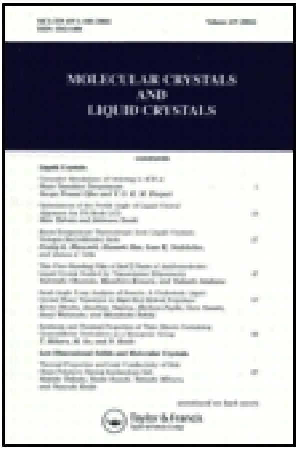

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^{2}H-NMR Spectral Patterns in Magneto-Aligned Smectic E and G Phases

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^{2}H-NMR Spectral Patterns in Magneto-Aligned Smectic E and G Phases[†]

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Unique ^{2}H-NMR spectral patterns can be obtained from biaxially ordered smectic E and G phases, where only one director of the phase is aligned by the magnetic field. Two effects on the shape of the deuterium spectral pattern are demonstrated: (1) The effect of a motionally induced asymmetry parameter in the time averaged deuterium quadrupole interaction, and (2) the effect when the principal z-axis of the time averaged interaction is not parallel to the aligned director. Spectral patterns for the S_G phase of the compound 4-n-pentoxybenzylidene-4-n'-heptylaniline selectively deuterated on one of the aromatic rings (50.7-d_4) were obtained for both unaligned and magneto-aligned samples. Both of these spectral patterns were consistent with that expected for an asymmetry parameter, $\eta \simeq 0.2$. Spectral patterns in the S_G phase of the compound 50.6 (24.7 wt.%) + 90.4-αd_2-γd_2 (75.3 wt.%) were studied showing a different behavior with respect to the spectral patterns obtained in 50.7. We believe that a shift in the orientation of the z principal axis relative to the sample c axis has occurred in this S_G phase. Spectral patterns were also recorded for the S_E phase in magneto-aligned samples of the mixture of compounds 4-cyano-4′-octyloxybiphenyl (8OCB) with 50 wt.% 40.8-d_4. These data also show a small asymmetry parameter but, in addition, a distribution in the orientation of the principal z-axis indicating that the time scale of the motion of the long molecular axis is in a regime where it is of the order of the ^{2}H-NMR measurement. Models for the smectic E and G phases based on these observations are discussed.

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I. INTRODUCTION

Almost all the information on the microscopic structure of smectic phases come from X-ray and optical studies.[1] While optical studies can distinguish uniaxial and biaxial ordering in liquid crystals, X-ray diffraction can provide detailed molecular structure such as the layer spacing, intermolecular distances and tilt angle. Often missed from X-ray studies are details on the orientational ordering of the molecules. Deuterium magnetic resonance (^{2}H-NMR) is a tool particularly suitable to yield information on the orientational order of the molecules.[2]

Among the phases which have been classified as "smectics", it is believed that the low symmetry smectic phases such as S_E, S_G and S_H are "crystalline" in the sense that they exhibit long-range 3-dimensional positional order. The S_G phase, for example, has a centered monoclinic cell with pseudo-hexagonal packing of molecules tilted towards an edge of the hexagon, while the S_E phase has an orthorhombic structure with a herringbone packing formed by the planes of the molecules. However, there is evidence that considerable dynamical disorder still exists in these phases. For instance, the observation[3] of low frequency dielectric dispersion in the S_E phase has differentiated this from a true 3-dimensional crystal. The observed dissimilarity in the X-ray diffraction patterns of a solid and S_G phase also offers a strong argument, according to Helfrich,[4] for a difference between ordinary solids and ordered smectics. The present study aims at understanding the nature of biaxial ordering in the S_E and S_G phase by means of ^{2}H-NMR.

II. THEORY

Since deuterium magnetic resonance experiments are performed with the sample in a large magnetic field, liquid crystalline materials are often aligned or partially aligned by the presence of the field. This is particularly true of polymorphic liquid crystals which exhibit a nematic phase. In this case the director of the long molecular axis will often align parallel to the direction of the magnetic field. When the sample is cooled from the aligned nematic phase into the smectic phases at lower temperatures, a partial alignment of the sample, which depends upon the specific smectic phase, will be maintained.

