order at the nematic-smectic transition.⁽³⁾ These differences have prompted us therefore to reinvestigate the molecular organization within the nematic and smectic A mesophases of 4-*n*-butyloxybenzylidene-4'-acetoaniline but with (3-spiro-[2'-N-oxyl-3',3'-dimethylloxazolidine]) 5 α -cholestane as a spin probe.⁽⁴⁾

The mesogen was synthesized⁽¹⁾ from 4-aminoacetophenone and 4-*n*-butyloxybenzaldehyde which was obtained by alkylating 4-hydroxybenzaldehyde.⁽⁵⁾ After three recrystallizations from

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ethanol the product melted at 84 °C, passed to the nematic phase at 98 °C and formed an isotropic melt at 110 °C, in good agreement with the literature values.⁽¹⁾ The transition temperatures were depressed by about two degrees on addition of the spin probe. The electron resonance spectra of the doped sample were recorded on a Varian E-3 spectrometer and the sample temperature was monitored with the aid of a copper-constantan thermocouple immersed in the sample. The spectra measured when the sample was in the isotropic and nematic phases contained the three relatively sharp lines expected for a nitroxide radical. However the form of the spectrum observed from the smectic A depended critically on the rate of cooling at the nematic smectic transition. For example if the sample is cooled rapidly ($\sim 0.5^\circ\text{C s}^{-1}$) in the magnetic field of 3.3 K gauss normally used to measure the spectrum then it contains five, and not the usual three hyperfine lines. The two additional lines are indicated by arrows in Fig. 1. The presence of these extra lines together with the shape of the other spectral lines clearly indicates that the smectic A phase is not perfectly oriented. In the nematic phase the director is parallel to the magnetic field but the magnetic free energy is presumably unable to maintain this alignment in the smectic phase

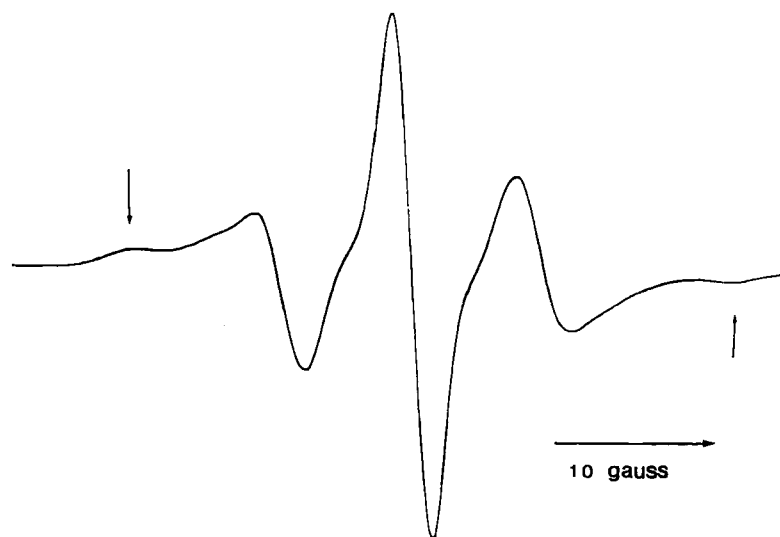


Figure 1. The electron resonance spectrum of the spin probe dissolved in a non-uniformly aligned sample of the smectic A mesophase.

because of the disrupting influence of surface and other forces at the nematic-smectic transition. Since this non-uniformity of the director might be difficult to observe when vanadyl acetylacetonate is used as a spin probe it may well be responsible for the unusual results obtained by Fryburg *et al.*⁽¹⁾ We were however able to obtain a homogeneous smectic A phase by coating the sample tube with plastic to reduce surface forces, using the maximum field of 6.5 K gauss obtainable on the E-3 and cooling at a rate of about 0.02 °C s⁻¹ at the nematic-smectic transition. We were therefore able to measure the nitrogen coupling constant in the isotropic melt and uniformly oriented nematic and smectic A phases as a function of temperature. The smectic phase is readily supercooled and it proved possible to obtain spectra at temperatures as low as 30 °C below the freezing point.

