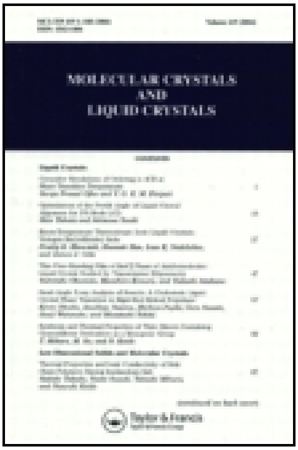

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Orientational Order of Spin Probe Molecules in Liquid Crystals

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Orientational Order of Spin Probe Molecules in Liquid Crystals[†]

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We report here measurements of hyperfine splittings and g values of two nitroxide spin probes 4',4'-dimethyl-spiro-(5α-cholestane-3,2'-oxazolidin)-3'-yloxyl and 2-(10-carboxydecyl)-2-hexyl-4,4-dimethyl-3-oxazolidinyloxyl methyl ester dissolved in p-azoxyanisole. Using the principal axes values of $\mathbf{g}$ and $\mathbf{A}$ tensors available, we have determined all three diagonal components of the orientational order parameter tensor $\mathbf{S}$ for these spin probe molecules. We find that for neither of the spin probes used here has this tensor $\mathbf{S}$ the cylindrical symmetry that is normally assumed to determine the orientational order parameter tensor $\mathbf{S}^{(p)}$ defined by the long molecular axis from such measurements. We show further that this conclusion about $\mathbf{S}$ is independent of any uncertainty in the principal axes values of the $\mathbf{g}$ and $\mathbf{A}$ tensors, and hence the relations between $\mathbf{S}$ and $\mathbf{S}^{(p)}$ normally used do not seem to be well justified. Probable relations are also suggested.

I. INTRODUCTION

The use of hyperfine splittings or g shifts or both to measure the orientational order parameter tensor $\mathbf{S}$ of spin probe molecules dissolved in liquid crystals is a standard practice.[1,2] Since the principal axes values of

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hyperfine-coupling-constant **A** and **g** tensors are known from measurements using the crystalline phase, it is convenient to express **S** in the principal axes x, y and z of these tensors fixed in the molecular frame and then to relate this **S** to $\mathbf{S}^{(p)}$ the orientational order parameter tensor defined by the long molecular axis about which molecules are assumed to execute rotational motions. This $\mathbf{S}^{(p)}$ for the uniaxial nematic phase has cylindrical symmetry about the director axis Z in the laboratory frame XYZ.

In other words, the long molecular axis is assumed to be the cylindrical symmetry axis of the whole molecule. Alternatively, $\mathbf{S}^{(p)}$ is generated by a unit vector along the long molecular axis. On the other hand, the diagonal components of **S** are defined by the three principal axes x, y and z assumed to be the same for both **g** and **A** tensors of nitroxide spin probes as observed with the solid phase. As we shall see shortly, to express **S** in this manner is equivalent to constructing it with a unit vector along the director axis Z in the xyz frame.

In relating **S** with $\mathbf{S}^{(p)}$, it is generally assumed that the former also has cylindrical symmetry or that its deviation from cylindrical symmetry can be ignored.[2] In our opinion, the standard procedure adopted in relating **S** with $\mathbf{S}^{(p)}$ is questionable even if **S** has the required cylindrical symmetry, since the two tensors are expressed in two different coordinate frames. The purpose of the present communication is two-fold: (i) to check the validity of the assumption that **S** has cylindrical symmetry, and (ii) to see how far it is justifiable to ignore its deviation from such a symmetry, if there is any, and to relate **S** with $\mathbf{S}^{(p)}$ as normally done. With these aims in view, we have measured all three diagonal components of **S** for two nitroxide spin probes dissolved in the same nematic liquid crystal. Prior to presenting our results, we give a brief description of the theory relating the diagonal components of **S** with the directly measured quantities used here.