In the case of quadrupole magnetic resonance, which is time averaged in the fast motion regime, the directors can be identified with the principal axes x, y, z of the electric field gradient tensor V_{ij} defined such that $|V_{xx}| \leq |V_{yy}| < |V_{zz}|$. In the nematic phase exhibited by aromatic compounds the z-axis aligns parallel to the direction of the magnetic field. Also, the nematic phase is uniaxial $V_{xx} = V_{yy} = -V_{zz}/2$. When the nematic is cooled into a uniaxial smectic (i.e. S_A or uniaxial S_B), this condition is observed to be maintained. On the other hand, when the material is cooled into a biaxial smectic or into a smectic where some aspects of the molecular motion are no longer in the fast motion regime, then two features can happen: (i) $V_{xx} \neq V_{yy}$ giving an asymmetry or biaxiality[5] and/or (ii) the principal z-axis may shift its orientation away from the direction of the magnetic field.[6]

In such a case, a deuterium two line spectrum of frequencies $\nu^{\pm}$ will follow the equation

$$
\begin{aligned}
\nu^{\pm} = \pm\frac{3}{4}\nu_Q\Bigg\{&\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right)\left[\frac{3}{2}\cos^2\theta - \frac{1}{2} + \frac{\eta}{2}\sin^2\theta\cos 2\psi\right]\\
&+ \frac{3}{4}\sin^2\theta_0\Bigg(\sin^2\theta\cos 2\phi + \frac{\eta}{3}\Big[(1+\cos^2\theta)\cos 2\psi\cos 2\phi\\
&\qquad\qquad - 2\cos\theta\sin 2\psi\sin 2\phi\Big]\Bigg)\\
&+ \frac{3}{4}\sin 2\theta_0\Bigg(\sin 2\theta\cos\theta + \frac{1}{3}\eta[-\sin 2\theta\cos 2\psi\cos\phi\\
&\qquad\qquad + 2\sin\theta\sin 2\psi\sin\phi]\Bigg)\Bigg\} \qquad (1)
\end{aligned}
$$

where $\nu_Q = \text{eq}\, V_{zz}/h$, $\eta = (V_{xx} - V_{yy})/V_{zz}$, and the Euler angles ϕ, θ, ψ give the orientation of the newly oriented principal axis (x, y, z) frame in the sample (a, b, c) frame. The sample frame is defined such that c is parallel to H when the sample was cooled into the smectic phase. When the smectic sample so prepared is then reoriented in the magnetic field, the angle θ_0 between c and H is in the a,c plane. A derivation of Eq. 1 can be found in Ref. 7.

We apply Eq. 1 to three specific cases we have examined in the laboratory: (i) the S_G phase as has been reported[8] to appear in the material 50.7; (ii) the S_G phase as has been identified[9] in mixtures of 50.6 and 90.4; and (iii) the S_E phase found[10] in mixtures of 8OCB and 40.8.

III. EXPERIMENTAL AND INTERPRETATION

A. Smectic *G* Phase 50.7

One form of biaxial ordering as observed in a magneto-aligned sample is illustrated by the ^{2}H-NMR spectra in Figure 1. Biaxial ordering is evidenced by the splitting of the lines at the 90° orientation of the sample relative to the direction of the magnetic field. The splitting at this orientation results from $V_{xx} \neq V_{yy}$ and, consequently, a finite value of η for Eq. 1.[11] When the sample is prepared by cooling from the uniaxial nematic in the presence of the magnetic field, the z principal axis remains aligned, $\theta = 0$, in which case Eq. 1 becomes:

$$\nu^{\pm} = \pm\frac{3}{4}\nu_Q\left\{\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right) + \frac{\eta}{2}\sin^2\theta_0\cos 2(\phi + \psi)\right\} \quad (2)$$

Furthermore, the x and y principal axes become randomly distributed whereby $\phi + \psi$ also take on random values. This situation results in a unique spectral pattern whereby each line breaks up into two edge singularities.[11] This pattern has been described elsewhere.[11] The experimental observation of such a pattern at $\theta_0 = 90°$ is illustrated in Figure 2 along with the simulated spectrum calculated from Eq. 2 with $\phi + \psi$ being randomly distributed. A value of $\eta = 0.2$ was obtained from the fit.

B. Smectic *G* Phase of 50.6/90.4 Mixtures

We shall show that the ^{2}H-NMR spectra are totally different in this S_G phase from that illustrated above in 50.7.