The symmetry and width of individual hyperfine lines shows that the rate of molecular reorientation, with respect to the director, is fast, with a correlation time of about 10⁻¹⁰ s. Further, since the spin probe is partially oriented by a pseudo-potential, which is cylindrically symmetric with respect to the director, the probe is equivalent to a static species with cylindrically symmetric magnetic interactions.^(6,7) For example the component of the hyperfine tensor \tilde{A} parallel to the director is

$$\tilde{A}_{\parallel} = a + (2/3)^{1/2} \sum_p (-1)^p A^{(2,p)} \mathcal{D}_{0,-p}^{(2)},$$

where a is the scalar coupling constant, $A^{(2,p)}$ is the anisotropic hyperfine tensor and the averaged Wigner rotation matrix $\mathcal{D}_{0,-p}^{(2)}$ measures the extent of solute alignment. The component perpendicular to the director is simply

$$\tilde{A}_{\perp} = a - (1/6)^{1/2} \sum_p (-1)^p A^{(2,p)} \mathcal{D}_{0,-p}^{(2)}.$$

In the case of nitroxides the important interactions are the electron and nitrogen Zeeman couplings, the electron-nuclear hyperfine interaction and the nitrogen quadrupole coupling. The form of the electron resonance spectrum for such a species is well known because of the previous studies of transition metal complexes in which the magnetic interactions were cylindrically symmetric with respect to a common axis.⁽⁸⁾ When the director is parallel to the magnetic field the spacing between hyperfine lines $\pm m$ is $2m\tilde{A}_{\parallel}$ where m is

the nuclear quantum number. The nitrogen hyperfine tensor for the spin probe is almost cylindrically symmetric⁽⁹⁾ and so the expression for \tilde{A}_i reduces to

$$\tilde{A}_i = a + A_{||}' \mathcal{D}_{0,0}^{(2)}.$$

In addition the spin probe possesses cylindrical symmetry about an axis orthogonal to the symmetry of the hyperfine tensor⁽¹⁰⁾ and so we may write

$$\tilde{A}_i = a - A_{||}' \bar{P}_2/2,$$

where $P_2(\cos \beta)$ is the second Legendre polynomial and β is the angle between the director and the molecular symmetry axis. The scalar nitrogen coupling constant was found to be 41.54 MHz in the isotropic melt of the mesogen and the tensor component $A_{||}'$ was determined from the spectrum of the radical dissolved in glassy o-terphenyl to be 51.3 MHz. We have therefore used our measurements of the nitrogen coupling constant to calculate the orientational order \bar{P}_2 of the probe dissolved in both mesophases of 4-*n*-butyloxybenzylidene-4'-acetoaniline. The results are plotted in Fig. 2 as a

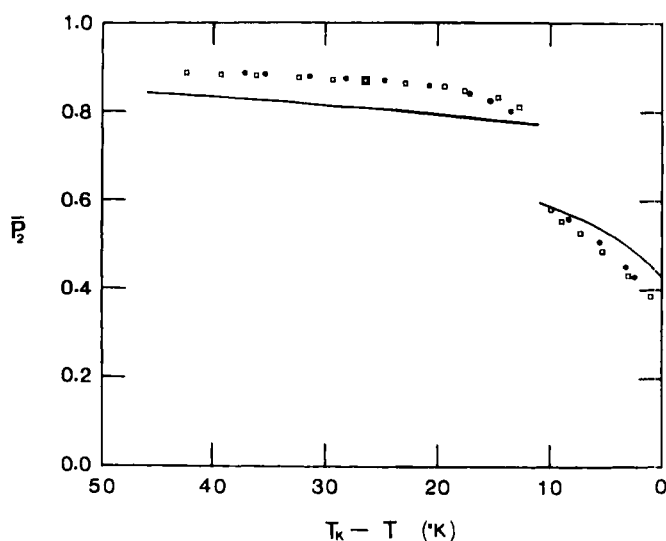


Figure 2. The temperature dependence of the orientational order \bar{P}_2 for the spin probe in the nematic and smectic A phases of 4-*n*-butyloxybenzylidene-4'-acetoaniline. The curves are obtained from a simple extension of the Maier-Saupe theory of the nematic mesophase.

function of $(T_K - T)$ where T_K is the nematic-isotropic transition temperature. This particular scale was chosen in order to compare samples whose different thermal histories had resulted in minor variations in the transition points.

The results in Fig. 2 show the strong temperature dependence of the orientational order expected⁽⁷⁾ when the probe is dissolved in the nematic mesophase. In contrast the orientational order in the smectic A mesophase is only slightly temperature dependent in agreement with the results for other mesogens.^(2,3) Finally the results exhibit a marked discontinuity in \bar{P}_2 , at the nematic-smectic transition, corresponding to an increase in orientational order of 0.17. We can understand these results by making a slight modification to the Maier-Saupe theory of the nematic mesophase.⁽¹¹⁾ According to this theory the orientational pseudo-potential takes the form