II. THEORY

With the director axis Z parallel to the applied magnetic field H as normally used in measurements with nematic liquid crystals, we can write[2,3]

$$A_N - A_L = (A_{zz} - A)S_{33} + (A_{xx} - A_{yy})(S_{11} - S_{22})/3 \qquad (1a)$$

$$g_N - g_L = (g_{zz} - g)S_{33} + (g_{xx} - g_{yy})(S_{11} - S_{22})/3 \qquad (1b)$$

where A_N, A_L, g_N and g_L are the directly measurable, effective, hyperfine-coupling-constant A and g factors for the nematic and isotropic liquid phases, for which the subscripts N and L are used; A and g are given by the relations: $A = (A_{xx} + A_{yy} + A_{zz})/3$, and $g = (g_{xx} + g_{yy} + g_{zz})/3$. The quantities A_N and A_L are measured from the splittings between the two lines at the wings of the three-line nitroxide spin probe spectrum, while g_N and g_L are measured from the position of the central line. From the definitions of the effective hyperfine-coupling-constant A and g factors, we expect $A = A_L$ and $g = g_L$, if these quantities do not depend on temperature and the host medium. But for the sake of consistency with our use of the principal axes values that are not measured here, we prefer A and g values obtained as above from the solid phase data. As we shall see, the conclusions of the present communication are not influenced by such a choice. The diagonal components S_{11}, S_{22} and S_{33} are defined as

$$S_{ii} = \langle 3\cos^2\theta_i - 1\rangle/2 \qquad (i = 1, 2 \text{ and } 3) \tag{2}$$

where θ_1, θ_2 and θ_3 are the angles made by H (in the present case, also the director axis) with the x, y and z axes respectively, and the angular brackets $\langle\cdots\rangle$ denote the thermodynamic average. In the notations of de Gennes,[4] these diagonal components are: $S_{11} = S^{xx}_{ZZ}$, $S_{22} = S^{yy}_{ZZ}$, and $S_{33} = S^{zz}_{ZZ}$. Thus it becomes quite evident that **S** is generated in the xyz frame with a unit vector along Z. It is the usual practice to measure S_{33} in the uniaxial nematic phase from the hyperfine splittings with the help of Eq. 1a, since $A_{xx} \simeq A_{yy}$ and $(A_{zz} - A) \gg (A_{xx} - A_{yy})$ for the nitroxide spin probes, and then to obtain $S^{(p)}$, the ZZ component of $\mathbf{S}^{(p)}$, from this S_{33}, assuming $S^{(p)} = 2S_{33}(3\cos^2\varphi_3 - 1)^{-1}$, where φ_3 is the angle between z and the long molecular axis. This angle φ_3 is estimated from the molecular geometry. Even where all three diagonal components have been determined and even though they clearly show that **S** has not cylindrical symmetry, similar relations[2] to the above have been used to determine $S^{(p)}$.

III. EXPERIMENTAL DETAILS

The nitroxide spin probes used in the present measurements are 4′,4′-dimethylspiro-(5α-cholestane-3,2′-oxazolidin)-3′-yloxyl (611) and 2-(10-carboxydecyl)-2-hexyl-4,4-dimethyl-3-oxazolidinyloxyl methyl ester (615) dissolved in *p*-azoxyanisole (PAA) in the molecular ratio of about one part per million; the numbers in parentheses on the right of each spin probe are those of the manufacturer (SYVA, Palo Alto, California, U.S.A.). The spin probes and PAA (obtained from Hoechst Italia, Italy) were used without further purification. The structural formula of the spin probes are shown in Figure 1. The first one (611) is known to have a more rigid structure than the second (615).

The quantities A_N, A_L, g_N and g_L were measured from the three-line spectra obtained by an X-band EPR spectrometer (Varian Model E-112)

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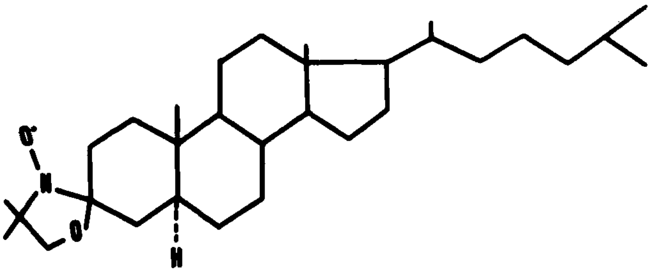

