

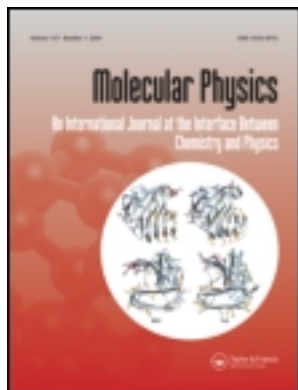
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## Zero field N.M.R. of uniaxial and biaxial smectic liquid crystals

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A study of three smectic liquid crystal systems is made through a comparison of the high field and zero field N.M.R. spectra of probe molecules. The motional averaging of the proton dipolar interaction of a  $\text{CH}_2\text{Cl}_2$  solute molecule reflects the local symmetry of Smectic *A*, *B* and *E* phases. In the Smectic *E* system, the onset of the biaxiality of the phase is clearly evident even in an unaligned sample.

### 1. Introduction

An interesting feature of some low temperature smectic liquid crystals [1] is that they are biaxial. The biaxiality of the smectic phases has been observed for the past few years by optical techniques as well as N.M.R. and N.Q.R. [2, 3] with many studies by deuterium N.M.R. [4, 5]. However, in many cases, the biaxial ordering is weak and may not be detectable in unaligned smectic phases. Therefore aligned samples have been used, produced by cooling the sample from the isotropic phase in a large magnetic field and then observing the N.M.R. spectrum at many different orientations with respect to the field. This is similar to single crystal experiments in high field N.M.R. Zero field N.M.R. now makes it possible to obtain spectra of polycrystalline or amorphous systems with the same resolution as for the aligned samples [6] and is therefore suited to the study of unaligned, powderlike smectic phases, where a multidomain distribution of the directors exists.

In this paper, a complete version of our earlier communication [7], the symmetry of different smectic phases has been studied through the ordering of a simple two spin  $I = 1/2$  solute molecule. The time averaged dipolar coupling tensor of the proton pair of the probe molecule clearly reflects the degree of ordering and the symmetry of the environment in which this averaging takes place. The advantage of studying the dipolar interaction derives from its inherent axial symmetry in the static principal axis system. Thus any asymmetry in the observed interaction, which is predicted as a consequence of the biaxiality of the phase, can be induced only by molecular motions in zero field. No assumptions as to the contributions of the inherent static symmetry versus motionally induced asymmetries need to be made as they are in the case of the quadrupolar interaction [8].

Smectic liquid crystals can be divided into those with no long range translational order in the layers (i.e. smectic *A* and *C* phases) and those which do not

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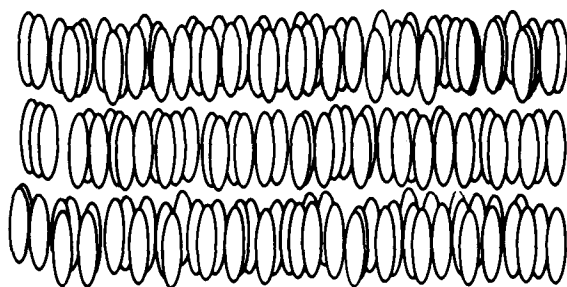


Figure 1. Illustration of the layering present in smectic liquid crystals. The elongated molecules arrange themselves in parallel layers. The preferred direction of the molecular long axes can be either parallel or tilted with respect to the layer normal. The molecules may be either translationally ordered or disordered within the layer planes.

display long range translational order (i.e. smectic *B*, *H*, *E* and *G* phases) [9]. Unlike the more common nematics, the elongated molecules of the smectic phases are arranged in parallel layers as shown schematically in figure 1. In the smectic *A*, *B* and *E* phases studied in this work, the average direction of the molecular long axes is perpendicular to the layer planes, but they differ significantly in the degree of translational order within the smectic planes and the orientational ordering about the long molecular axes. Such phases have been investigated intensively during the past several years by X-ray diffraction [10, 11, 12], miscibility methods [13], and neutron scattering [14].

