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# Remarks on the Proton NMR of Di-Heptyloxyazoxybenzene in the Smectic-C Phase

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# Remarks on the Proton NMR of Di-Heptyloxyazoxybenzene in the Smectic-C Phase

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It is suggested that the ideal smectic-C reorientation model be modified to include both some rotational slipping of the smectic-C domains and hindered reorientation of a small percentage of molecules to account for the behaviour of proton NMR in smectic-C di-heptyloxyazoxybenzene. The calculated poly-domain line shapes are rather insensitive to the characteristic biaxial order parameter predicted by molecular models of the smectic-C phase.

The behaviour with rotation of the applied magnetic field ($\gtrsim 10$ kG) of NMR spectra of smectic-C liquid crystals has been interpreted by means of a model in which molecules in different domains are free to reorient subject to a fixed tilt angle.[1,2] In this note it is pointed out that the proton NMR spectra of smectic-C di-heptyloxyazoxybenzene (DHAB) in a field of 24 kG[2] are in poor agreement with the above reorientation model and that one way to improve the agreement very markedly is to allow for two quite plausible deviations from the original ideal model.

In the high field approximation the effective spin Hamiltonian, $\mathscr{H}$, for a molecule of DHAB may be written,[3]

$$\mathscr{H} \approx (\text{Zeeman energy of protons}) + \eta[(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}) - \tfrac{1}{4}V\sin 2\theta] \times (\text{Spin operator}), \tag{1}$$

where $V = \mu_c/\eta$, $\eta$ is the Maier–Saupe order parameter, $\mu_c$ is a biaxial order parameter and $\theta$ is the angle between the magnetic field and the nematic axis of a particular domain ($|\theta| \leq \pi/2$).

The angle $\theta$ is given by the relation[2] (using a tilt angle of 45°)

$$\cos\left(\frac{\pi}{4} + \theta\right) = \frac{1}{\sqrt{2}}|\sin\delta\cos\varphi + \cos\delta|. \tag{2}$$

Here $\varphi(0 \leq \varphi \leq 2\pi)$ is an azimuthal angle of the domain's plane normal, measured with the initial field direction as the polar axis.[2] The angle $\delta$ is the rotation of the magnetic field from the direction it had originally during cooling of the sample into the smectic-C phase. Eq. (1) neglects biaxial order parameters other than the basic $\mu_c$[4,5] and assumes uniform rotation of the two halves of the DHAB molecule about the respective para axes.[3]

The smectic-C spectrum for a given $\delta$ is obtained from the $\delta = 0°$ spectrum by scaling with the square factor of Eq. (1) and summing over all the values $\theta(\varphi, \delta)$, corresponding to a uniform distribution of domains in $\varphi$, in the manner described by Luz and Meiboom.[2]

Figure 1 shows the experimental spectra of DHAB at 75°C, obtained from Ref. 2, for $\delta = 0°, 40°, 60°$ and $90°$. Figure 2 shows the corresponding curves calculated with the ideal reorientation model.[6] There is a marked qualitative difference in the shapes of calculated and experimental spectra, especially for $\delta = 40°$. Also, the experimental peak heights increase monotonically with $\delta$ but the calculated peak heights do not—the calculated peak height for $\delta = 60°$ is greater than for $\delta = 90°$.

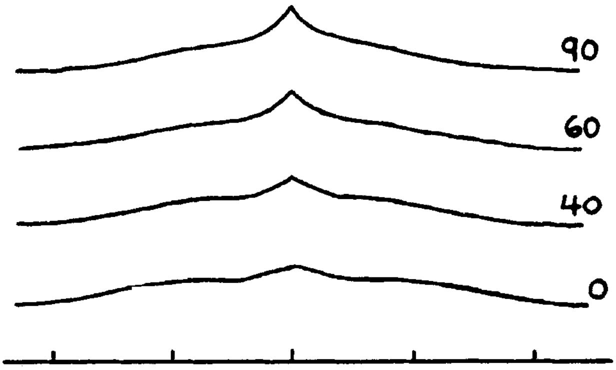

FIGURE 1 Experimental proton NMR spectra of DHAB in the smectic-C phase at 75°C (from Ref. 2). The numbers labeling the curves are the values of magnetic field rotation $\delta$. The marker spacing is 10 kHz.

