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Saul Meiboom [a] & Zeev Luz [a]
[a] Bell Laboratories, Murray Hill, New Jersey, 07974
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Nuclear Magnetic Resonance Study of Smectic Phases†

SAUL MEIBOOM and ZEEV LUZ

Bell Laboratories
Murray Hill, New Jersey 07974

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Abstract—Proton NMR spectra of oriented smectic phases of terephtal-*bis*-(*p*-*n*-butylaniline) (TBBA) are reported. Spectra of the liquid crystal, as well as of methylenechloride dissolved as a probe molecule in this material, were taken. In both cases the behavior as function of temperature and under sample rotation relative to the magnetic field was studied. Each of the smectic *A*, *B* and *C* phases exhibits a typical behavior. That in the smectic *C* phase can be explained in terms of a model in which the molecular orientation can adjust freely on a cone while maintaining a constant tilt angle with respect to the smectic layers. It is concluded that NMR may be a useful tool in classifying smectic phases.

1. Introduction

The purpose of the work reported here was to explore the usefulness of NMR spectroscopy in elucidating the structure of the different smectic phases. Most of the work has been on terephtal-*bis*-(*p*-*n*-butylaniline) (TBBA), which exhibits, in addition to a nematic phase, at least three smectic phases, according to the diagram[1]

$$\text{Solid} \xrightarrow{113.0} \text{Sm}B \xleftrightarrow{144.1} \text{Sm}C \xleftrightarrow{172.5} \text{Sm}A \xleftrightarrow{199.6} \text{Nem} \xleftrightarrow{236.5\,^{\circ}\text{C}} \text{Iso.}$$

Two types of studies were made: In one approach the wide-line proton NMR spectra of the neat liquid crystalline compounds were observed‡. In the second approach a small amount of a " probe " compound—CH_2Cl_2 in the present investigation—was added to

† Presented at the Fourth International Liquid Crystal Conference in Kent, August 21–25, 1972.

‡ The adjective " neat " is used here in the regular meaning of " not mixed with anything ", to differentiate samples not containing a probe compound from those containing one. No reference to the so-called neat phase of lyotropic liquid crystals is intended.

the liquid crystal, and its high-resolution spectrum, rather than that of the liquid crystal itself, was studied. In both cases the behavior of the NMR spectra as function of temperature and of orientation of the sample relative to the magnetic field was studied.

As a result of the direct dipolar interaction between the two protons of the probe molecule, its proton NMR spectrum consists of two equal peaks, with a frequency spacing given by[2]

$$\Delta = C(3\cos^2\phi - 1). \tag{1}$$

In deriving this equation, it is assumed that the probe molecule tumbles rapidly in an essentially uniaxial environment; ϕ is then the angle between the axis of the environment and the direction of the magnetic field. The coefficient C depends on the geometry of the probe molecule, and, for a given probe, is proportional to the order parameter.

2. NMR Spectra of Probe Molecules

In the traces of Fig. 1, the two narrow lines constitute the proton spectrum of the CH_2Cl_2 probe in TBBA, recorded at 100 MHz proton frequency. It should be noted, when comparing this figure with later ones of the neat material, that the transition temperatures, as well as many other properties, are altered to some extent by the presence of the probe, and thus quantitative comparisons should only be made with reservations. In the frequency range of these traces, the TBBA molecules contribute only to the broad background signal, and will be disregarded here. It is apparent that, on cooling from the nematic in the 24 kGauss magnetic field of the spectrometer, the peaks remain quite sharp throughout the smectic phases. This, as well as the rotation results given below, show that the liquid crystal remains well oriented throughout. The spacing of the two peaks as function of temperature is plotted in Fig. 2. It is of interest to note that the nematic to smectic A transition is evidenced by a small discontinuous increase in the spacing (barely visible on the scale of Fig. 2), while the smectic C to smectic B transition involves a very large change. The smectic A to smectic C transition is not accompanied by a detectable discontinuity, and thus could be of second order, or very nearly so. These observations

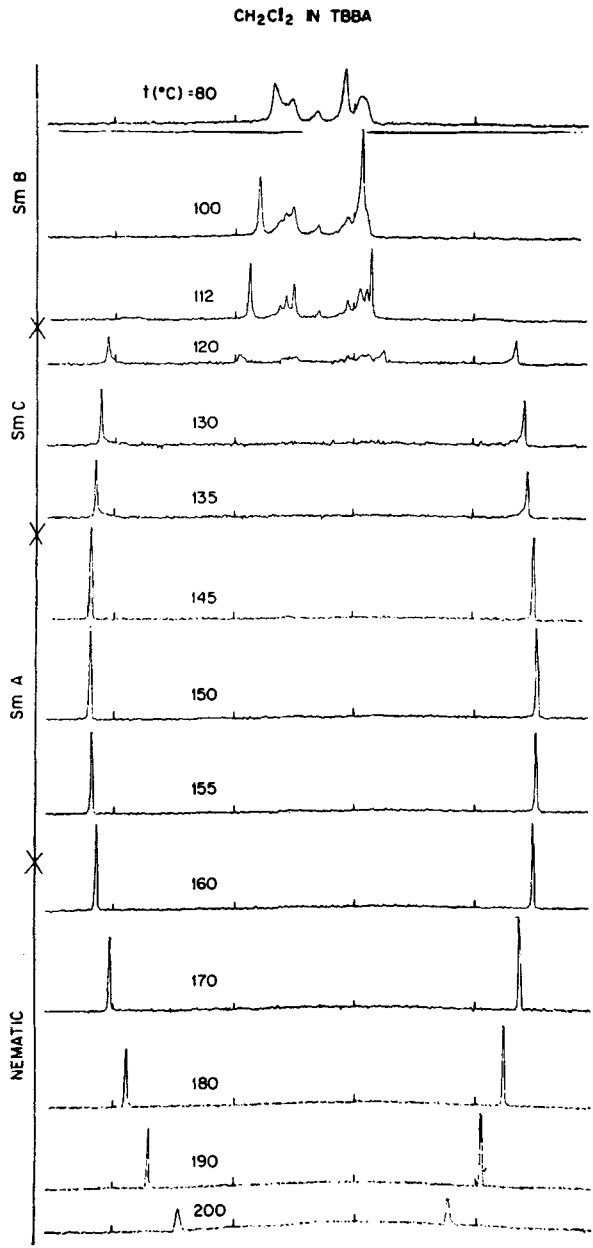


Figure 1. 100 MHz proton NMR of a 5.3 wt. % solution of CH_2Cl_2 in TBBA as function of temperature. The sample was oriented by cooling from the nematic phase. The frequency markers are spaced 1 kHz apart.