The smectic *A* phase resembles a two-dimensional fluid since there is long range translational disorder of the molecular positions within the layer and the molecules exhibit free rotation about their long axes as shown in figure 2. The phase is optically uniaxial with the optical axis along the layer normal. The uniaxial smectic *B* phase has its constituent molecules arranged in layers with the molecular centres positioned in a hexagonally packed array as shown in figure 2. The molecules still experience rapid rotation about their long axes but with some cooperation between the rotations of neighbouring molecules [10, 11]. Most of the smectic *B* phases

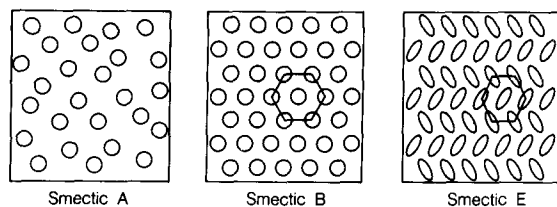


Figure 2. Cross-sectional representations of the smectic layer planes. At left, the molecules of the smectic *A* phase are depicted by rods with circular cross-sections which represent the space swept out by the free rotation about their long axes. There is no translational order within the plane and the phase is uniaxial. The smectic *B* phase shown in the centre, with the molecules aligned parallel to the layer normal, is also uniaxial. Rotation about the long molecular axes is still allowed while the molecular centres are fixed in a hexagonal array. When there is a contraction of such a molecular arrangement, a smectic *E* phase results. The molecules can no longer rotate freely about their long molecular axes but instead oscillate by angles less than  $180^\circ$  as illustrated schematically by the ellipses at right. The molecules can then be expected to occupy one of the two sites in the herringbone-like pattern. Due to the restricted rotational freedom, the smectic *E* phase is expected to be biaxial.

involve no inter-layer correlations [12]. The difference between the smectic *B* and smectic *E* phase arises from the herringbone structure sometimes accompanied by a contraction in one direction of the two-dimensional hexagonal network, resulting in an orthorhombic arrangement [1] as shown in figure 2. This contraction accounts for the biaxial properties of the phase. Full rotation about the long molecular axes is no longer possible in this close packed arrangement and the molecules undergo oscillations about their long axes through angles of less than  $180^\circ$  [5]. Although this reorientational motion is rapid ( $10^{11} \text{ s}^{-1}$ ), the molecules can still be regarded as spending most of the time in the two fold disordered herringbone arrangement which is depicted in figure 2(c). In addition to molecular positional and orientational correlations within the layer, correlations between the neighbouring smectic layers are also present [12].

## 2. Experimental

The systems under investigation consisted of a  $\text{CH}_2\text{Cl}_2$  solute dissolved in smectic *A*, *B* and *E* phases. Binary mixtures of 40·8 (4-*n*-butyloxy-benzylidene-4'-*n*-octylaniline, Frinton Laboratories) and 80CB (4-*n*-octyloxy-4'-cyanobiphenyl, EM Chemicals/BDH) can be used to prepare stable room temperature smectic *B* and *E* phases [15]. The smectic *B* phase was prepared by mixing 60 wt per cent of 40·8 and 40 wt per cent 80CB with  $\sim 5$  wt per cent  $\text{CH}_2\text{Cl}_2$ . A 50 : 50 wt per cent ratio of the same compounds with  $\sim 7$  wt per cent  $\text{CH}_2\text{Cl}_2$  was used for the smectic *E* phase. No binary mixture of these compounds was found to form a stable smectic *A* phase [15]. Therefore, the smectic *A* phase consisted of a closely related liquid crystal 8CB (4-*n*-octyl-4'-cyanobiphenyl, EM Chemicals) mixed with approximately 2 wt per cent of  $\text{CH}_2\text{Cl}_2$ . The samples were made homogeneous by heating them to above the clearing temperature and mixing thoroughly. Cooling the samples to room temperature in the absence of a magnetic field produces a random distribution of liquid crystal directors. In highly viscous smectic *B* and *E* phases, this distribution is preserved when a large magnetic field is applied, while a smectic *A* phase may become uniformly aligned.

Zero field N.M.R. experiments were performed on a homebuilt 180 MHz ( $^1\text{H}$ ) spectrometer which is described in detail elsewhere [16]. The field cycles used in the experiments are illustrated in figure 3. The samples are adiabatically demagnetized to an intermediate field of approximately 100 G. Sudden removal of this field, as shown in figure 3(a), initiates evolution in zero field for unaligned, powderlike phases, where the initial condition of magnetization evolves in the presence of the zero field hamiltonian [6]. In the case of an aligned phase, orthogonal dc magnetic field pulses as illustrated in figure 3(b) must be employed to alter the initial spin state in zero field and thereby produce zero field signal. This situation is identical to that in aligned nematic liquid crystals characterized by positive magnetic susceptibility anisotropy ( $\Delta\chi > 0$ ) which have been described elsewhere [17, 18]. In analogy to a Hahn spin echo experiment in high field [19], a  $\pi$  pulse can also be applied in the middle of the zero field evolution period in order to remove the effects of residual fields in the zero field region.