Figure 3 gives the curves we obtain on allowing for some rotational slipping of the smectic-C domains. The shape of the curves is improved a little and the peak height increases monotonically with $\delta$. The overall agreement with experimental is still rather poor, e.g., the peak heights at $\delta = 60°$ and $\delta = 90°$ are too small.

The method we used to allow for slipping is very crude but simple. The domains are divided into five classes according to their (initial) values of $\varphi$: (1) $0 \leq \varphi \leq 20$; (2) $20 \leq \varphi \leq 75$; (3) $75 \leq \varphi \leq 108$; (4) $108 \leq \varphi \leq 135$; (5) $135 \leq \varphi \leq 180$. (These particular classes were chosen because they are

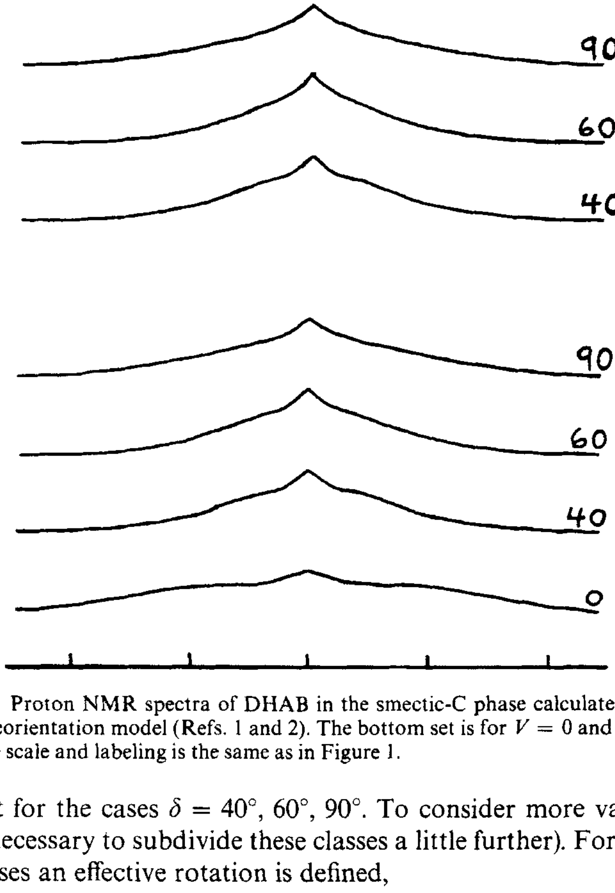

FIGURE 2 Proton NMR spectra of DHAB in the smectic-C phase calculated on the basis of the ideal reorientation model (Refs. 1 and 2). The bottom set is for $V = 0$ and the top set for $V = 0.2$. The scale and labeling is the same as in Figure 1.

convenient for the cases $\delta = 40°, 60°, 90°$. To consider more values of $\delta$ it might be necessary to subdivide these classes a little further). For each of the above classes an effective rotation is defined,

$$\delta^i_{\text{eff}} = \delta - X_i, |X_i| \leq 20,$$

where $X_i$ is so chosen that none of the domains in class $i$ have $\theta$ (calculated according to Eq. (2) with $\delta^i_{\text{eff}}$ replacing $\delta$) greater than about 30°. After a rough fitting procedure we chose the following set of values $X_i$ for each $\delta$ (where no explicit value is given for an $X_i$ it is set equal to zero):

$$\delta = 40°;\ X_1 = 20, X_5 = 20$$
$$\delta = 60°;\ X_1 = -15, X_4 = 15, X_5 = -15$$
$$\delta = 90°;\ X_1 = -5, X_3 = 15, X_4 = -5, X_5 = -5$$

The ease with which the domains can slip, to follow the magnetic field, decreases as $\delta$ increases (the domains start "getting into each other's way").