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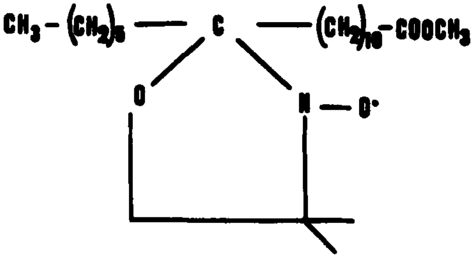

FIGURE 1 Structural formulae of spin probes used: (1) 4′,4′-dimethylspiro-(5α-cholestane-3,2′-oxazolidin)-3′-yloxyl, and (2) 2-(10-carboxydecyl)-2-hexyl-4,4-dimethyl-3-oxazolidinyloxyl methyl ester.

operated in the field frequency lock mode. The g values were obtained with respect to g of perylene$^+$ placed inside the cavity, but outside the Dewar, at a position from a side precalibrated with respect to the field at the actual sample position. The precalibration was necessary to ensure that g shifts were measured truly with respect to g_p (g of perylene$^+$), since PAA and perylene$^+$ could not be placed at the same H. The following procedures were adopted in actual measurements. First, the field at the lateral perylene$^+$ sample with respect to the sweep center was determined by placing another perylene$^+$ sample at the sample position inside the Dewar and obtaining the signal due to this sample at the sweep center by the field off-set. The field difference between the two signals gave the required calibration with respect to the sweep center, at which position the field was measured by a gaussmeter believed to be within a few milligauss of the actual value. This latter sample of perylene$^+$ was then replaced by the PAA sample of interest. The sample temperature was raised to bring it to the isotropic liquid phase and the difference between g_L and g_p was obtained using the relation: $g_L - g_p = g_p\Delta H/(H_0 + \Delta H)$, where H_0 is the field at the sweep center and ΔH is the position of the central line of the three-line spectrum measured from the sweep center. The observation of the signal from the lateral perylene$^+$ sample with respect to the sweep center ensured us that $g_L - g_p$ was truly measured. The central line was then positioned at the sweep center by the field off-set, and the g_N at different temperatures were determined in the same way as above, keeping always a check on the position of the perylene$^+$ signal from the sweep center. The magnetic field H_0 in all cases was measured by an NMR gaussmeter (Magnion Model G-502). The temperature of the sample was controlled with the help of a Varian temperature control unit (Model E-257) and was measured by a thermocouple to within ±0.2 K. Each sample was degassed by the freeze-

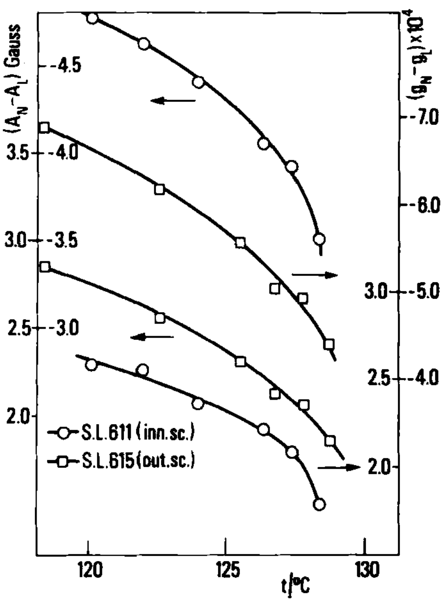

FIGURE 2 Experimental data on $A_N - A_L$ and $g_N - g_L$ vs temperature for the two spin probes shown in Figure 1 dissolved in PAA; 611 and 615 refer to the probes (1) and (2), respectively. Note that $A_N - A_L$ and $g_N - g_L$ have opposite signs for either of the spin probes.

thaw technique and sealed under vacuum in a quartz tube of 3 mm i.d.; the sample length was about 3 mm.

