On the Ordering Matrix for the Spin Probe (3-spiro[2'-N-oxyl-3',3'-dimethyloxazolidine])-5α-cholestane, in the Nematic Mesophase of 4,4'-dimethoxyazoxybenzene.

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Spin probes, such as (3-spiro[2'-N-oxyl-3',3'-dimethyloxazolidinc])-5α-cholestane (in Figure 1) have proved to be extremely valuable for studies of the long range orientational order and rates of molecular reorientation in a wide variety of liquid crystals. Their value stems, in part from their elongated form which results in a high alignment of the long molecular axis in an anisotropic environment. The extent of alignment is invariably described by a single order parameter associated with the long axis. This implies that the ordering matrix for the spin probe is cylindrically symmetric and such a description has considerable advantages for the theoretical analysis of both the spectral linewidths and the order parameter. However the spin probe does not possess a three-fold or higher symmetry axis and so the cylindrical symmetry of the ordering matrix must be established by direct measurement. There have been several investigations of I in lyotropic mesophases which conclude that the ordering matrix exhibits significant deviations from cylindrical symmetry.[1] This conclusion contrasts with the cylindrically symmetric ordering matrix found for I in a thermotropic liquid crystal.[2] We believe that this disagreement is caused by the use of different principal coordinate systems for the ordering matrix in these

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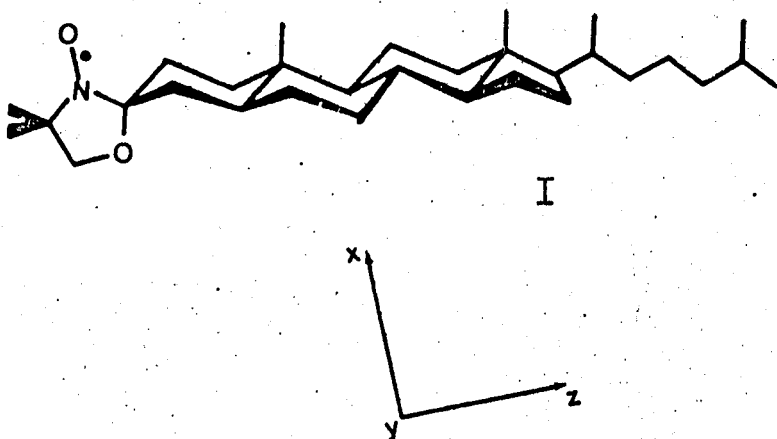
FIGURE 1 The structure of the spin probe (3-spiro[2'-N-oxyl-3',3'-dimethyloxazolidine])-5α-cholestane together with the principal coordinate system for the g and hyperfine tensors.

investigations, rather than the nature of the mesophase. In this Paper we present the results of a detailed investigation of I dissolved in the nematic mesophase of 4,4'-dimethoxyazoxybenzene and justify, with the aid of theory, our choice of principal coordinate system in which the ordering matrix is found to approximate closely to cylindrical symmetry.

The spin probe (I) was synthesised[3] from 5α-cholestan-3-one; the nematogen was purchased from Sherman Chemicals Ltd. and was purified by recrystallisation from an acetone/ethanol mixture (T_{S-N} 118°C; T_{N-I} 135°C). The electron resonance spectra were measured as a function of temperature on a Varian E-3 spectrometer; the klystron frequency, ν, was monitored with a Hewlett-Packard frequency counter (52452) fitted with a frequency converter (5256A). The magnetic field strength was measured with an AEG magnetometer.

The spectra contain the three sharp lines expected for a nitroxide spin probe; the nitrogen hyperfine coupling was determined from half the spacing between the outer spectral lines to avoid second order corrections.[4] The g factor was calculated from the position, B_0, of the central line, which for a nematic mesophase with the director parallel to the magnetic field, is

$$h\nu = \tilde{g}_{\|}\beta B_0\left(1 + \frac{\tilde{A}_{\perp}^2}{\tilde{g}_{\|}^2\beta^2 B_0^2}\right). \tag{1}$$

Here $\tilde{g}_{\|}$ is the component of the partially averaged g tensor parallel to the director and $\tilde{A}_{\perp}$ is the component of the partially averaged nitrogen hyperfine tensor perpendicular to the director.[4] The component, $\tilde{A}_{\perp}$, is calculated

from the scalar coupling constant, a, and the parallel component, $\tilde{A}_\|$, determined from the line separation.