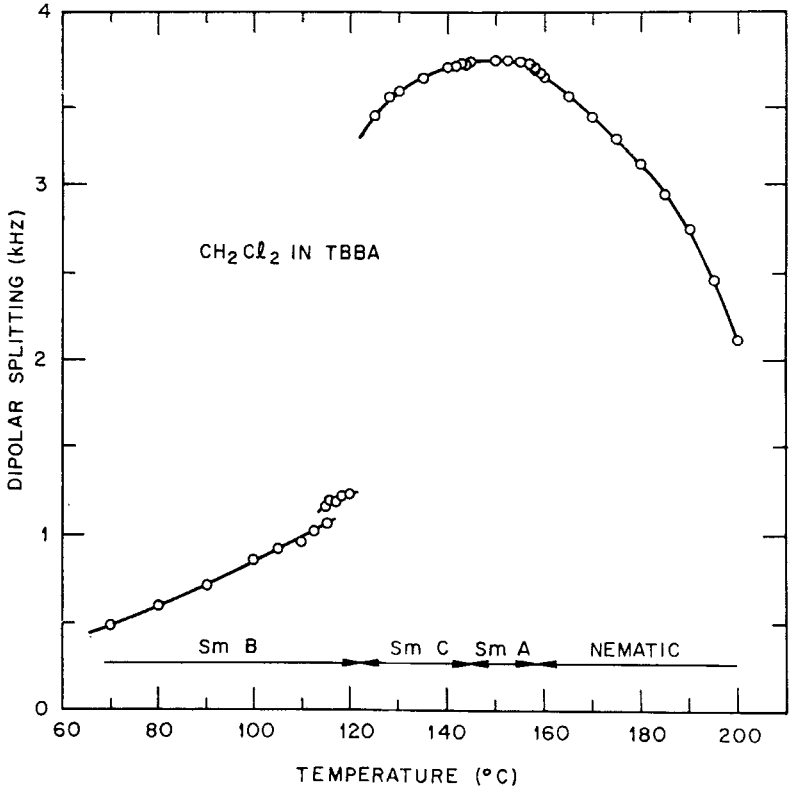


Figure 2. The doublet spacing of the CH_2Cl_2 spectra as function of temperature. The solution is the one referred to in the caption of Fig. 1.

are in agreement with DSC results,[1] in which the latent heat for the smectic B to smectic C transition is much larger than that for the smectic A to nematic, while no peak at all appears at the smectic C to smectic A transition.

We next discuss the behavior of the probe spectra under rotation of the sample in the magnetic field. In the nematic phase the director will rapidly readjust itself parallel to the field, and no changes in the spectrum are observed. However, after cooling into the smectic A phase, the spacing as function of rotation angle ϕ is in accordance with Eq. (1). Some typical spectra are shown in Fig. 3, and a plot of the spacing as function of ϕ is given in Fig. 4. The curve in this figure has been calculated from Eq. (1), the quantity C

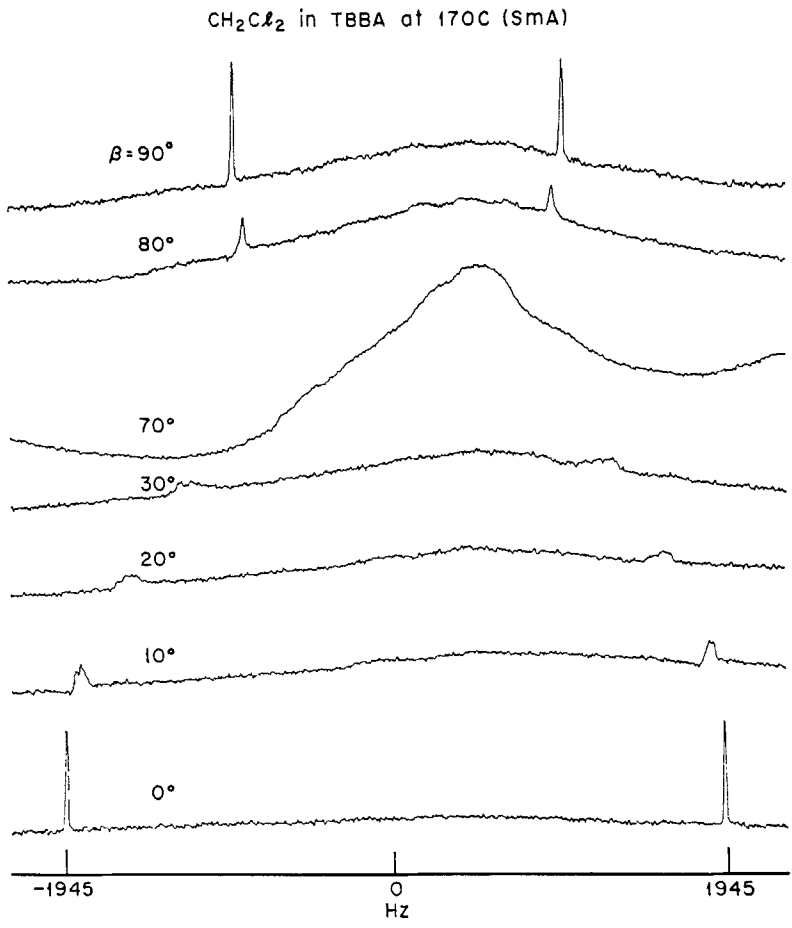


Figure 3. Proton NMR spectra of CH_2Cl_2 in the smectic A phase of TBBA as function of the rotation angle ϕ. This solution contained 2 wt. % CH_2Cl_2.

being the only adjustable parameter. The same behavior of a probe spectrum in a smectic A phase under rotation was reported previously by Yannoni,[3] and we have found it in four other compounds with smectic A phases, with no exceptions. In all these compounds it was found that the smectic A phases can be oriented by cooling in a strong magnetic field (24 kGauss) from the nematic, or directly from the isotropic phase, and that this orientation is preserved under rotation in the magnetic field.