IV. RESULTS AND DISCUSSIONS

We show in Figure 2 the results of our measurements of $A_N - A_L$ and $g_N - g_L$ for the spin probes 611 and 615 at different temperatures. It is interesting to note that $A_N - A_L$ and $g_N - g_L$ for each spin probe have opposite signs, suggesting that the first terms in Eqs. 1a and 1b are the most important ones in accordance with the available principal axes values of **A** and **g** tensors. Using Eqs. 1a and 1b and the principal axes values of **A** and **g** tensors given below,[5] we have determined S_{33} and $S_{11} - S_{22}$ for both the spin probes from the measured $A_N - A_L$ and $g_N - g_L$ shown in Figure 2. The principal axes values used are: $g_{xx} = 2.0089$, $g_{yy} = 2.0058$, $g_{zz} = 2.0021$, $A_{xx} = 5.8$, $A_{yy} = 5.8$, $A_{zz} = 30.8$ for 611, and $g_{xx} = 2.0088$, $g_{yy} = 2.0061$, $g_{zz} = 2.0027$, $A_{xx} = 6.3$, $A_{yy} = 5.8$, $A_{zz} = 33.6$ for 615; the A components are given in Gauss. Our measured values of g_L are 2.00592 and 2.00593 respectively for 611 and 615 with an

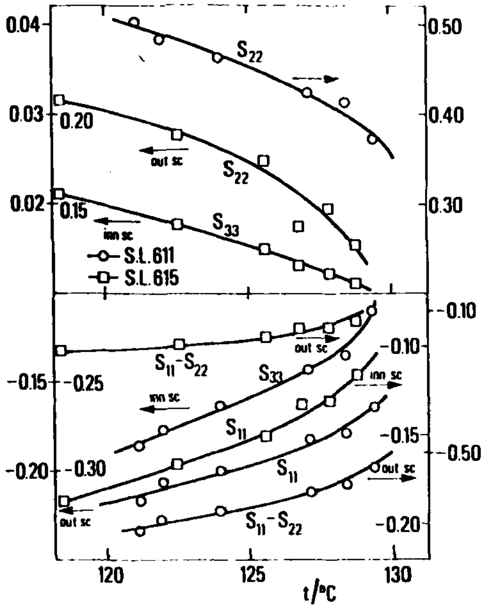

FIGURE 3 Temperature dependence of $S_{11} - S_{22}$, S_{33}, S_{11} and S_{33} obtained here for both spin probes. See the text for details.

error in each case of ±0.00001. These values are fairly close to those obtained for the solid phase. The corresponding measured values of A_L are 14.90 and 14.75 Gauss (compare 14.1 and 15.2 Gauss obtained for the solid phase). Such differences are known to be due to media[2] and have not been taken into account here, as noted earlier. The results for S_{33} and $S_{11} - S_{22}$ are shown in Figure 3. It should be noticed that both S_{33} and $S_{11} - S_{22}$ for either of the spin probes have comparable magnitudes, but are not equal, suggesting that **S** cannot have cylindrical symmetry. To confirm this conclusion, we have determined all three diagonal components using the traceless property of **S**. These results are also included in Figure 3. It should be noticed that no two components of **S** are equal, in contrast to the usual assumption of its cylindrical symmetry made by measuring S_{33} only. Since **S** has not cylindrical symmetry, it cannot be defined completely without the knowledge of the other three components.[6] If we assume that **S** has the diagonal form in the present representation, we can easily find its deviation from cylindrical symmetry by defining an asymmetry parameter $\eta = (|S_{11} - S_{22}|)/(|S_{33}|)$, where S_{33} is to be the maximum component with respect to the absolute value. We find this η to be temperature dependent

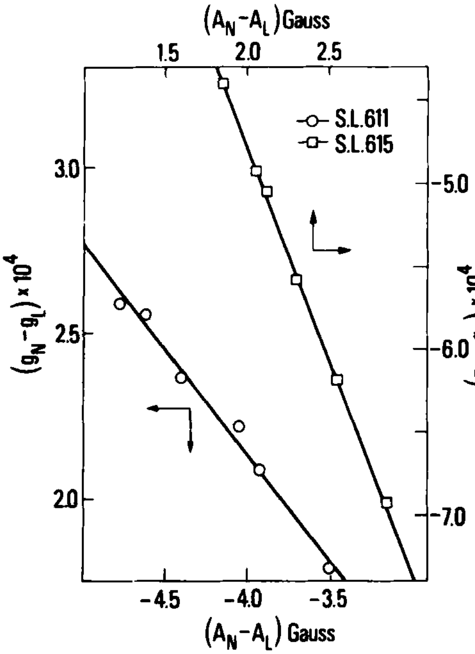

FIGURE 4 Plots of $g_N - g_L$ vs $A_N - A_L$ together with the least squares fits to a relation of the form: $y = mx + b$. See Table I for the results of such fits.