Figure 3 shows the spectral pattern in the G phase (at 56.3°C) of a magneto-aligned sample of 24.7 wt.% 50.6 in 90.4-d_4 deuterated in the α and γ position of the four segment alkyl chain. The γd_2 have smaller intensity because they are partially deuterated. It is obvious that unlike the previous case the spectral lines at $\theta_0 = 90°$ exhibit no break-up into a pattern. On the other hand, the lines do break up into spectral patterns at small angles, $\theta_0 \approx 20°$. We believe this situation occurs because of a change in the orientation of the principal z-axis relative to the sample c axis. If in Eq. 1 we set $\psi = 0$ we obtain:

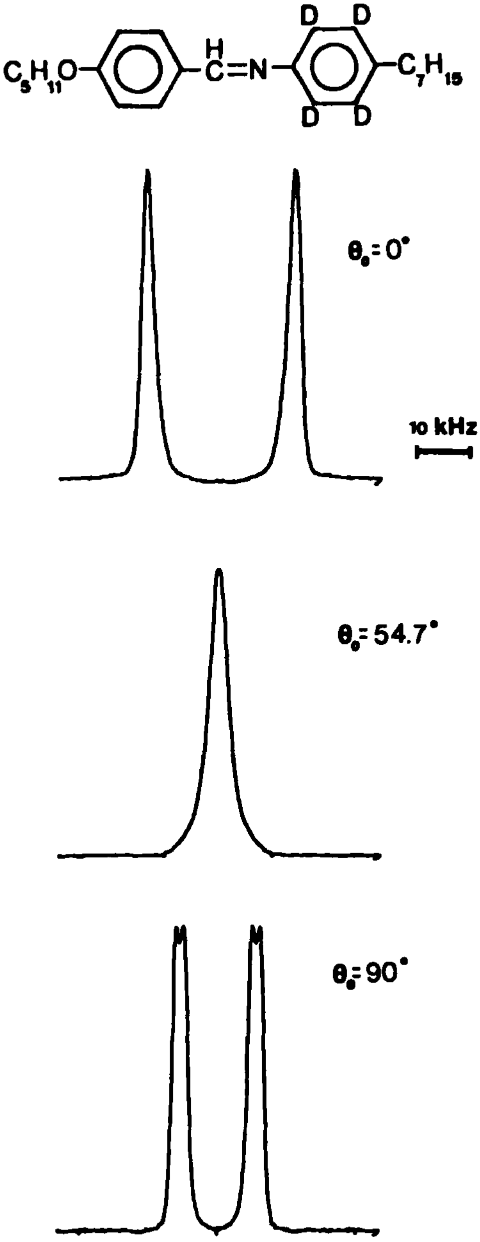

FIGURE 1 Experimental angular dependence of the ^{2}H-NMR spectrum in the S_G phase of 50.7-d_4 at 31°C. Each single line breaks up into two edge singularities at $\theta_0 = 90°$.

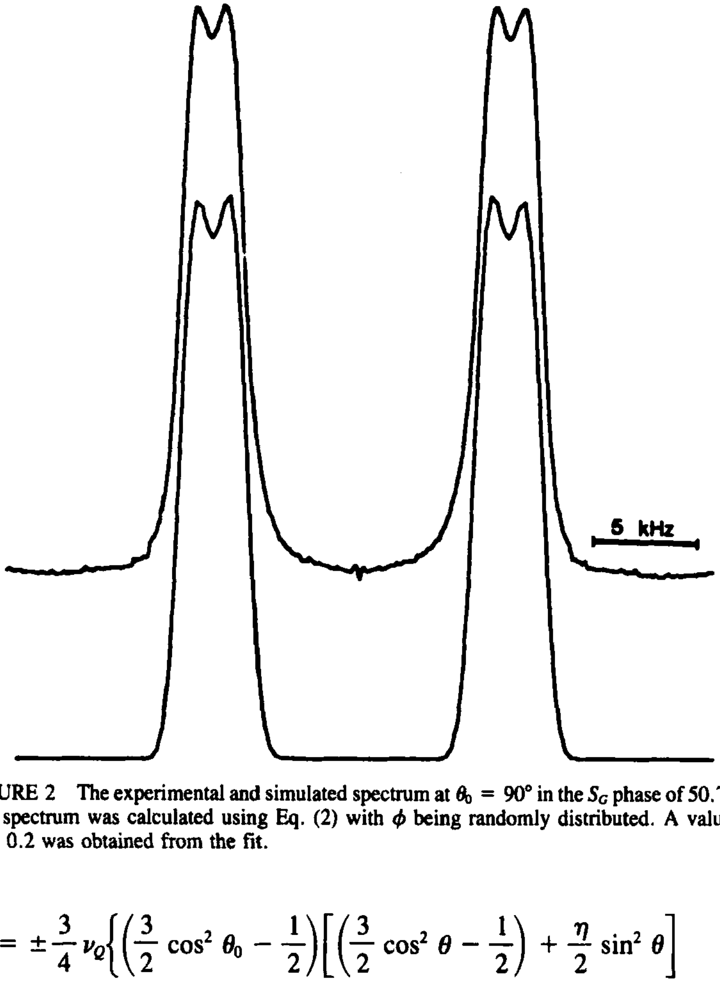

FIGURE 2 The experimental and simulated spectrum at $\theta_0 = 90°$ in the S_G phase of 50.7-d_4. The spectrum was calculated using Eq. (2) with ϕ being randomly distributed. A value of $\eta = 0.2$ was obtained from the fit.