It is apparent in Fig. 3 that a very appreciable broadening of the

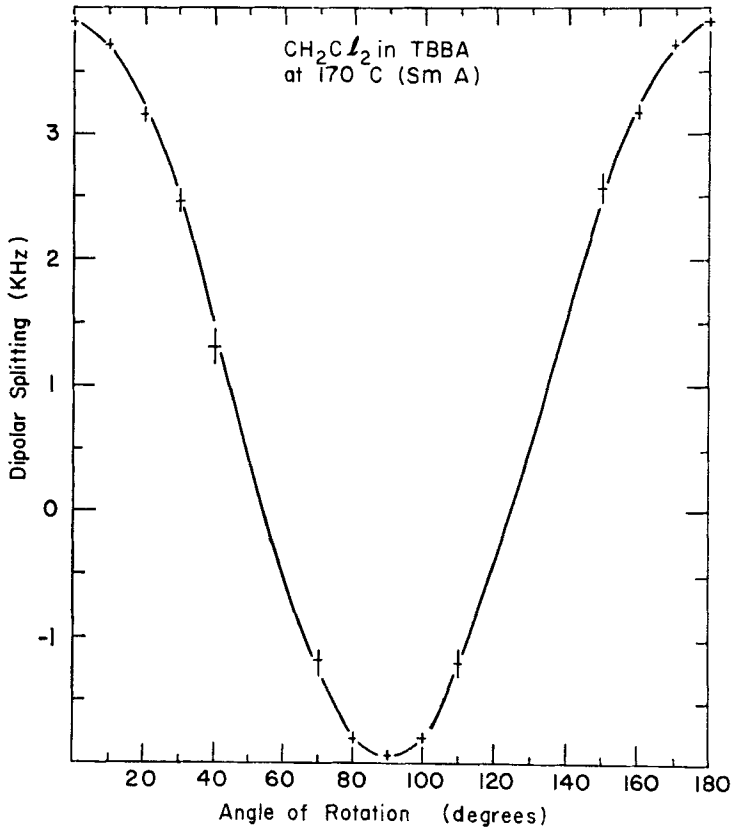


Figure 4. The doublet spacing of the CH_2Cl_2 spectra as function of the rotation angle ϕ of the solution referred to in the caption of Fig. 3. The curve is calculated from Eq. (1) with the constant C adjusted to fit the experimental result at $\phi = 0°$.

probe peaks occurs on rotation of the sample. This is the result of incomplete alignment of the liquid crystal. The assumption of a Gaussian distribution of the direction of alignment, with a standard deviation of 2 to 3 degrees, accounts for the observed broadening. In Fig. 3 only spectra for angles ϕ near 0° and 90° are shown. For intermediate angles the probe spectrum is hard to observe, both because of its increased linewidth and because of interference by the liquid crystal spectrum, which becomes narrow near the " magic angle " (the angle for which $3\cos^2\phi - 1 = 0$, i.e., $\phi \approx 55°$).

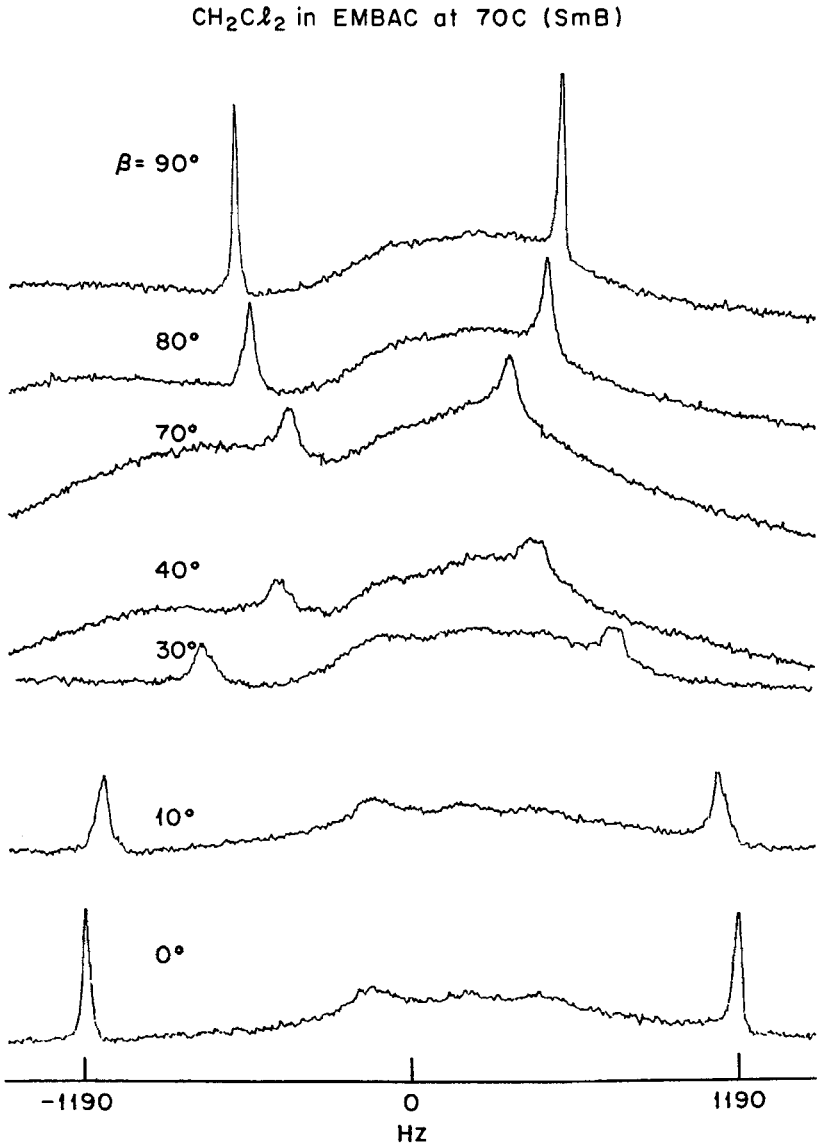


Figure 5. Same as Fig. 3 for a 2.7 wt. % solution of CH_2Cl_2 in the smectic *B* phase of EMBAC.

The same behavior of the probe spectrum under rotation was found in the smectic phases of ethyl[(methoxybenzylidene)amino] cinnamate (EMBAC). Figures 5 and 6 show spectra and rotational behavior of its smectic B phase. It is believed that this behavior is typical for uniaxial smectic B phases. It is not expected that biaxial smectic B phases will accurately follow Eq. (1), and indeed

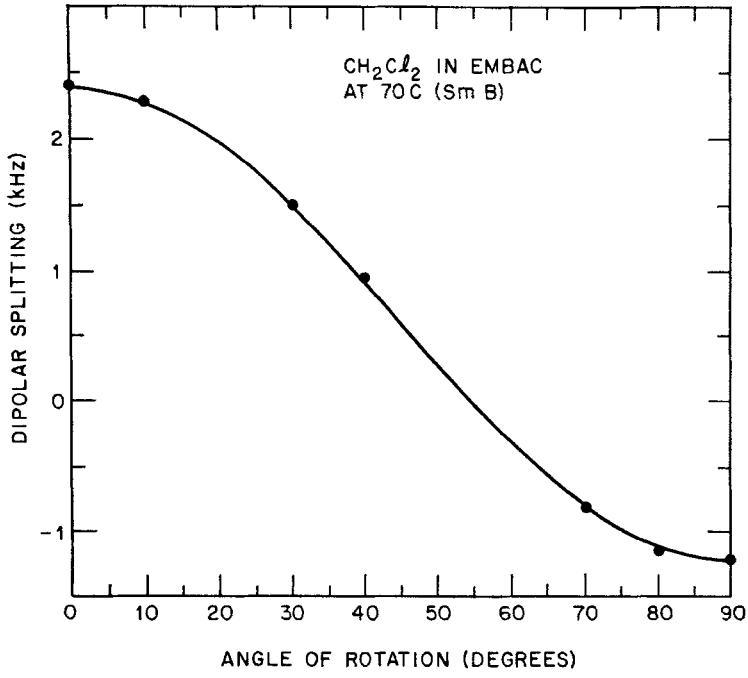


Figure 6. Plot of the results of Fig. 5 as function of the rotation angle ϕ.

the probe spectra of the smectic B phase of TBBA (Fig. 7) show appreciable deviations from this equation. Note, for instance, that the spacing at 90° rotation is larger than half the spacing at 0°.