for both the spin probes, suggesting the symmetry does not remain invariant. The mean η estimated from our measurements are 0.14 ±0.01 and 0.69 ±0.03 for the spin probes 611 and 615, respectively. The variations in the mean η are of the same order found in any component of **S**. From these considerations, it is quite evident that **S** is neither cylindrically symmetric nor even diagonal in its representation. Hence, the method currently in use to determine $\mathbf{S}^{(p)}$ from **S** does not seem quite justified.

The conclusion about **S**, except for some small variations in the values of the diagonal components obtained above, is independent of the principal axes values of the **A** and **g** tensors. This has been checked with different principal axes values available in literature.[5] A further check on the above conclusions about **S** is given below and is based on the following considerations. Any two of the diagonal components must be proportional to each other if **S** has cylindrical symmetry. On the other hand, S_{33} and $S_{11} - S_{22}$ must be independent variables if it does not have cylindrical symmetry. These are the general properties of a traceless symmetric tensor of rank two. With these considerations, we have plotted $g_N - g_L$ vs $A_N - A_L$ as shown in Figure 4 together with the least squares fits (lsf) to a straight line relation of the form $y = mx + b$. It should be noticed that the fits are quite good for both the spin probes. The results of these fits are given in Table I. For none of the spin probes is b zero, suggesting that **S** cannot have cylindrical symmetry. These results are independent of the choice of principal axes values. The good straight line fits from Eqs. 1a and 1b suggest that $S_{11} - S_{22}$ can be considered to be essentially temperature independent, together with $A_{xx} \approx A_{yy}$. Alternatively, the ratio $(S_{11} - S_{22})/S_{33}$ is constant, in contrast to their being independent variables. We shall come back to this latter point shortly. It is interesting to note that the m obtained by the lsf for the two spin probes differ by a factor of about four. This four-fold variation in m for the two probes is difficult to understand from the known variations of principal axes values of nitroxide radicals in different media. With the conditions noted above, we have $m = (g_{zz} - g)/(A_{zz} - A)$. With the principal axes values noted earlier, we get $m = -2.1 \times 10^{-4}$ and

TABLE I

Parameters obtained by the least squares fits shown in Figure 4

Spin Probe	$m \times 10^5$ Gauss^{-1}	$b \times 10^5$	Correlation coefficient	$m \times 10^5$ Gauss^{-1} from Eqs. 1a and 1b
611	−6.35	−4.02	0.993	−21.0
615	−25.6	−3.35	0.999	−17.2

-1.72×10^{-4} Gauss^{-1} for 611 and 615 respectively; the latter is fairly close to our experimental value, but not the former. Furthermore, if we estimate the average values of $S_{11} - S_{22}$ for these spin probes, using the expression for b obtained from Eqs. 1a and 1b and the corresponding b obtained from the lsf, we get -0.039 and -0.037 respectively for 611 and 615. Such small values of $S_{11} - S_{22}$ may tempt us to approximate **S** to having cylindrical symmetry, but other evidence noted earlier is in strong contradiction, particularly when we take note of S_{33} and its temperature dependence.

As we have noted earlier, it is the standard practice[1,2] to determine $S^{(p)}$ from the measured S_{11}, S_{22} or S_{33} value, multiplying by a factor involving the angle φ_i between the long molecular axis and the ith principal axis. Molecular models[1,3,7] similar to that of Maier and Saupe[8] have also been proposed to understand such $S^{(p)}$. Some discrepancies between such theories and experimental results have also been noticed recently[9] and these have been attributed to the uncertainty in the estimation of the angle mentioned above.[10] As we have noted already, to derive $S^{(p)}$ from the measured S_{11}, S_{22} or S_{33} in the usual way involves the assumption that both $S^{(p)}$ and **S** have cylindrical symmetry in the same frame. Our results show