$$\begin{aligned}\nu^{\pm} = \pm\frac{3}{4}\nu_Q\Bigg\{&\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right)\left[\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right) + \frac{\eta}{2}\sin^2\theta\right]\\ &+ \sin^2\theta_0\cos 2\phi\left[\frac{\eta}{2} - \left(\frac{\eta-3}{4}\right)\sin^2\theta\right]\\ &+ \sin 2\theta_0\cos\phi\left(\frac{\eta+3}{4}\right)\sin 2\theta\Bigg\} \qquad (3)\end{aligned}$$

where, like in the previous case, the angle ϕ is also probably randomly distributed as there is no interaction to align the x and y principal axes. While in this paper we show no actual fittings to Eq. 3, we can demonstrate that the third term in Eq. 3 which is the principal difference between this equation and Eq. 2 is responsible for the splittings observed in the indi-

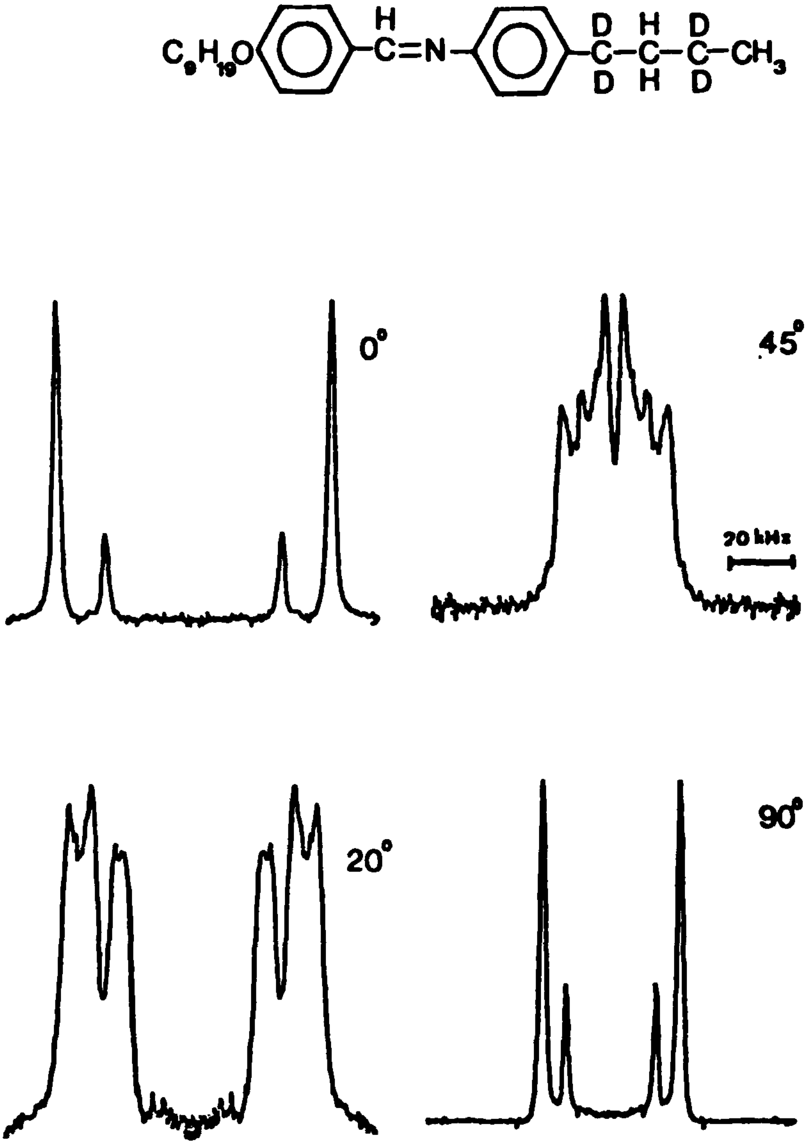

FIGURE 3 Observed spectra at different θ_0 in the S_G phase of the system 50,6 (24.7 wt.%) + 90.4 (75.3 wt.%). A schematic representation of the 90.4 molecule and the deuterated sites is also shown. It is obvious that the spectral lines have no splitting into edge singularities at θ_0 = 90°. On the other hand spectral patterns recorded at small angles exhibit a break up into two edge singularities.

vidual lines in Figure 3 at small angles. In Figure 4 we have plotted the splittings between the singularities of the pattern vs sin $2\theta_0$. The linearity of these plots demonstrates that the third term of Eq. 3 and hence a shift in the orientation of the z principal axis has occurred in this S_G phase. It also shows that the contribution of the second term in Eq. 3 is very small.