$$U(\beta) = \bar{u}_2 \bar{P}_2 P_2(\cos \beta),$$

where the parameter \bar{u}_2 is given by⁽¹²⁾

$$\bar{u}_2 = (1/\rho) \int \sum_n u_{22:n}(r) n^{(2)}(r) dr.$$

In this expression ρ is the number density, r is the intermolecular separation, $n^{(2)}(r)$ is the pair distribution function and $u_{22:n}(r)$ is a measure of the strength of the pairwise intermolecular interaction. The orientational order is calculated from the pseudo-potential by taking the appropriate Boltzmann average and so \bar{P}_2 is determined by the parameter \bar{u}_2 . We suppose therefore that the greater order in the smectic phase is caused by an increase in $|\bar{u}_2|$ at the nematic-smectic transition. This assumption is entirely reasonable since some long range spatial order is introduced at this transition. However to calculate the orientational order in both phases it is necessary to know the values of \bar{u}_2 in each phase. The parameter $\bar{u}_2^{(n)}$ for the nematic mesophase is readily obtained for, according to the Maier-Saupe theory, $\bar{u}_2^{(n)}$ is directly proportional to the nematic-isotropic transition temperature:

$$\bar{u}_2^{(n)} = -4.541kT_K.$$

We have estimated the parameter $\bar{u}_2^{(s)}$ for the smectic A phase in the following way. The orientational order in the nematic phase at the nematic-smectic transition may be calculated from $\bar{u}_2^{(n)}$; the order in the smectic phase, at the same temperature, is then calculated for a

range of $\bar{u}_2^{(s)}$ until the difference in the orientational order corresponds to the experimental value of 0.17. This procedure gives the reasonable value for $-\bar{u}_2^{(s)}/4.541k$ of 435 °K which should be compared with 383 °K found for $-\bar{u}_2^{(n)}/4.541k$. The theoretical temperature dependence of \bar{P}_2 obtained from these parameters, after allowing for their slight volume dependence,⁽¹²⁾ is shown as the solid lines in Fig. 2. Since no attempt was made to allow for solute-solvent interactions⁽¹³⁾ or for higher order terms in the pseudo-potential⁽¹²⁾ the theoretical curves cannot be expected to agree quantitatively with the orientational order observed for the spin probe. None the less our simple model does appear to account fairly successfully for the temperature dependence of \bar{P}_2 in both the nematic and smectic mesophases. The agreement is not quite so good at the smectic-nematic transition where the orientational order of the probe in the smectic A phase decreases more rapidly than the theory predicts. However this rapid decrease may well be associated with a pretransitional effect.

We have also measured the angular dependence of the electron resonance spectrum of the probe dissolved in the smectic A phase at 60 °C. For all orientations the spectrum contained just three lines, as expected for a uniformly aligned sample, and the angular dependence of one half the spacing, $2\bar{a}(\gamma)$, between the first and last spectral lines is shown in Fig. 3. Provided rotation of the sample tube through an angle γ rotates the director by the same amount then we can calculate the angular dependence of $\bar{a}(\gamma)$ from⁽⁸⁾

$$\bar{a}(\gamma) = K + \frac{\bar{Q}^2}{K} \left(\frac{\tilde{A}_\parallel \tilde{A}_\perp \tilde{g}_\parallel \tilde{g}_\perp}{K^2 g^2} \right)^2 \sin^2 \gamma \cos^2 \gamma + \frac{\bar{Q}^2}{K} \left(\frac{\tilde{A}_\perp \tilde{g}_\perp}{Kg} \right)^4 \sin^4 \gamma,$$

$$\text{where } K^2 g^2 = \tilde{A}_\perp^2 \tilde{g}_\perp^2 + (\tilde{A}_\parallel^2 \tilde{g}_\parallel^2 - \tilde{A}_\perp^2 \tilde{g}_\perp^2) \cos^2 \gamma,$$

and

$$g^2 = \tilde{g}_\perp^2 + (\tilde{g}_\parallel^2 - \tilde{g}_\perp^2) \cos^2 \gamma.$$

The g tensor for the static molecule $\tilde{\mathbf{g}}$ has components given by equations similar to those for the hyperfine tensor $\tilde{\mathbf{A}}$. The quadrupole interaction has no scalar component and so can be described by a single parameter \bar{Q} for the fictitious static molecule:

$$\bar{Q} = (2/3)^{1/2} \sum_p (-1)^p Q^{(2,p)} \mathcal{D}_{0,-p}^{(2)},$$

where $Q^{(2,p)}$ is the total quadrupole tensor. The ability to change the orientation of the director is of some importance. Thus when the