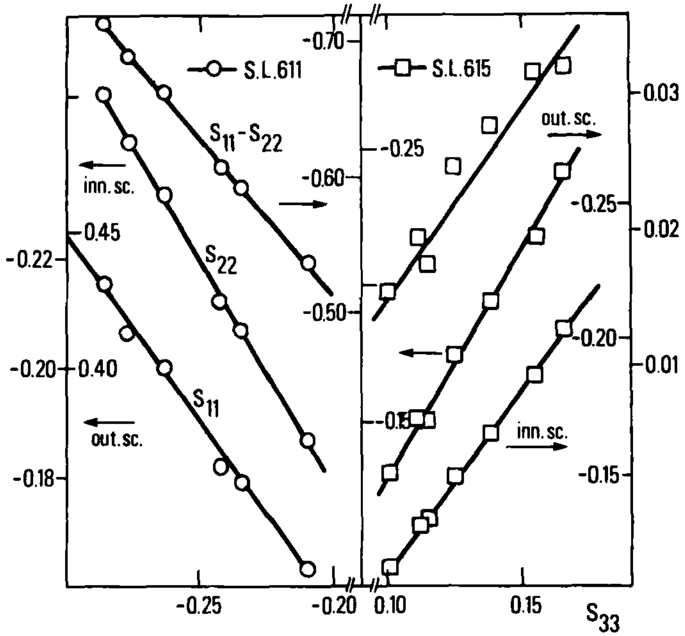

FIGURE 5 Plots of $S_{11} - S_{22}$, S_{11} and S_{22} separately against S_{33} together with the least squares fits to a relation of the form $y = mx + b$. The results of such fits are given in Table II.

TABLE II

Parameters obtained by the least squares fits shown in Figure 5. The subscripts 12, 1 and 2 are for fits to $S_{11} - S_{22}$, S_{11} and S_{22}, respectively. Correlation coefficients in each of the fits are better than 0.99

Spin Probe	m_{12}	m_1	m_2	b_{12}	b_1	b_2
611	2.36	0.682	−1.68	−0.0385	−0.0192	0.0192
615	−1.67	−1.33	0.334	0.0371	0.0183	−0.0186

clearly that such a condition is not satisfied. In order to check the assumption involved in relating $S^{(p)}$ with S_{11}, S_{22} or S_{33}, we have plotted $S_{11} - S_{22}$, S_{11} and S_{22} separately against S_{33} as shown in Figure 5, together with the lsf to a straight line of the form $y = mx + b$. The results of such fits are given in Table II. The correlation coefficient in each case is better than 0.99. It should be noticed that b in no case can be taken to be zero, confirming our earlier results. In conformity with our earlier results discussed above, this non-zero b for both the spin probes cannot be understood from the small uncertainty in the principal axes values of the **A** and **g** tensors. Neither of these results can be understood from the uncertainty in the angle noted earlier. On the other hand, all the results can be well understood with a relation of the form: $S_{ii} = m_i S^{(p)} + b_i$, a relation similar to that used to understand the quadrupole splittings in long chain molecules.[11] The origin of such a relation and its consequence have been given elsewhere.[12]

V. CONCLUSIONS

We have shown here that the orientational order parameter tensor **S** determined from measurements by the EPR technique does not have the cylindrical symmetry usually assumed. Neither is it diagonal. Hence, it is essential to determine the other three components to determine **S** completely. The relations normally used to determine $S^{(p)}$ from the measured components of **S** do not seem to be well justified. On the other hand, our results are in complete conformity with the relation proposed to understand the quadrupole splittings in long chain molecules forming liquid crystals.

Finally, we would like to note that similar conclusions to ours can be derived from results where all three diagonal components of **S**, such as in the measurements of Schindler and Seelig[3] or of Hemminga and Berendsen,[9] have been determined. Our results show clearly the limitations of determining $S^{(p)}$, a characteristic of the phase and an essential parameter to test any microscopic theory. A possible way out, in conformity with other observations, is also suggested. It is to be noted that an exactly similar behavior of **S** to that presented here has also been observed for two other nitroxide spin probes dissolved in PAA.[13]

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