C. Smectic *B* and *E* Phases of 40.8/8OCB Mixtures

The angular dependence of the ^{2}H-NMR spectrum of a mixture of 8OCB (50 wt.%) and 40.8-d_{21} aligned in a magnetic field was studied in its S_B and S_E phase.[10] Typical spectra in the S_B (at 63°C) and S_E (at 40°C) phases are shown in Figure 5. A plot of the linewidth at the magic angle ($\theta_{MA} = 54.7°$) vs the reciprocal temperature is shown in Figure 6.

The angular dependence in the S_B phase of all the deuterated sites is consistent with $\theta = \eta = 0$ in Eq. 1 which reduces to the well known equation:

$$\nu^{\pm} = \pm\frac{3}{4}\nu_Q\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right) \tag{4}$$

The orientational order of this S_B phase is clearly similar to that of the uniaxial nematic and S_A phases.

It is clear from Figure 5, on the other hand, that in the S_E phase the situation is different. In the S_E phase, the lines become significantly broadened leading to a poor resolution of the lines. At the magic angle the spectrum is again structureless consisting of a single line of half width $\Delta\nu_{MA}$. Whereas $\Delta\nu_{MA}$ is nearly constant in the S_B phase, the linewidth jumps at the S_B–S_E phase transition and continues to increase with decreasing temperature. This observation supports the idea of a thermal-activated motional process with an activation energy of 11 kcal/mole in the S_E phase. Since there appears no structure on the spectrum at the magic angle in the S_E phase, it is apparent that the angular dependence roughly follows Eq. 4. The other terms in Eq. 1 appear to contribute only toward the broadening of each line.

To simulate the angular dependence of the line shape in the S_B phase we assumed a Gaussian distribution of the director orientation around $\theta = 0$ in Eq. 1 with a standard deviation $\sigma = 0.5°$. The azimuthal angle ϕ of the director was uniformly distributed because there is axial symmetry in the usual ϕ sample about the direction of the magnetic field during the cooling process. Furthermore, to simulate the narrow peak on the broad "background" for θ_0 near θ_{MA}, a superlorentzian ($p < 1$) broadening