## 3. Results

Both high and zero field spectra of the  $\text{CH}_2\text{Cl}_2$  solute were obtained for all the smectic phases at room temperature. To observe only the solute signal, and not that

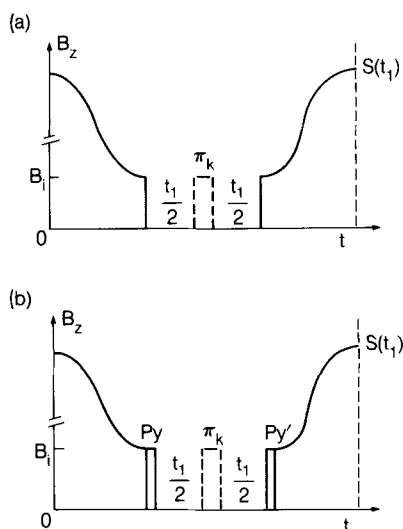


Figure 3. Schematics of the experimental zero field N.M.R. field cycles. In both (a) and (b), the sample originates in a large polarizing magnetic field ( $\sim 40$  kG) and is adiabatically demagnetized to an intermediate field,  $B_i$ , of  $\sim 100$  G in the laboratory  $z$  direction. The state of the nuclear spin system at this point is proportional to  $I_{z, \text{lab}}$ . A sudden transition in the field initiates evolution in zero field, as in (a), if the initial state and the zero field hamiltonian do not commute as in a powder-like sample. Evolution continues for a time  $t_1$ , which may be divided in half by a  $\pi_k$  ( $k = x, y, z$ ) pulse in analogy to a high field echo sequence. Reapplication of the intermediate field terminates evolution in zero field and preserves the  $z$  component of magnetization. The sample is remagnetized to high field where the magnitude of the signal is detected. Repeating the field cycle for incremented intervals of  $t_1$  produces the time domain signal,  $S(t_1)$ . Alternatively, as illustrated in (b), pulsed dc magnetic fields,  $P_y$ , may be required to initiate evolution in zero field in analogy to an rf pulse in a high field experiment. A second pulse applied at the end of the  $t_1$  period is included to stop evolution before the remagnetization and detection stages.

of the liquid crystal itself, the longer  $T_2$  component of the signal was sampled with an echo sequence in high field. The degree of ordering of the solute in the liquid crystalline matrix with and without the presence of an external magnetic field is compared whenever this information is extractable from the high field spectrum. Figure 4(a) represents a high field dipolar spectrum of  $\text{CH}_2\text{Cl}_2$  in smectic  $A$  phase and shows a doublet indicative of an aligned sample. The zero field spectrum of the same compound, employing the field cycling scheme of figure 3(b) with  $\pi_x$  echo pulse in the middle, is depicted in figure 4(b). The spectrum consists of two lines appearing at the characteristic frequency of the two proton dipolar interaction,  $\pm 3\nu_D/2 = 3\gamma^2 hS/8\pi^2 r^3$ , scaled by the order parameter,  $S$  which is a measure of the degree of ordering of the solute in the uniaxial liquid crystalline environment [17]. The calculated order parameter in zero field,  $S = 0.074 \pm 0.001$ , is equal to the value obtained in high field,  $S = 0.077 \pm 0.002$ , within the experimental error.

The high and zero field spectra of  $\text{CH}_2\text{Cl}_2$  in the uniaxial smectic  $B$  phase are presented in figure 5(a) and 5(b). The singularities of the high field orientationally broadened powder spectrum of the axially symmetric two proton dipolar interaction are reasonably well defined. Thus an order parameter of  $S = 0.041 \pm 0.002$  can be easily calculated. Using the version of the field cycle shown in figure 3(a), the zero