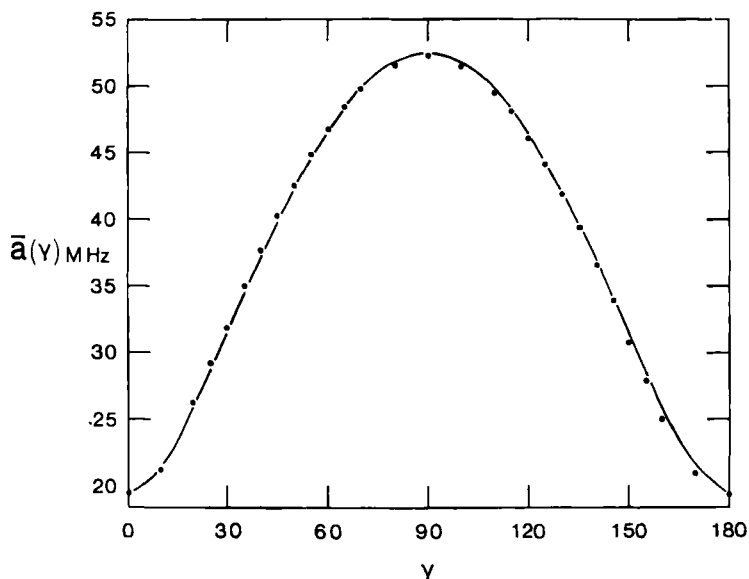


Figure 3. The angular dependence of the line separation $\bar{a}(\gamma)$ in the smectic A phase; the theoretical curve was calculated using the parameters given in the text.

director is parallel to the magnetic field the quadrupolar coupling does not influence the line positions⁽¹⁴⁾ but this is not so when the director is inclined to the field, as the expression for $\bar{a}(\gamma)$ shows. It should therefore be possible to estimate the quadrupole couplings in quite complex radicals by employing a smectic A mesophase as the solvent. Unfortunately the accuracy of such measurement may be limited since \tilde{Q} only effects the line positions in second order. In contrast ENDOR studies of radicals dissolved in liquid crystals, even when the director is parallel to the field, are capable of far greater accuracy because the relevant nuclear transitions are effected in first order.⁽¹⁵⁾ A further advantage of such angular dependent measurements in, for example, a smectic phase is that both components of the hyperfine tensor $\tilde{\mathbf{A}}$ can be determined. It is then possible to extract from these the scalar hyperfine coupling constant a for the radical dissolved in the mesophase. Usually this parameter may only be obtained from measurements in the isotropic melt, as a consequence we can gauge the magnitude of environmental effects by

measuring both quantities. Such comparisons are not expected to reveal the existence of a large environmental effect in electron resonance unless the radical is non-rigid. This technique could however be of considerable importance in nuclear magnetic resonance where the scalar interactions are much more dependent on the nature of the environment.

The parameters occurring in the theoretical expression for the separation $\bar{a}(\gamma)$ were obtained in the following. A previous study⁽²⁾ of a similar spin probe dissolved in a smectic A phase has shown that the components of \tilde{g} are virtually identical. We have therefore ignored the anisotropy in the g tensor when fitting the expression for $\bar{a}(\gamma)$ to the experimental points. The least squares fitted values of the parameters are:

$$\tilde{A}_{\parallel} = 19.31 \text{ MHz},$$

$$\tilde{A}_{\perp} = 52.21 \text{ MHz},$$

and

$$\tilde{Q} = 3.8 \text{ MHz}.$$

The theoretical angular dependence calculated with these parameters is in excellent agreement with the experimental results as the curve in Fig. 3 shows. The scalar coupling a calculated from the hyperfine tensor is 41.24 MHz which is close to the value of 41.54 MHz obtained from measurements in the isotropic melt. The environmental effects for this spin probe are clearly rather small. As we anticipated the error in \tilde{Q} turned out to be quite large and probably as great as $\pm 50\%$. However the result is in broad agreement with the values found for other nitroxide radicals using the ENDOR technique.⁽¹⁵⁾

In conclusion we compare the exact expression for $\bar{a}(\gamma)$ with that given by Fryburg *et al.*⁽¹⁾ They chose to ignore the anisotropy in the g tensor and the quadrupole coupling, which is reasonable for their spin probe. They then obtain, in our notation,

$$\bar{a}(\gamma) = \tilde{A}_{\perp} + (\tilde{A}_{\parallel} - \tilde{A}_{\perp}) \cos^2 \gamma,$$

by ignoring the important pseudo-secular hyperfine terms in the spin hamiltonian; this result should be compared with the corresponding exact form

$$\bar{a}(\gamma) = \{\tilde{A}_{\perp}^2 + (\tilde{A}_{\parallel}^2 - \tilde{A}_{\perp}^2) \cos^2 \gamma\}^{1/2}.$$

Since both expressions contain the same number of parameters there would seem to be no virtue in employing the approximate form for $\bar{a}(\gamma)$ especially as it can lead to considerable numerical errors unless $(\bar{A}_{\parallel} - \bar{A}_{\perp})/a$ is considerably less than unity.

Acknowledgements

We are grateful to the Science Research Council for a grant towards the cost of the equipment. M. Setaka wishes to thank the Royal Society and the Japan Society for the Promotion of Science for the award of a Research Fellowship.

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