The behavior of the probe spectra in the smectic C phase is quite different from that of the A and B phases. Referring to the experimental spectra for TBBA in Fig. 8, it will be seen that, at the smaller angles of rotation, the peaks do not move in, but rather develop a sharp edge at their original position, while tailing away towards the inside. This behavior is consistent with the following model.

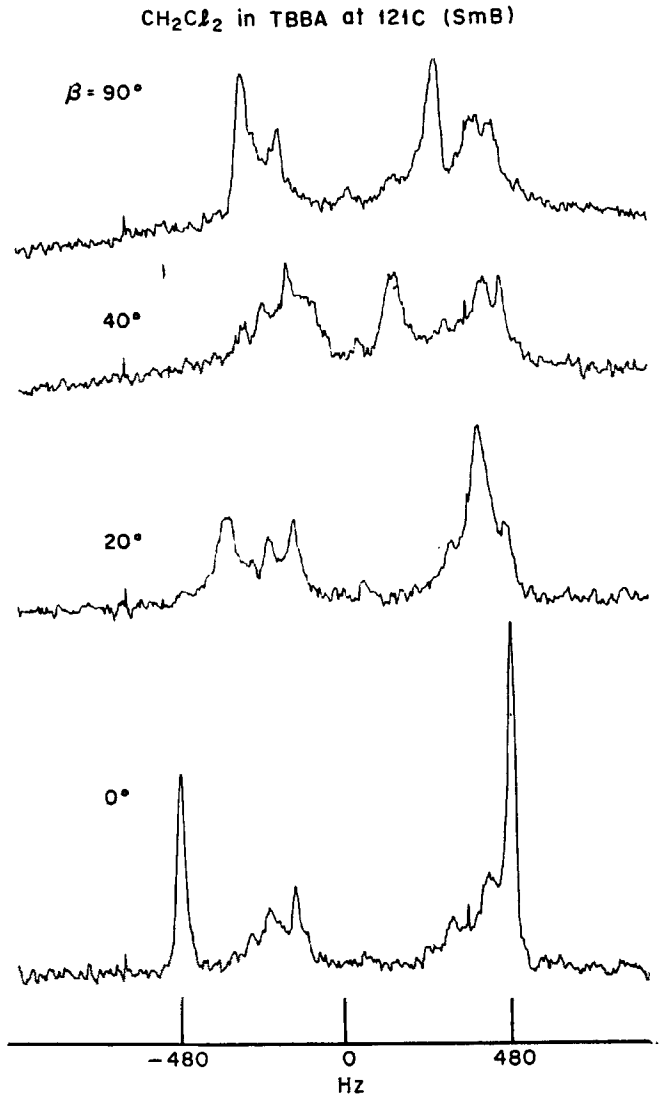
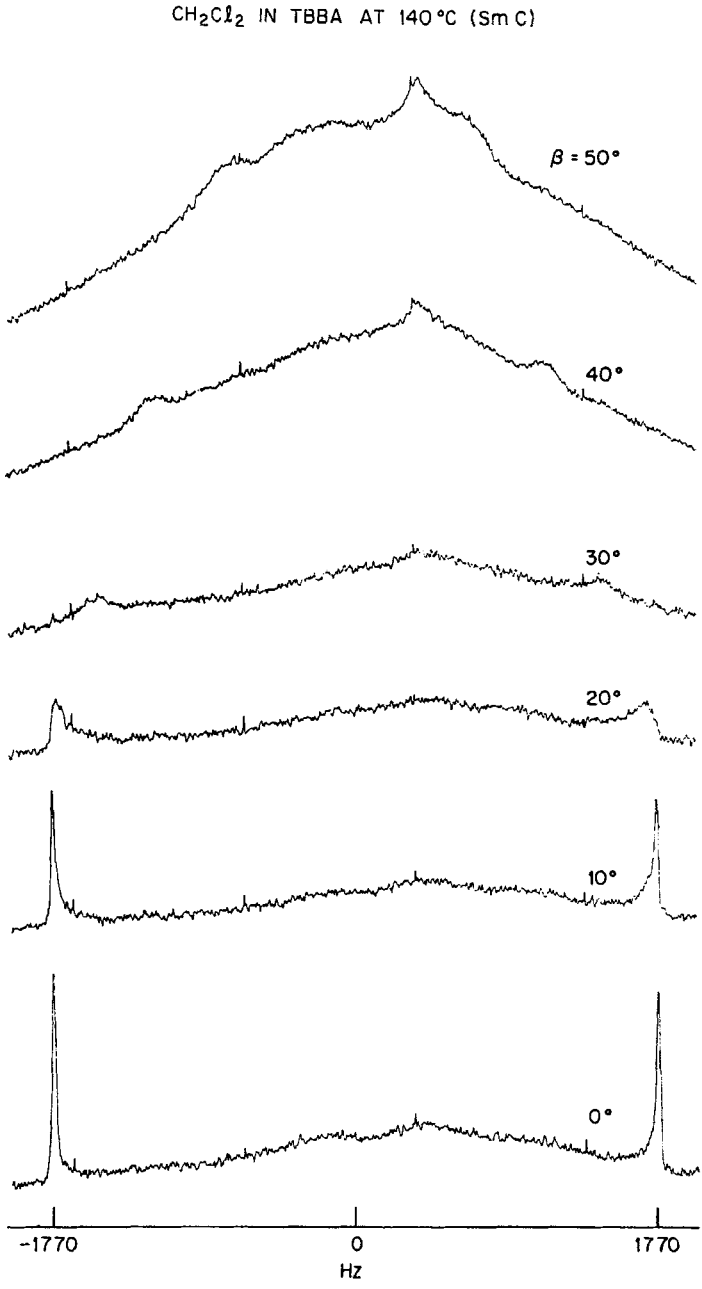


Figure 7. Same as Fig. 3 for a 2.7 wt. % solution of CH_2Cl_2 in the smectic B phase of TBBA. The rotationally invariant background spectrum is due to the separation of an isotropic phase, consisting of a solution of TBBA in CH_2Cl_2.