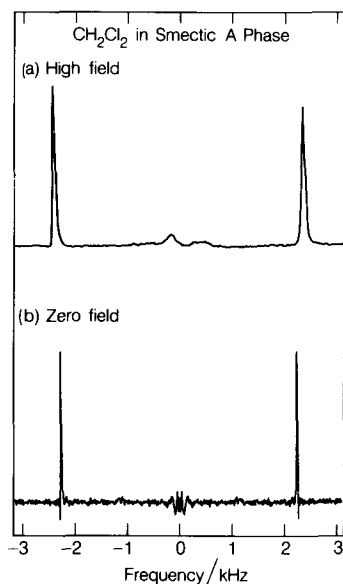


Figure 4. High field (a) and zero field (b) N.M.R. spectra of  $\text{CH}_2\text{Cl}_2$  in smectic *A* phase. A doublet pattern in high field is indicative of an aligned sample. The peak separation is related to the dipolar coupling scaled by the uniaxial order parameter,  $S$ . In zero field, the field cycle of figure 3(b) is required to initiate evolution. A  $\pi_x$  refocusing pulse produces the narrow line spectrum (b) and allows for precise determination of the order parameter in the absence of a magnetic field. The order parameters found in high and zero fields agree within experimental error.

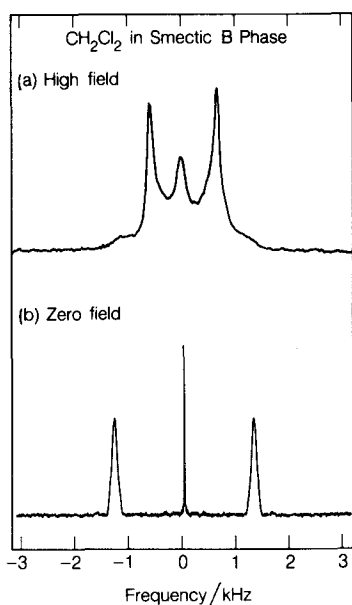


Figure 5. High field (a) and zero field (b) N.M.R. spectra of  $\text{CH}_2\text{Cl}_2$  in smectic *B* phase. The high field spectrum shows the typical orientationally broadened powder pattern of the axially symmetric two proton dipolar interaction. The peak in the centre of the powder spectrum is most likely due to residual liquid crystal signal not removed by the high field echo sequence. The zero field spectrum (b) was obtained using the field cycle of figure 3(a) with no echo pulse. From the frequencies of the lines at  $\pm 3\nu_D/2 = 3\gamma^2 h S / 8\pi^2 r^3$ , a value of the order parameter can be calculated.

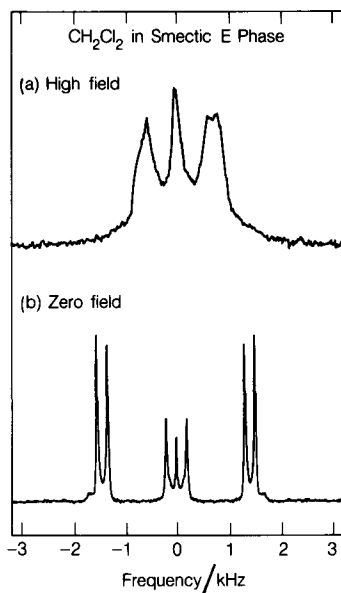


Figure 6. High field (a) and zero field (b) N.M.R. spectra of CH<sub>2</sub>Cl<sub>2</sub> in smectic *E* phase. The broadened singularities of the high field powder pattern are indicative of an asymmetry in the dipolar interaction. The zero field spectrum consists of narrow lines whose separation is directly related to the magnitude of  $\eta$ . This spectrum was obtained using the field cycle of figure 3(a) with no refocusing pulse and taken under identical conditions as for the smectic *B* spectrum. The narrow lines are the result of a quenching effect of the residual fields by the presence of a nonzero asymmetry parameter.

field spectrum consists of three lines occurring at zero frequency and  $\pm 3\nu_D/2$ . The spectrum is similar to that of the isolated proton pairs of polycrystalline samples [6] differing only in the scaling of the dipolar interaction by the order parameter,  $S$ . Hence,  $S$  can be directly deduced from the spectral splitting with  $S = 0.042 \pm 0.002$  in agreement with the value from high field. The fact that  $S$  is lower in the smectic *B* phase than it is in the smectic *A* phase may indicate that the probe has changed its environment in the smectic layers. The differences in the linewidths in the zero field spectrum are not characteristic of the phase but rather are due to the effect of residual field inhomogeneities and can be removed through using a refocusing pulse in the field cycle [20].