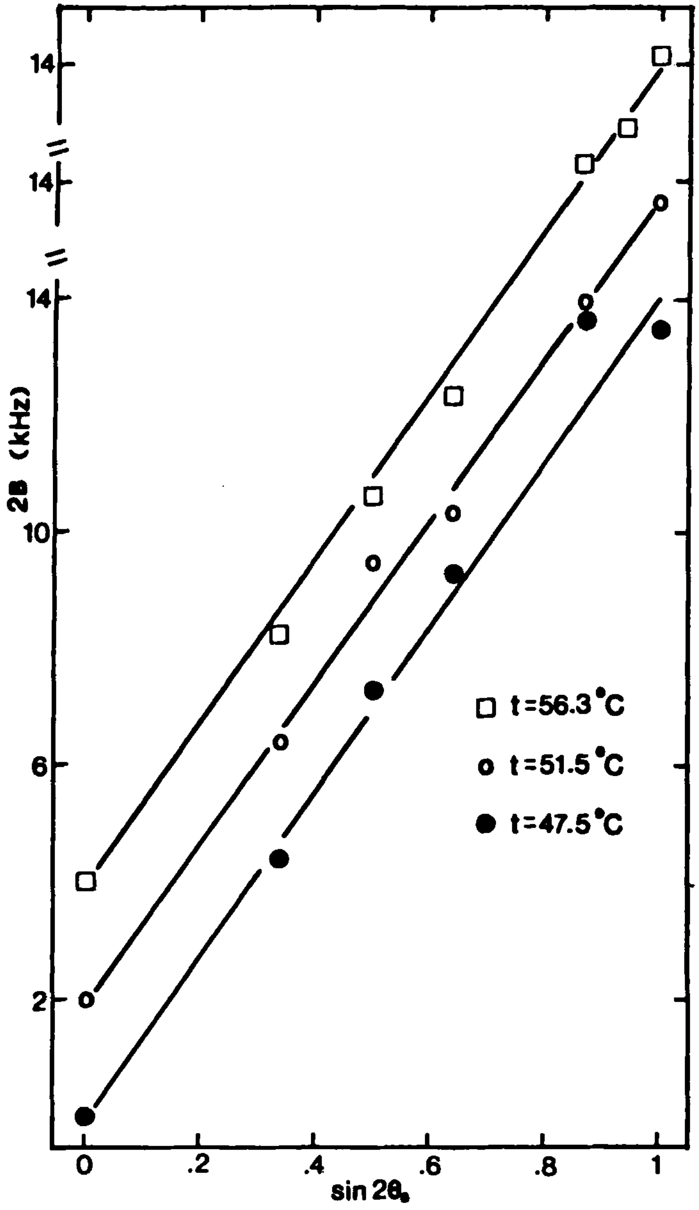

FIGURE 4 Plot of the separation between the two edge singularities vs sin $2\theta_0$ in the S_G phase of 50.6 (24.7 wt.%) + 90.4 (75.3 wt.%). The linearity of this plot and sin $2\theta_0$ (the third term of Eq. (3)) demonstrates that a shift in the orientation of the z principal axis has occurred in this S_G phase.

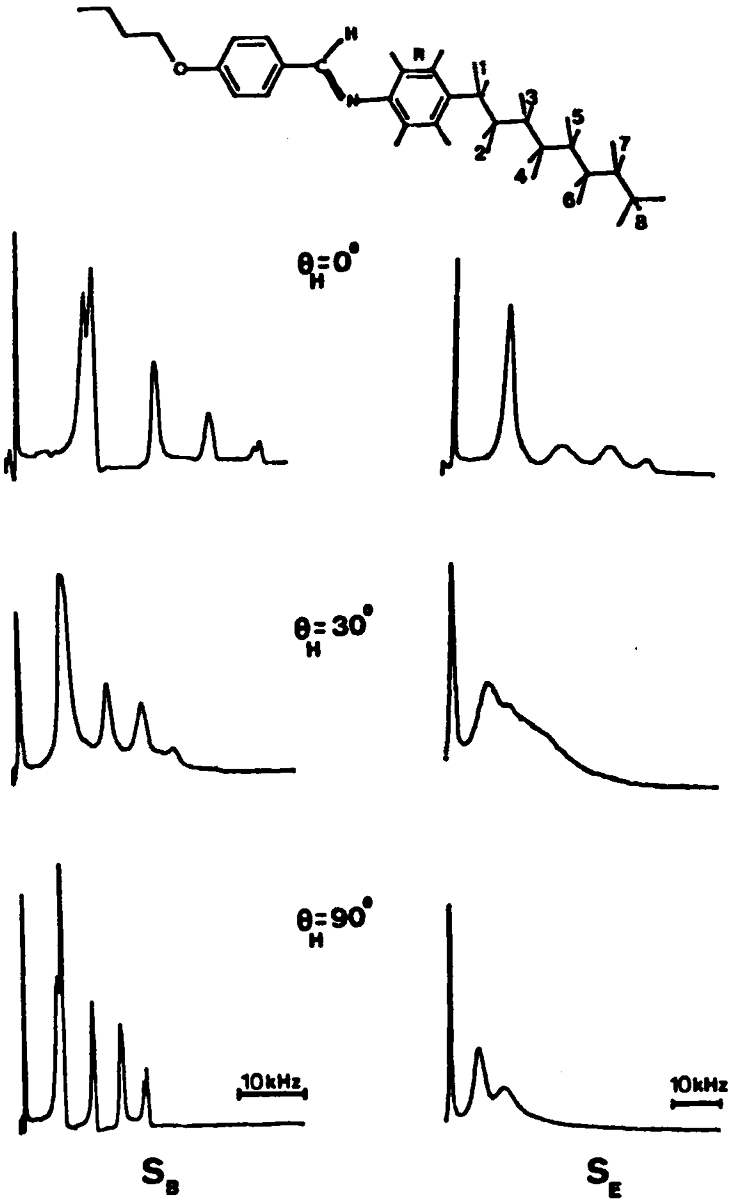

FIGURE 5 Experimental angular dependence of one-half of the ^{2}H-NMR spectrum in the S_B (63°C) and S_E (40°C) phases of the system 40.8 (50 wt.%) + 8OCB (50 wt.%). A schematic representation of the deuterated sites of the 40.8-d_{21} molecule is shown. The S_B spectra exhibit uniaxial behavior [see Eq. (1)]: (i) all sites have the same principal axis; (ii) $\eta_i = 0$ for all i sites. The S_E spectra show different angular behavior from S_B.