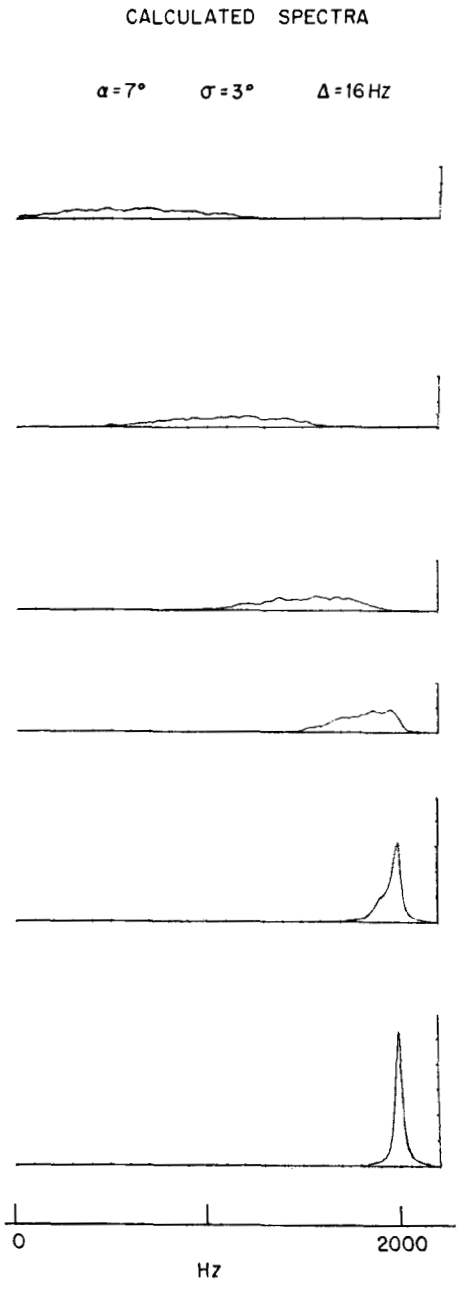


Figure 8. Same as Fig. 3 for a 1.5 wt. % solution of CH_2Cl_2 in the smectic *C* phase of TBBA at 140 °C. The spectra on the right are calculated as explained in the text.

On cooling of the sample into the smectic C phase, the long axes of the molecules stay aligned along the strong magnetic field. Since this axis is inclined to the smectic planes (by an angle α), the sample breaks up into domains, in which the smectic planes make an angle α with the magnetic field direction, but the orientation of which is otherwise evenly distributed about this direction. Referring to Fig. 9, the normals on the smectic planes thus fall on the inner

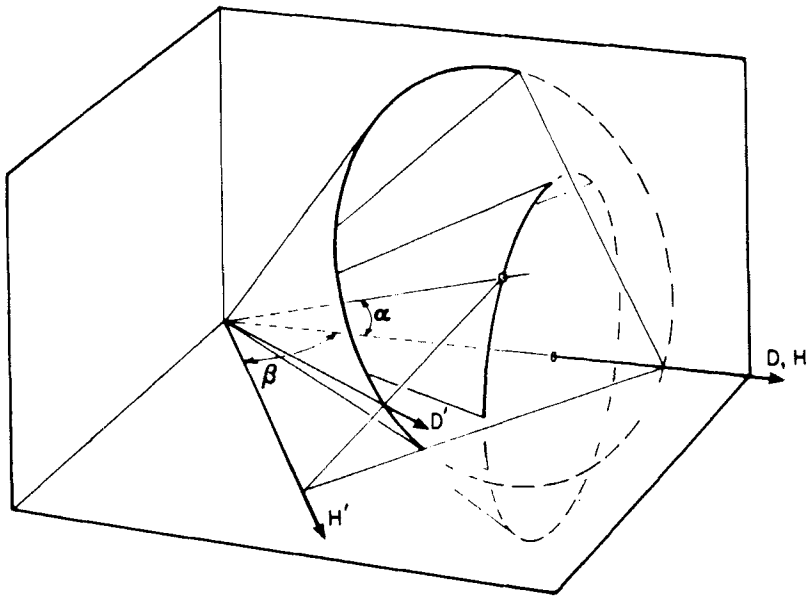


Figure 9. Coordinate system used to describe the smectic C model.

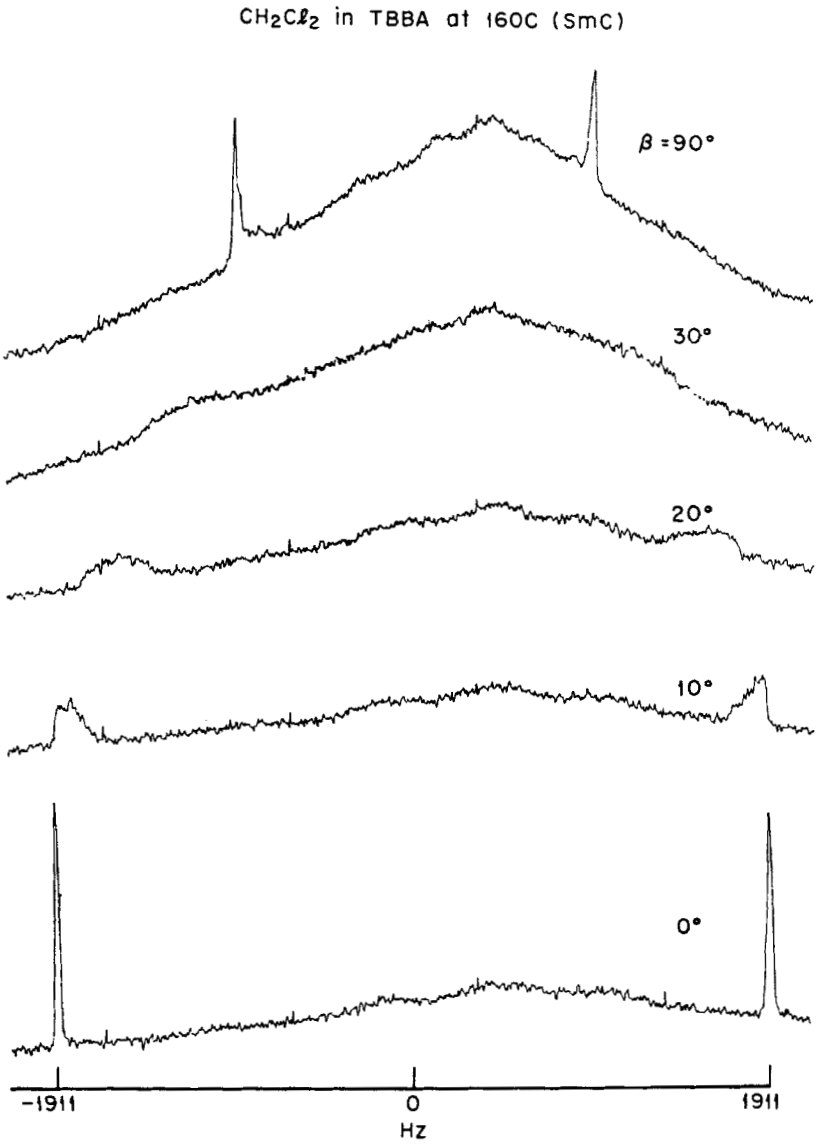
cone, having H as axis and 2α as apex angle. It is further assumed that in each of these domains the direction of the long axis of the molecules (indicated by D in the figure) is free to rotate about the normal to the plane, while keeping a constant tilt angle α. In Fig. 9, the outer cone indicates the locus of the possible molecular orientations for a given domain. The axis of this cone is the normal for that domain, and the cones for the different domains are evenly distributed around H.