The high field powder spectrum of CH<sub>2</sub>Cl<sub>2</sub> in smectic *E* phase appears in figure 6(a). Here, unlike the smectic *B* phase, a broadening of the singularities is evident and can be attributed to a motionally induced asymmetry in the dipolar coupling. Only by clearly resolving the features of the powder pattern can values of the dipolar coupling, order parameter and asymmetry parameter be obtained in analogy to a spin  $I = 1$  system [21, 8]. In contrast, in figure 6(b), sharp line splittings appear in zero field spectrum of the same smectic *E* sample. The line at zero frequency is also due to residual field inhomogeneities in the zero field region [20]. The other six lines may be attributed to the motionally induced asymmetry ( $\eta \neq 0$ ) in the dipolar coupling which splits each of the three lines of figure 5(b). The differences in linewidths between the smectic *B* and *E* spectra can be explained as a quenching effect of the residual fields in the presence of a nonzero asymmetry parameter [20]. The positions and separations of the lines are directly proportional



to the asymmetry parameter and scaled dipolar coupling so that values of  $\eta = 0.208 \pm 0.002$  and  $S = 0.045 \pm 0.001$  can be easily extracted from the spectrum. The observed zero field dipolar spectra in the different smectic phases can be explained on the basis of the motional averaging of the zero field spin hamiltonian as explained in the following section.

#### 4. Motional averaging of the spin hamiltonian in zero field

Due to different types of molecular motion, the spatial terms in the nuclear spin interactions become time-dependent and only the motionally averaged interactions are detected. In the case of the intermediate regime of motions, when the correlation times are comparable to the N.M.R. interaction, the lineshapes themselves will be affected. In such cases, the motional effects on zero field spectra can be calculated by stochastic Liouville method [22]. Zero field spectra in the fast motional regime, which account for all the current experiments, consist of sharp lines at frequencies characteristic of the time averaged interaction tensors. The hamiltonian of the dipolar spin interaction can be written in a general spherical tensor representation [23]

$$H_D = \sum_m (-1)^m \langle A_{2m} \rangle T_{2-m}, \quad (1)$$

where the irreducible tensor operators  $A_{2m}$  and  $T_{2m}$  represent the spatial and spin parts of the hamiltonian, respectively. The brackets on the  $\langle A_{2m} \rangle$  term indicate that the spatial part is always time averaged in a liquid crystal. In conventional high field N.M.R. the spin part of the hamiltonian is truncated by the large magnetic field and only the secular ( $m = 0$ ) terms remain. However, in the absence of a field, truncation of the hamiltonian can still occur through the spatial terms due to molecular motions [17, 18]. The effect of motional averaging on the zero field hamiltonian will be treated separately for axially symmetric (uniaxial) and nonaxially symmetric (biaxial) liquid crystalline phases.

*Uniaxial phases.* Two coordinate frames must be defined to describe the effects of molecular motion on the dipolar hamiltonian. One is the principal axis system (PAS) of the interaction with the  $z$  axis along the internuclear vector of the two protons of the solute molecule. This frame is related by the Euler angles  $(\alpha, \beta, \gamma)$  to the director frame. Because of the fluctuations of the direction of the interproton vector with respect to director itself, the angles  $(\alpha, \beta, \gamma)$  are time dependent. The director frame is fixed on average with respect to the liquid crystal molecules and has its  $z$  axis normal to the smectic planes as shown in figure 7(a). Expressing the spatial part of the hamiltonian in equation (1) in terms of its PAS components, the dipolar hamiltonian in the director frame becomes

$$H_D^{\text{dir}} = \sum_m \sum_{m'} (-1)^m \langle D_{mm'}^2(\alpha\beta\gamma) \rangle A_{2m'}^{\text{PAS}} T_{2-m}^{\text{dir}}, \quad (2)$$

where the  $D_{mm'}$  terms represent Wigner rotation matrix elements [23]. Due to the axial symmetry of the dipolar tensor in its PAS, only the terms with  $m' = 0$  survive. Furthermore, the uniaxial symmetry of the phase means invariance with respect to the angle  $\alpha$ , so that under the motion, only  $m = 0$  remains, and equation (2) simplifies to

$$H_D^{\text{dir}} = - \frac{\gamma^2 h S}{2\pi r^3} (3I_{z1} I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2), \quad (3)$$