The spectrum therefore contains two pieces of information, $\tilde{g}_\|$ and $\tilde{A}_\perp$, and so, because of the low molecular symmetry, it is impossible to determine the five independent elements of the ordering matrix. However, the g and hyperfine tensors do share a principal coordinate system, denoted by xyz in Figure 1, and consequently it is possible to evaluate the diagonal elements of S in this system. These elements are related to the observables by[4]

$$\tilde{g}_\| = g + S_{zz}g'_{zz} + \frac{(S_{xx} - S_{yy})(g'_{xx} - g'_{yy})}{3}, \qquad (2)$$

with an analogous expression for $\tilde{A}_\|$; the primes here denote the anisotropic part of the tensor. The same coordinate system has also been assumed[1] to diagonalise the ordering matrix but, as we shall see, this assumption leads to principal components which are at variance with a statistical mechanical calculation of S. The magnetic tensors used to extract the diagonal elements of the ordering matrix from $\tilde{g}_\|$ and $\tilde{A}_\|$ were[5]

$$A_{zz} = 5.85 \pm 0.1\,\text{G}, \qquad g_{zz} = 2.0060 \pm 0.0001,$$
$$A_{xx} = 6.32 \pm 0.1\,\text{G}, \qquad g_{xx} = 2.0090 \pm 0.0001,$$
$$A_{yy} = 31.90 \pm 0.02\,\text{G}, \qquad g_{yy} = 2.0024 \pm 0.0001.$$

The difference, $(S_{xx} - S_{yy})$, which is a measure of the deviation of S from cylindrical symmetry, is plotted against S_{zz} in Figure 2. The deviation from such symmetry is seen to be large and to increase almost linearly with S_{zz}; the slope of this line is about 0.26. Quite similar behaviour has been observed for the same spin probe dissolved in dipalmitoyllecithin–cholesterol multi-bilayers where the slope varies from 0.13 to 0.18, depending on the cholesterol concentration.[1] To investigate the sensitivity of our results to the choice of g and A we have repeated the calculations using the slightly less accurate values[6]

$$A_{zz} = 5.8 \pm 0.5\,\text{G}, \qquad g_{zz} = 2.0058 \pm 0.001,$$
$$A_{xx} = 5.8 \pm 0.5\,\text{G}, \qquad g_{xx} = 2.0089 \pm 0.001,$$
$$A_{yy} = 30.8 \pm 0.5\,\text{G}, \qquad g_{yy} = 2.0021 \pm 0.001,$$

with the results shown as closed triangles in Figure 2. It is clear that although the absolute magnitudes are changed the linear increase of $(S_{xx} - S_{yy})$ with S_{zz} is preserved with the same slope. We shall now see how these results compare with a statistical mechanical theory of S.

In the molecular field theory of non-cylindrically symmetric particles, exhibiting a uniaxial mesophase, the orientational pseudo-potential[7] is, to lowest order,

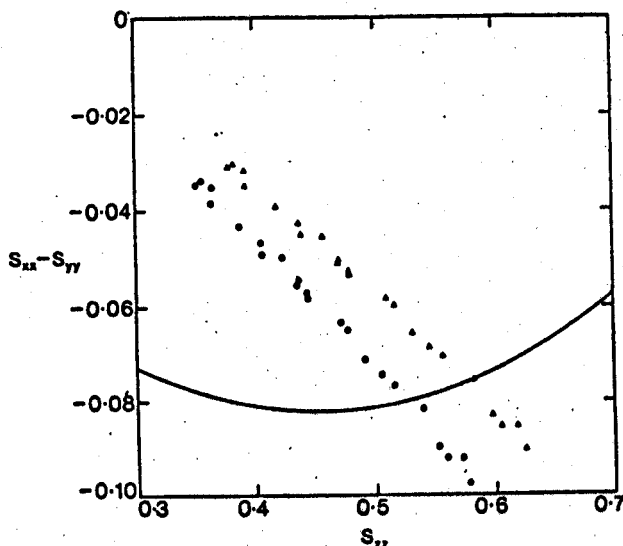$$U(\beta\gamma) = -kT\{ad_{0,0}^{(2)}(\beta) + bd_{0,2}^{(2)}(\beta)\cos 2\gamma\}. \qquad (3)$$

FIGURE 2 The dependence of $(S_{xx} - S_{yy})$ on S_{zz}, calculated from two sets of magnetic tensors (● Reference 5) and (▲ Reference 6). The curve was calculated from the pseudo-potential in Eqns. (3) and (4) with λ equal to 0.2.

where $d^{(2)}_{0,n}(\beta)$ is a reduced Wigner rotation matrix.[8] The Euler angles,[8] β and γ, define the orientation of the director in the molecular coordinate system which diagonalises the ordering matrix. The coefficients a and b, depend on the orientational order as well as the parameters in the anisotropic intermolecular potential.[7] Fortunately we need not be concerned with this dependence except to note that for particles interacting via dispersion forces[9]

$$b = 2\lambda a, \tag{4}$$

where λ is determined entirely by the deviation of the molecule from cylindrical symmetry and is therefore independent of temperature. The ordering matrix is obtained from the pseudo-potential by taking the appropriate Boltzmann average; in this notation[9] we have

$$S_{zz} = \overline{d^{(2)}_{0,0}(\beta)}, \tag{5}$$

and

$$S_{xx} - S_{yy} = \sqrt{6}\,\overline{d^{(2)}_{0,2}(\beta)\cos 2\gamma}. \tag{6}$$