The behavior of this model can qualitatively be seen as follows: On rotation of the magnetic field through an angle β, from H to H', the molecular axes will reorient so as to minimize the magnetic energy. That is, they will rotate on the outer cone to the direction D' as near to H' as possible. For values of $\beta < 2\alpha$ there are always two domains for which D' coincides with H', i.e., for which $\phi = 0$. These domains, and the ones with neighboring orientations, produce the outer edges of the spectrum. For values of $\beta > 2\alpha$, no such domains exist and the probe peaks move in.

The model discussed is the same as that advanced by Gelerinter and Fryburg[4] from EPR observations in the smectic C phase of 4,4′-di-*n*-heptyloxyazoxybenzene, except that they conclude that, in strong magnetic fields, the smectic planes realign on rotation. Our NMR evidence indicates that no such reorientation occurs.[5]

A computer program for calculating theoretical spectra based on this model was written. The results of this program were made more realistic by incorporating a Gaussian distribution of the orientation of the smectic planes, similar to the one discussed above for the smectic A spectra. A standard deviation of 2° for this distribution was adopted, as well as a natural linewidth of 16 Hz (half width at half height). In applying this model to the probe spectra, use is made of Eq. (1), which assumes an axially symmetric local potential for the probe molecule. This is obviously not rigorously true for the smectic C, and the results should therefore be interpreted only in a qualitative or semi-quantitative way. Calculated spectra, in which the angle α was taken as an adjustable parameter, are shown in Figs. 8 and 10 for TBBA at respectively, 140 and 160 °C. Best fit to the experimental spectra was obtained for $\alpha = 7°$ and $\alpha = 3°$, respectively. Although the trend of these values is probably significant, they should, for the reason given above, not be taken as giving the inclination of the liquid crystal molecules quantitatively.

Similar results for 4,4′-di-*n*-heptyloxyazoxybenzene (DHAB) are shown in Fig. 11, with theoretical curves for $\alpha = 40°$.



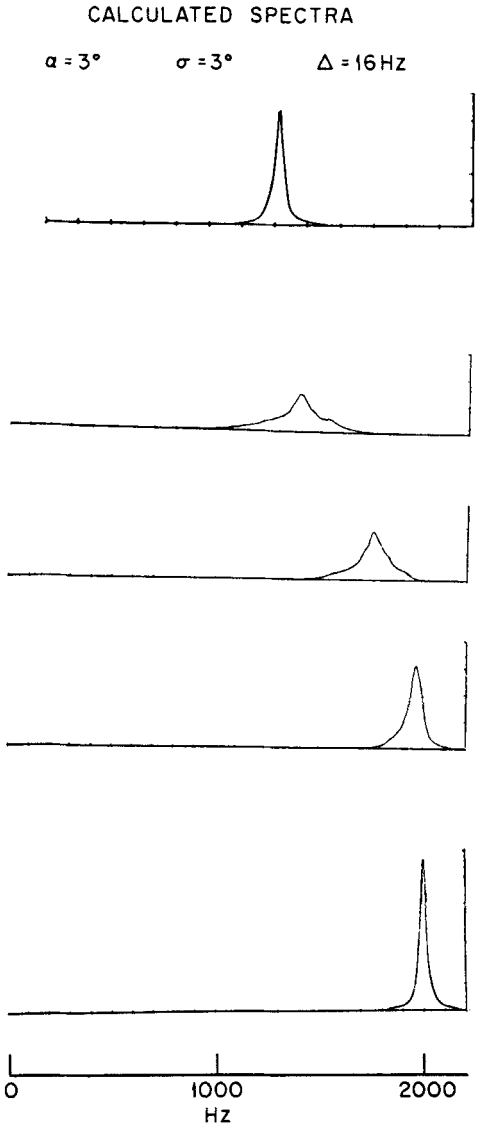


Figure 10. Same as Fig. 8 for a temperature of 160 °C.

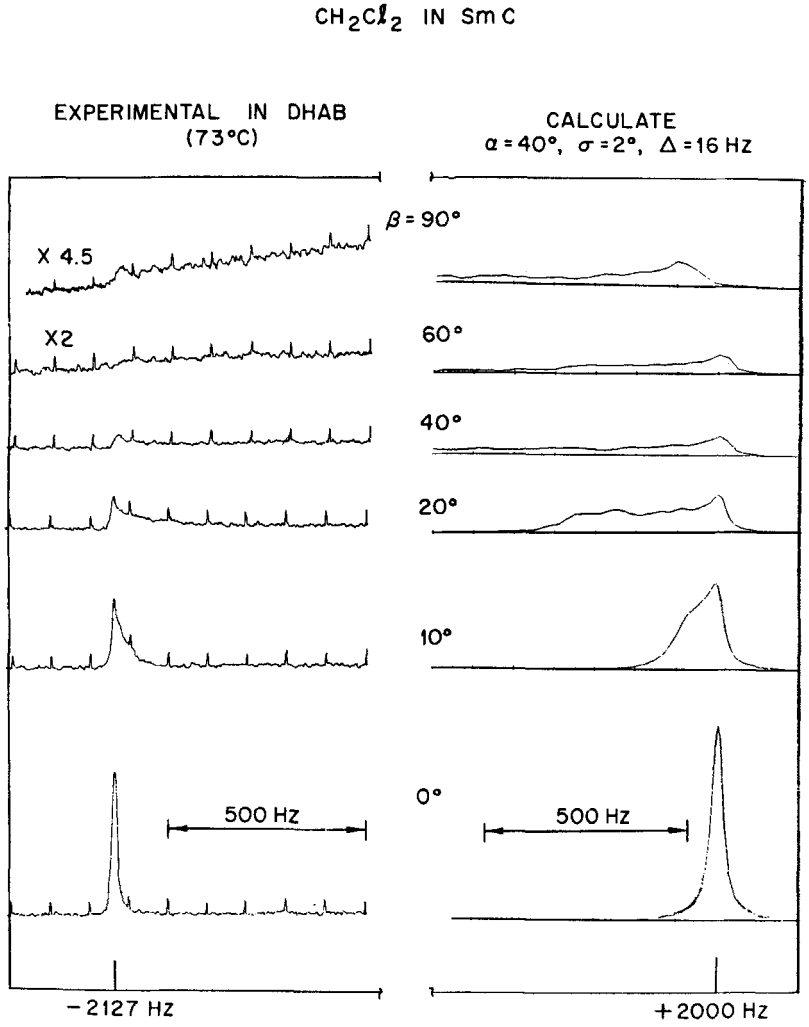


Figure 11. Same as Fig. 8 for a 1.8 wt. % solution of CH_2Cl_2 in DHAB at 73 °C.