Finally, Figure 4 shows the line shapes obtained when one allows a small fraction of the total number of molecules to be distributed uniformly

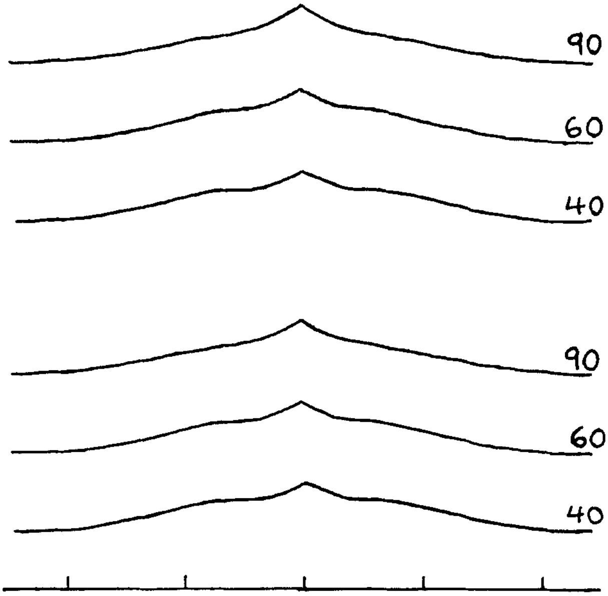

FIGURE 3 Same as Figure 2 but allowing for some rotational slipping of the smectic-C domains.

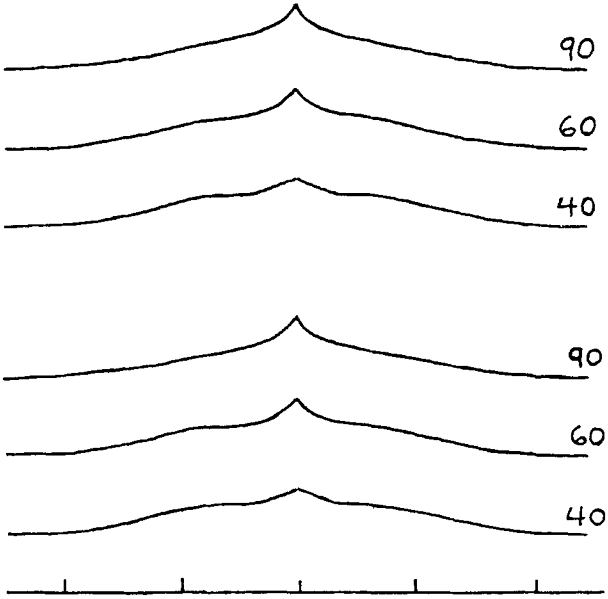

FIGURE 4 Same as Figure 2 but allowing for both slipping of domains and a small percentage of molecules with random direction of tilt (2.7% for $\delta = 40°$, 4% for $\delta = 60°$ and 6% for $\delta = 90°$).

in $0 \leq \theta \leq \delta$. We imagine that molecules near the surface of domains, or all the molecules in very small domains, follow the magnetic field (according to the reorientation model) for some distance, but keep dropping out in a random way as they get fixed by neighbouring domains. Adjusting the fraction of deviant molecules to fit the calculated peak height at $\delta = 90°$ (for $V = 0$) to the experimental value, gives 6%. The corresponding percentages at $\delta = 60°$ and 40°, taken to be proportional to the value of $\delta$, are 4% and 2.7%. It may be worth noting here that Wise, Smith and Doane have commented that for good agreement with their experiments (at 10 kG) it suffices that 90% of the molecules follow the reorientation model.[1]

The spectrum of the deviant smectic-C regions was calculated by using, as before, the square factor of Eq. (1) (with $V = 0$)[7] as a scaling factor, and summing over $\theta = 2, 4, 6, \ldots, \delta$.

The agreement between the curves of Figure 4 and the experimental spectra of Figure 1 is surprisingly good. We see that the $V = 0$ and $V = 0.2$ curves are practically the same. (Only for $V > 0.3$ do the curves begin to differ significantly from the $V = 0$ ones—the line shapes become too narrow, especially at $\delta = 90°$ and 60°.)

It would be very useful for the investigation of the biaxial order parameter $\mu_c$ if the domains could be eliminated by using very thin films, or if the reorientation phenomena could be avoided by doing pulsed NMR experiments, as suggested by Doane.[8]

## Acknowledgements

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6. Our curves for $V = 0$ agree essentially with the spectra calculated by Luz and Meiboom (Ref. 2 above), except that owing to a peculiarity of their data-processing program the area under their curves decreases by about 50% between $\delta = 0°$ and $\delta = 90°$ (it is constant within 10% for the experimental spectra). We thank Dr. S. Meiboom for correspondence on this matter.
7. For random direction of tilt, $V$ does not affect the sum spectra to first order.
8. J. W. Doane (private communication).