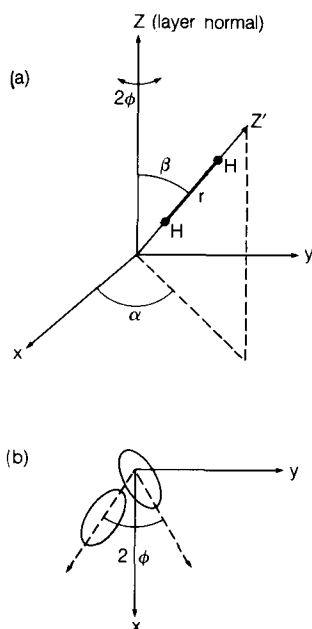


Figure 7. Frames of reference used for describing the dipolar interaction in the liquid crystalline phases in zero field. The PAS frame of the dipolar interaction is shown in (a) with the  $z$  axis along the H-H internuclear vector. Only the angles  $\alpha$  and  $\beta$  are required to relate this axially symmetric interaction to the liquid crystal director frame ( $x, y, z$ ). A third frame, with its  $Z$  axis colinear to the director/layer normal frame ( $\theta \approx 0$ ), is used to describe the two site jumps of the molecules in a biaxial phase. The  $x$  axis of this frame, as shown in (b), is rotated by an angle of  $\pm\phi$  with respect to the symmetry axis of the liquid crystal director frame.

where  $r$  is the interproton distance and  $S = 1/2\langle 3 \cos^2 \beta - 1 \rangle$  measures the degree of ordering of the interproton vector with respect to the local liquid crystal director. Since there is no externally defined field direction, the truncation of the hamiltonian does not depend on a particular orientation of the domain, that is, it is independent of the bulk alignment of the sample.

For a nonaligned sample, the field cycle of figure 3(a) produces an initial zero field state proportional to  $I_z$  and initiates evolution with the sudden transition in field. The signal as a function of the evolution time,  $t_1$ , in zero field can be calculated from

$$S(t_1) = \text{Tr} \{ R I_z R^{-1} \exp(-iH_D t_1) R I_z R^{-1} \exp(iH_D t_1) \}, \quad (4)$$

where  $R = \exp(-i\Phi I_z) \exp(-i\Theta I_y)$  relates the zero field frame to the laboratory frame with its  $z$  axis along the external magnetic field. Integrating over the powder distributions of the liquid crystalline domains (and local directors), the normalized signal is

$$S(t_1) = 1/3 + 2/3 \cos(3\omega_D t_1/2), \quad (5)$$

with  $\omega_D = \gamma^2 h S / 2\pi r^3$ . The Fourier transform of this time domain signal consists of three lines of equal intensity as seen for the smectic  $B$  phase in figure 5. The frequency separation is directly proportional to the order parameter,  $S$ .

*Biaxial phases.* Due to the lack of motional freedom of the liquid crystalline molecules about their long axes, the biaxial smectic phases cannot be described by a single director. The change of symmetry of the phase is clearly reflected in the spin interaction of the probe molecule. The averaging of the two proton dipolar coupling is caused not only by onsite fluctuations (tumbling) of the probe molecule with respect to the layer normal/director, but also by rapid diffusion between the two inequivalent sites in the herringbone lattice. The probabilities of occupying each of these two sites is assumed to be the same. This fast dynamic equilibrium (on an N.M.R. timescale) between the two sites is taken into account by introducing additional frame of reference with its  $z$  axis along the layer normal/director ( $\theta \approx 0$ ) [5], and its  $x$  axis rotated by an angle  $\pm\phi$  with respect to the symmetry axis in the smectic plane as shown in figure 7(b). The dipolar hamiltonian in this averaged director/zero field frame can be written as follows

$$H_D^{\text{dir}} = \sum_m \sum_n (-1)^m \langle D_{mn}^2(\phi 00) D_{n0}^2(\alpha\beta) \rangle A_{20}^{\text{PAS}} T_{2-m}^{\text{dir}}, \quad (6)$$

where we have already taken into account the axial symmetry of the dipolar interaction in its PAS. We define the time averages of  $D_{mn}$ s as the order coefficients in the orientational distribution function [25], namely the order parameters, as

$$S_m = \sum_n \langle D_{mn}^2(\phi 00) D_{n0}^2(\alpha\beta) \rangle. \quad (7)$$