We have calculated $(S_{xx} - S_{yy})$ as a function of S_{zz} for a wide range of values for λ but were unable to find agreement with the experimental results shown in Figure 2. The curve, shown in this figure, was obtained with λ equal to 0.2 and illustrates the major discrepancy between theory and experiment.

The form of the pseudo-potential is determined largely by symmetry and, in addition, has been successfully applied to other systems.[7,9] We therefore suspect that the failure to find agreement results from an incorrect assignment of the principal coordinate system for the ordering matrix. This view is supported by an inspection of molecular models which suggests that the long axis lies in the oxazolidine ring but is not orthogonal to the N—O bond. If this is so then the principal components of S will be related to the observed components by[4]

$$S_{zz} = S_{z'z'} \sin^2 \theta + S_{x'x'} \cos^2 \theta, \tag{7}$$

$$S_{xx} = S_{z'z'} \cos^2 \theta + S_{x'x'} \sin^2 \theta, \tag{8}$$

$$S_{yy} = S_{y'y'}, \tag{9}$$

where the prime denotes a principal axis and θ is the angle between the N—O bond and the long axis. This angle cannot be determined unambiguously and values of $110°$[2] and $106°$[10] have been reported. We have therefore calculated the principal components of S from our results for various values of θ and selected the one which gives good agreement with the theoretical ordering matrix. The angle chosen in this way was $110°$ and the derived values of $(S_{x'x'} - S_{y'y'})$ are plotted as a function of $S_{z'z'}$ in Figure 3. We see that the ordering matrix now exhibits a small deviation from cylindrical symmetry in contrast to the conclusions of previous studies. The curves shown in Figure 3 demonstrate the good agreement between theory and experiment which is significant even though this was optimised when selecting θ. Our results show that λ is approximately 0.09 but at present
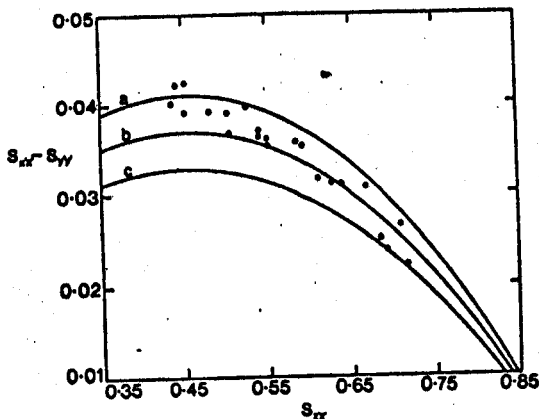

FIGURE 3   The dependence of $(S_{x'x'} - S_{y'y'})$ on $S_{z'z'}$ where the prime indicates the principal coordinate system for the ordering matrix. The curves were calculated from the pseudo-potential with λ equal to (a) 0.1, (b) 0.09 and (c) 0.08.

there is no way in which we may confirm this value because the relationship between λ and the molecular structure has not been established.

Although the angle of 110°, determined by a comparison of the experimental and theoretical ordering matrices, is supported by an intuitive inspection of molecular models a more quantitative estimate seems desirable. Now it has been discovered that the ordering matrix and moment of inertia tensor share a principal coordinate system for many molecules dissolved in a nematic mesophase.[11] Of course it is impossible to prove that the principal coordinate systems should be common none-the-less this result is not entirely unexpected since the moment of inertia tensor reflects the molecular shape which is related to the polarizability tensor[12] and both factors influence the anisotropic intermolecular potential. We have therefore calculated the moment of inertia tensor for the spin probe using standard bond lengths and angles for the steroidal residue.[13] The structure of the oxazolidine ring was however taken from the results of an X-ray investigation of the biradical 1,4-bis(spiro-[2'-N-oxyl-3',3'-dimethyloxazolidine]) cyclohexane.[14] The moment of inertia tensor is found to approximate closely to cylindrical symmetry and in addition the angle between the major axis and the N—O bond is 108° in agreement with our estimate of this angle.

We conclude therefore that the principal coordinate system of the ordering matrix is not parallel to those of the g and hyperfine tensors. The angle between the long molecular axis and the N—O bond is about 110° and that in this principal coordinate system the deviation of the ordering matrix from cylindrical symmetry is small.

Acknowledgements

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