3. NMR Spectra of Neat TBBA

Proton spectra for neat TBBA at a number of different temperatures are shown in Fig. 12. Due to the large number of protons in the liquid crystal molecule, these spectra consist of very many overlapping and unresolved lines, and no sharp features can be

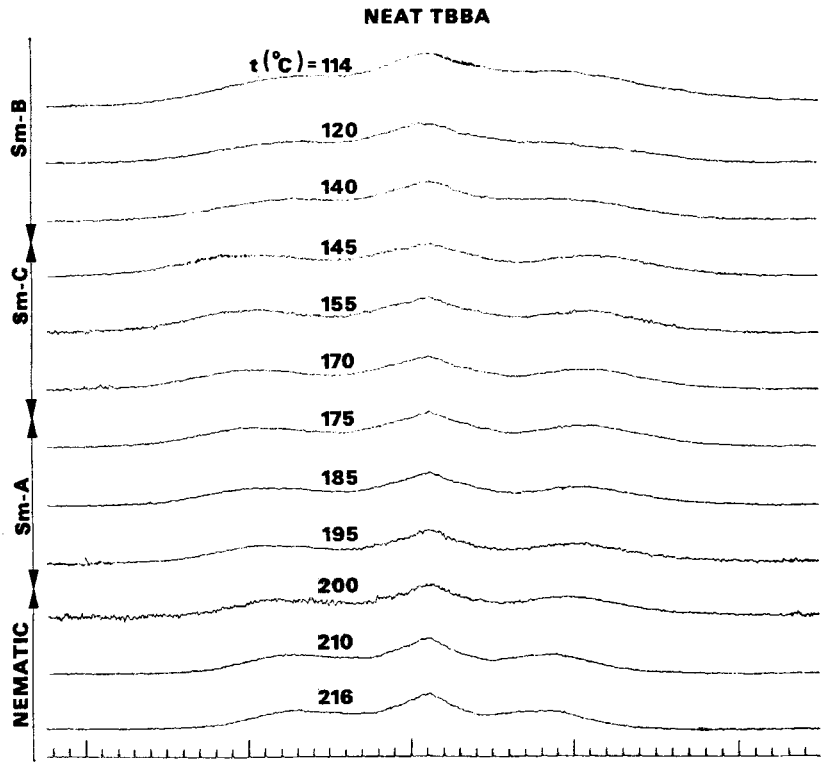


Figure 12. Proton NMR spectra of neat TBBA as function of temperature. The small frequency markers at the bottom of the figure are spaced 1 kHz apart.

isolated. For this reason no accurate frequency measurements can be made, but the general behavior of the spectral width in the different phases is quite similar to that shown in Fig. 1 for the probe spectra.

Upon rotation of the sample, no change of the spectrum is observed in the nematic phase, as expected. The behavior under rotation in the smectic *A* phase is shown in Fig. 13, and fits the one predicted by Eq. (1): Almost total collapse of the spectrum occurs near the magic angle (55°), where the dipolar interactions vanish and the chemical shift of the different protons becomes apparent. Note also that the spectral width at an angle of 90° is just one half that at 0°.

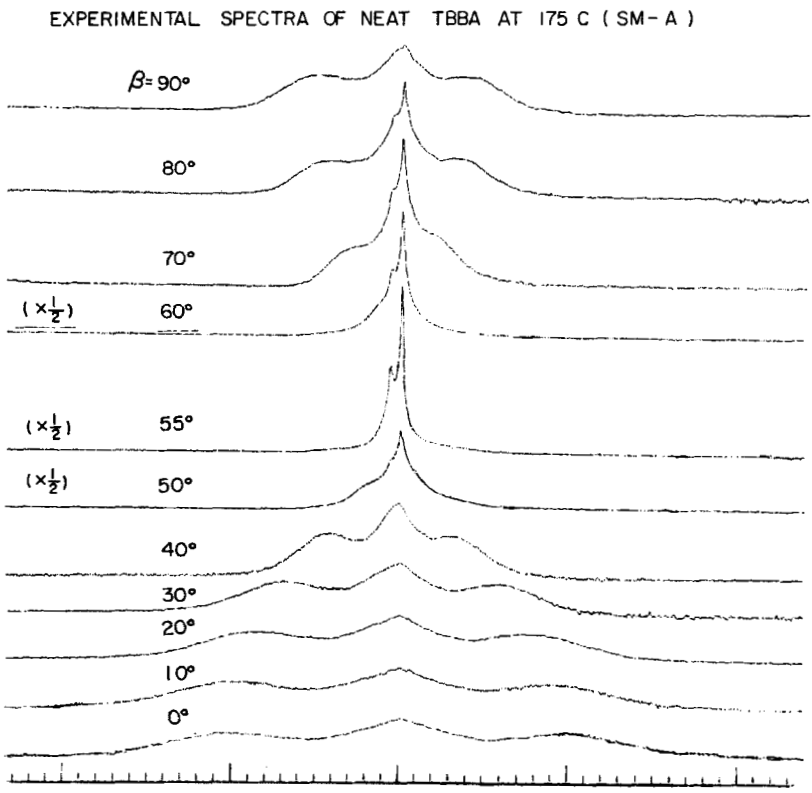


Figure 13. Proton NMR spectra of neat TBBA in the smectic A phase as function of the rotation angle ϕ.

A similar set of spectra for the smectic B phase is shown in Fig. 14 for two different temperatures. On comparison with the previous figure for smectic A, the following facts stand out: the minimum spectral width still occurs near the magic angle, but the residual line-width is much larger and increases at the lower temperature. Two reasons for this behavior can be advanced: (i) There is good evidence that in the smectic B phase of TBBA the long axes of the molecules are inclined to the smectic planes, probably even more so than in the smectic C phase.[6] The NMR spectra of Fig. 12 show that an appreciable contraction in the overall spectral width occurs on going from smectic C to smectic B, indicating that in the latter phase the long axes of the molecules make a larger angle with the