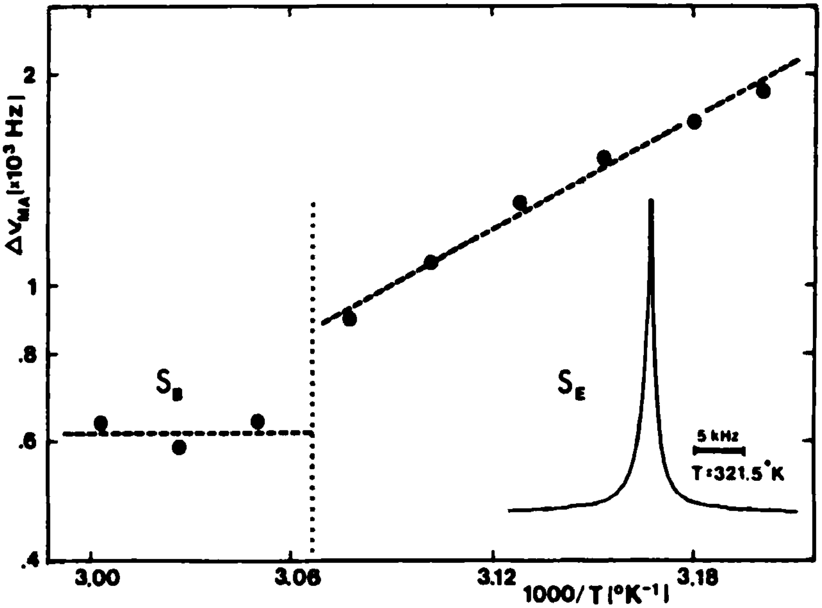

FIGURE 6 A plot of the line width at the magic angle, $\Delta\nu_{MA}$, vs the reciprocal temperature in the S_B and S_E phases of the system 40.8 (50 wt.%) + 8OCB. A typical spectrum at the magic angle in the S_E phase is shown. The temperature dependence of $\Delta\nu_{MA}$ in the S_E phase has an activation energy of 11 Kcal/mole suggesting that a thermal activated motional process takes place in the S_E phase which affects $\Delta\nu_{MA}$.

$$\frac{T_2}{(1 + \omega^2 T_2^2)^p}$$

of the individual lines gave good fit. The assignment of the splittings to the different ^{2}H-sites in 40.8 was done according to earlier workers.[12]

The general features of the experimental spectrum in S_B were simulated rather well, confirming again that all ^{2}H-sites in the molecule share the same principal axis frame and have a vanishing asymmetry parameter. The distribution of the director is narrow, clearly less than 1 degree, indicating a well aligned sample. Whereas, the width of the individual lines of the spectra in S_B diminishes or remains constant when θ_0 changes from 0° to 90°, the lines in the S_E spectra broaden significantly when θ_0 is increased (Figure 5). Furthermore, the spectrum for $\theta_0 = 90°$ clearly cannot be obtained from the $\theta_0 = 0°$ spectrum by a simple scaling procedure (as in S_B) even after including line broadening. This indicates that either $\eta^{lc} \neq 0$ at least for some of the deuterated sites in the molecule and/or that the PAF-EFG's of different sites do not coincide. Figure 7 shows the simulated general features of the ^{2}H-NMR spectrum at $\theta_0 = 90°$. Figure 7c shows