Taking into account the symmetry relation for the Wigner rotation matrices, such that

$$D_{mn}^L(\alpha\beta\gamma) = (-1)^{m-n} D_{-m-n}^L(\alpha\beta\gamma) \quad (8)$$

and replacing the  $T_{2m}$  terms by their cartesian counterparts, the two proton dipolar coupling hamiltonian is

$$H_D^{\text{dir}} = -\frac{\gamma^2 \hbar S_0}{2\pi r^3} \left[ 3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2 + \frac{3S_2}{2S_0} (I_{x1}I_{x2} - I_{y1}I_{y2}) \right], \quad (9)$$

where  $S_0 = S = 1/2 \langle 3 \cos^2 \beta - 1 \rangle$  and  $S_2 = \langle \sin^2 \beta \cos 2\alpha \cos 2\phi \rangle$  are the two order parameters describing the effect of the biaxial phase on the probe molecule.

The above hamiltonian is completely analogous to the quadrupolar hamiltonian for a spin  $I = 1$  nucleus for which a similar derivation can be found in reference [2]. We can rewrite equation (9) in the more familiar form,

$$H_D^{\text{dir}} = -\frac{\gamma^2 \hbar S_0}{2\pi r^3} [3I_{z1}I_{z2} - \mathbf{I}_1 \cdot \mathbf{I}_2 + \eta(I_{x1}I_{x2} - I_{y1}I_{y2})], \quad (10)$$

where the asymmetry parameter  $\eta$  is defined by

$$\eta = 3S_2/2S_0 = 3 \langle \sin^2 \beta \cos 2\alpha \cos 2\phi \rangle / \langle 3 \cos^2 \beta - 1 \rangle. \quad (11)$$

The asymmetry term results from the restricted rotational freedom of the molecules in the biaxial environment. The uniaxial order parameter,  $S = S_0$ , is contained in the dipolar coupling constant as before, while the asymmetry parameter containing  $S_2$  is an indication of the biaxiality of the phase.

The corresponding transitions for this hamiltonian, within the triplet manifold, are

$$\left. \begin{aligned} \omega_{12} &= \eta\omega_D, \\ \omega_{32} &= (3 - \eta)\omega_D/2, \\ \omega_{31} &= (3 + \eta)\omega_D/2, \end{aligned} \right\} \quad (12)$$

with  $\omega_D = \gamma^2 h S_0 / 2\pi r^3$  and  $\eta$  defined in equation (11). The normalized signal function calculated as from equation (4) and integrated over the powder distribution of the liquid crystal domains yields

$$S(t_1) = 1/3\{\cos[\eta\omega_D t_1] + \cos[(3 - \eta)\omega_D t_1/2] + \cos[(3 + \eta)\omega_D t_1/2]\}, \quad (13)$$

which consists of six lines at positive and negative frequencies with their separation depending upon the values of  $\eta$  and  $\omega_D$ . This interferogram reduces to the one in equation (5) when  $\eta = 0$ . The contributions of the uniaxial and biaxial order parameters in the smectic *E* case presented can be separated and calculated to be  $S_0 = 0.045 \pm 0.001$  and  $S_2 = 0.006 \pm 0.001$ . As expected,  $S$  for the probe molecule is much smaller than it would be for the molecules of the liquid crystal itself [5], making the apparent value of  $\eta$  larger. The derived values of the order parameters are in reasonably good agreement with the values obtained by high field deuterium N.M.R. studies of deuteriochloroform in a smectic *G* phase (8).

## 5. Conclusions

The zero field N.M.R. method and its applications to unaligned smectic liquid crystals is appealing for many reasons. Firstly, it allows one to probe the solute-liquid crystal system without a perturbing external field. Secondly, zero field N.M.R. has the capability of obtaining well resolved, crystal-like spectra in orientationally disordered materials. Zero field N.M.R. spectra are very sensitive to small motional effects [22, 26] so that a small motionally induced anisotropy in the dipolar interaction is easily detected. The motionally induced asymmetry is clearly manifested as a splitting of the narrow zero field N.M.R. lines. Zero field N.M.R. is thus potentially useful for gaining an accurate measure of the very small effects of biaxialities which may not be detectable by conventional N.M.R. methods. Of course, no information is gained concerning the orientation of the averaged tensor interaction which does require aligned samples.

The use of solute molecules has proved to be a very sensitive probe of the biaxiality of the liquid crystalline phase. It is advantageous using such systems due to the simplicity of the spin system and its corresponding spectrum without requiring isotopic labelling. A future goal of zero field N.M.R. is to probe the motions of the liquid crystal molecules themselves rather than solute molecules and to obtain some insight into the mechanisms that are responsible for the biaxiality.