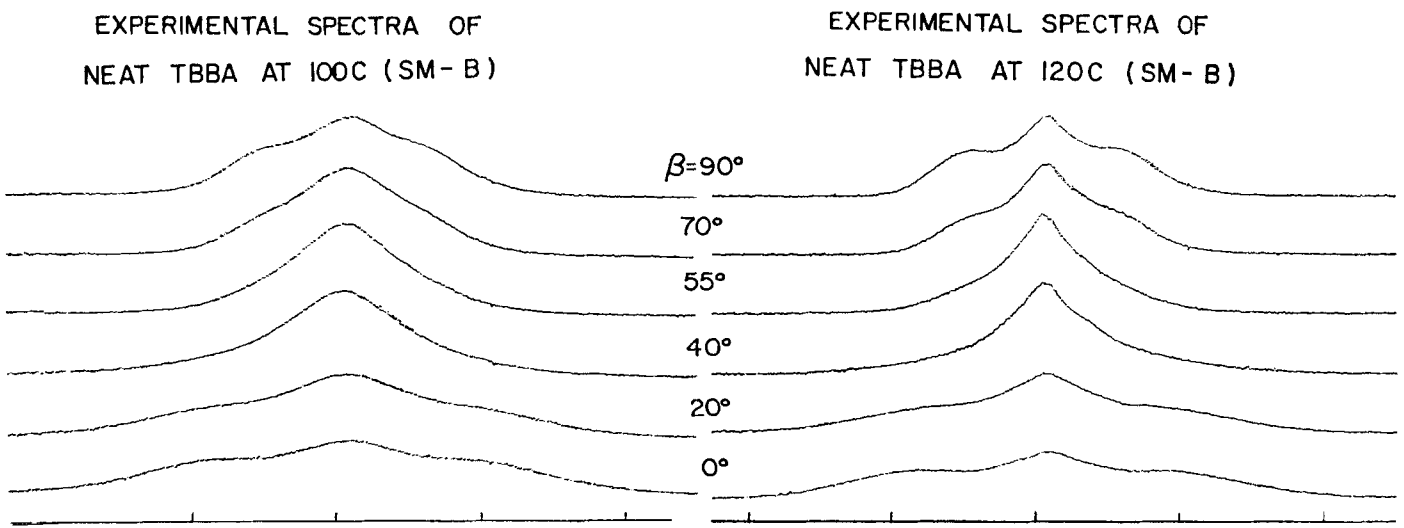


Figure 14. Proton NMR spectra of neat TBBA in the smectic B phase.

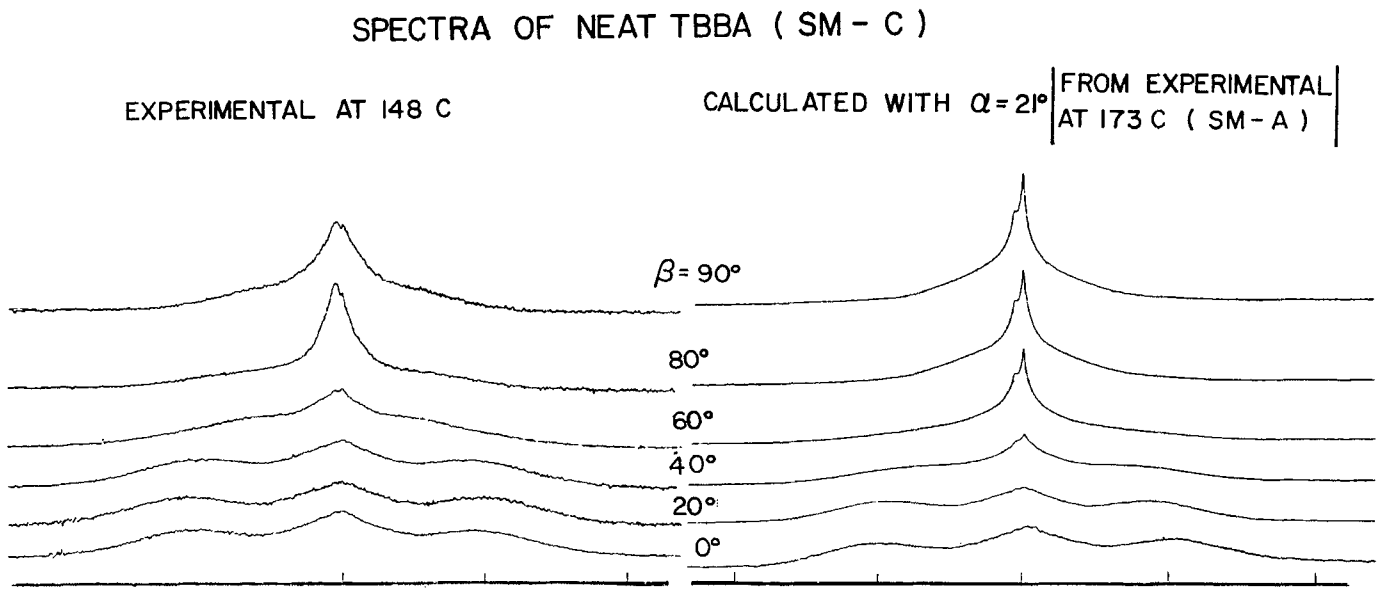


Figure 15. Proton NMR spectra of the smectic *C* phase of TBBA as function of the rotation angle ϕ at 148 °C. The spectra on the left are experimental; those on the right are calculated as explained in the text.

direction of the magnetic field. Like in the smectic C, the sample will be made up of differently oriented domains, but in the present case no freedom of movement of the molecular alignment should be assumed. This model leads to an inhomogeneous broadening on rotation of the sample, because the axes of different domains will be differently oriented. (ii) A second possible contribution to the increased width is from intermolecular dipolar interactions. In contrast to smectic A and C, where rapid molecular diffusion within the layers takes place, such diffusion may be much slower in the more highly ordered smectic B phase. The strong temperature dependence of the broadening (compare for instance the widths at the magic angle), which is absent in the other smectic phases, provides evidence for such an effect: At the lower temperatures slower diffusion increases the average intermolecular dipolar interaction.

The behavior under rotation of the smectic C phase is again very different from that of the A and B phases, as is evident from the spectra shown in Fig. 15. The smectic C model, described above in connection with the probe spectra, can again explain the major features. In the present case it is impractical to calculate a theoretical spectrum for the large number of protons in the liquid crystal molecule (as could easily be done for the two protons in the probe). However, one can get around this problem by observing that, in the model, each domain gives a spectrum contribution that is essentially identical to the spectrum observed in the smectic A phase at an angle of rotation equal to the angle between H' and D' appropriate for that domain. One should thus be able to " synthesize " a given smectic C spectrum by superposing smectic A spectra, the distribution of the rotation angles to be used being calculated from the model. The single adjustable parameter for this process is again the smectic C inclination angle α. Results for such superpositions are given under the heading " calculated " in Fig. 15.

4. Conclusions

The results described here indicate that NMR spectroscopy may be a useful tool in classifying the different smectic phases. Particularly, the behavior under rotation of both the probe spectra and those of the neat liquid crystal appear to be quite specific. We have indeed

found the same behavior in a number of other liquid crystals, to be reported on at a later date.

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