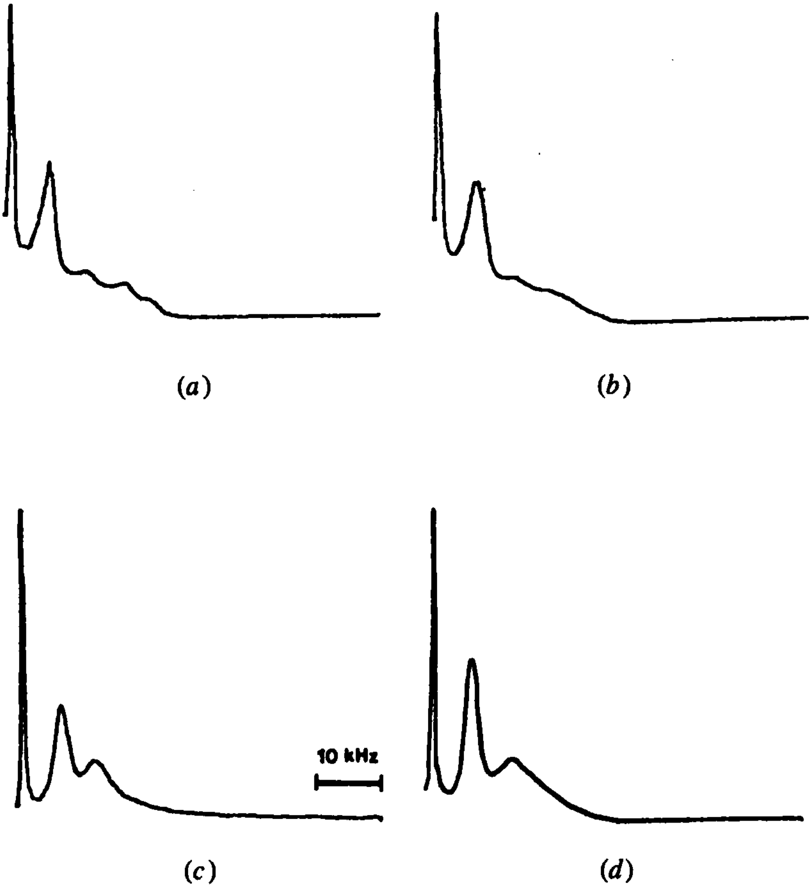

FIGURE 7 Comparison of simulated to experimental spectra for $\theta_0 = 90°$ of Eq. (4) in the S_E phase of the system 40.8 (50 wt.%) + 8OCB. The influence of the width of the distribution, σ, and the asymmetry parameter η in the simulation process is shown: (a) $\sigma = 20°$ for all the sites, $\eta_i = 0$ for all it sites; (b) $\sigma = 20°$ for all the sites, $\eta_i = 0.1$ for all i sites; (c) the experimental spectrum; (d) the simulated spectrum obtained by distributing the width σ along the chain: $\sigma = 20°$ for sites 1, 2, 3; $\sigma = 8°$ for the remaining sites. The asymmetry parameter: $\eta_i = 0.1$ for all i sites.

the experimental spectrum. Figure 7a shows a simulated spectrum using $\sigma = 20°$ and $\eta = 0$. It is evident that the spectral lines with large quadrupolar splitting are not well fitted. Figure 3c shows a simulated spectrum using $\sigma = 20°$ and $\eta = 0.1$. Attempts to improve the fit failed when the values of η or σ were assumed not to be distributed along the chain. The effect of increasing η is to broaden the lines, but the value of η is limited because when the value of $\eta \approx 0.2$ the lines split. Figure 7d shows a simulation where to the two larger splittings (at $\theta_0 = 0$) we assigned a distribution of $\sigma = 20°$ and, to the remaining lines, a distribution of $\sigma = 8°$. We found that a small value of $\eta = 0.1$ is essential to improve the fit.

A larger value in the distribution σ for the larger splittings is consistent with a model where the fluctuations in the orientation of the long molecular axis occurs on a time scale comparable to the ^{2}H-NMR measurement. The larger splittings have larger values of ν_Q and thus are associated to shorter measurement times, $[\nu_Q]^{-1}$. A large splitting means less time averaging and, therefore, the site can be related to a large distribution of principal axes, σ. Conversely, small splittings can be related to more time averaging and, therefore, to a small distribution, σ.

These results suggest that in the S_E phase the time scale of the motion of the long molecular axis is comparable to the values of $[\nu_Q]^{-1}$ associated with the spectral splitting of that phase. In fact, the motion appears to be more comparable for the large splitting $[\nu_Q]^{-1} \approx 2 \times 10^{-5}$ sec but fast as compared to the smallest splitting $[\nu_Q]^{-1} \approx 3 \times 10^{-4}$ sec, which is associated with the methyl group. This motion also appears to be responsible for the line broadening at the magic angle.

IV. CONCLUSIONS

These data show that what has been reported to be the same phase (S_G phase) in 50.7 and in 50.6/90.4 mixtures may actually be two different phases. A microscope examination under cross polarizers shows them to have the same textures, both characteristic of the S_G phase.[13] The orientational order on the other hand appears to be different. More studies are underway to extract the order parameters from measured values of ν_Q, η and θ. To do this requires the measurement of these values for different deuterated sites.[14,15]

The motional averaging in the S_G plane of these two materials appears to be in the fast motion regime for ^{2}H-NMR. Our data in the S_E phase of 80CB/40.8 show that it is weakly biaxial ordered. Unlike the S_G phase, the orientation of the long molecular axis in the S_E phase fluctuates on a time scale which is not in the fast motion regime but comparable to the ^{2}H-NMR time scale of the measurement ($\sim 10^{-5}$ s).

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