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### References

- [1] GRAY, G. W., and GOODBY, J. W., 1984, *Smectic Liquid Crystals* (Heyden). LUZ, Z., and MEIBOOM, S., 1973, *J. chem. Phys.*, **59**, 275.
- [2] DOANE, J. W., 1979, *Magnetic Resonance of Phase Transitions*, edited by F. J. Owens, C. P. Poole and H. A. Farach (Academic Press), and references therein.
- [3] SELIGER, J., OSREDKAR, R., ZAGAR, V., and BLINC, R., 1977, *Phys. Rev. Lett.*, **38**, 411.
- [4] DOANE, J. W., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (D. Reidel), chaps. 18 and 19.
- [5] VAZ, N. A., VAZ, M. J., and DOANE, J. W., 1984, *Phys. Rev. A*, **30**, 1008.
- [6] ZAX, D. B., BIELECKI, A., ZILM, K. W., PINES, A., and WEITEKAMP, D. P., 1985, *J. chem. Phys.*, **83**, 4877. PINES, A., *Lectures of Pulsed N.M.R., Proceedings of the 100th Fermi School of Physics*, edited by B. Maraviglia (in the press).
- [7] THAYER, A. M., LUZAR, M., and PINES, A., 1987, *Liq. Crystals*, **2**, 241.
- [8] BARBARA, T., and DAILEY, B. P., 1982, *Molec. Crystals liq. Crystals*, **87**, 239.
- [9] HELFRICH, W., 1979, *J. Phys. Paris, Colloq.*, C3, **40**, 105.
- [10] DOUCET, J., and LEVELUT, A. M., 1977, *J. Phys., Paris*, **38**, 1163. DE JEU, W. H., and DE POORTER, J. A., 1977, *Physics Lett. A*, **61**, 114.
- [11] DOUCET, J., LEVELUT, A. M., LAMBERT, M., LIEBERT, L., and STRZELECKI, L., 1975, *J. Phys., Paris, Colloq.*, C1, **36**, 13.
- [12] LEADBETTER, A. J., MAZID, M. A., and MALIK, K. M. A., 1980, *Molec. Crystals liq. Crystals*, **61**, 39.
- [13] GOODBY, J. W., and GRAY, G. W., 1979, *J. Phys., Paris*, **40**, 363.
- [14] LEADBETTER, A. J., RICHARDSON, R. M., and FROST, J. C., 1979, *J. Phys., Paris, Colloq.*, C3, **40**, 125.
- [15] CLADIS, P. E., 1981, *Molec. Crystals liq. Crystals*, **67**, 177.
- [16] BIELECKI, A., ZAX, D. B., ZILM, K. W., and PINES, A., 1986, *Rev. scient. Instrum.*, **57**, 393.
- [17] THAYER, A. M., MILLAR, J. M., LUZAR, M., JARVIE, T. P., and PINES, A., 1986, *J. phys. Chem.*, **90**, 1577.
- [18] THAYER, A. M., LUZAR, M., and PINES, A., 1987, *J. phys. Chem.*, **91**, 2194.
- [19] HAHN, E. L., 1950, *Phys. Rev.*, **80**, 580.
- [20] LUZAR, M., THAYER, A. M., and PINES, A., 1987, *J. magn. Reson.*, **73** (in the press).
- [21] BARNES, R. G., 1972, *Advances in Nuclear Quadrupole Resonance*, edited by J. A. S. Smith (Heyden), p. 342.
- [22] JONSEN, P., LUZAR, M., PINES, A., and MEHRING, M., 1986, *J. chem. Phys.*, **85**, 4873.
- [23] MEHRING, M., 1983, *Principles of High Resolution N.M.R. in Solids* (Springer-Verlag). HAEBERLEN, U., 1976, *High Resolution N.M.R. in Solids, Selective Averaging, Advances in Magnetic Resonance*, Suppl. 1 (Academic Press).
- [24] ROSE, M. E., 1957, *Elementary Theory of Angular Momentum* (John Wiley).
- [25] ZANNONI, C., 1985, *Nuclear Magnetic Resonance of Liquid Crystals*, edited by J. W. Emsley (D. Reidel), chap. 1.
- [26] MILLAR, J. M., THAYER, A. M., ZAX, D. B., and PINES, A., 1986, *J. Am. chem. Soc.*, **108**, 5113.