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SOME PARTIALLY RESOLVED PROBLEMS IN NMR OF MIXED LIQUID CRYSTALS OF OPPOSITE DIAMAGNETIC ANISOTROPIES

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NMR spectra of molecules dissolved in mixed liquid crystals of opposite diamagnetic anisotropies have been extensively used in the determination of chemical shift anisotropy and other useful information which is normally difficult to derive without the help of such experiments. However, studies on systems such as methanol, tetramethylsilane and the observation of two spectra at the critical concentration and temperature are only partially understood. Details of such investigations are presented with critical up-to-date evaluation of the experiments.

1. INTRODUCTION

The use of NMR spectroscopy of oriented molecules in the determination of chemical shift anisotropy and the study of deformations and orientation of tetrahedral molecules has attracted the attention of various groups.[1,2] The information derived and the theories presented so far do not provide unique answers to these problems. As far as the determination of chemical shift anisotropy using

this technique is concerned, various improvements in the method of obtaining the differences in the chemical shifts between the isotropic and the nematic phases have been proposed from time to time in order to reduce the errors due to solvent effects. However, every method suggested suffers from one or more disadvantage(s) with the result that the values derived for the same compound are rarely in agreement with each other particularly for the proton chemical shift anisotropy. The NEMIX method[3], proposed by Khetrapal and Kunwar[4-6], utilizing a critical mixture of two liquid crystals of opposite diamagnetic anisotropies avoids the use of a reference compound and hence the additional effects in this case are reduced compared to those in other methods. However, the 'local effects', present even in this method need to be considered in order to obtain the 'true' values. In certain cases the effects are so large that their presence becomes obvious from the 'ridiculous' values of the derived parameters if the effects are neglected[7]. The quantitative determination of such effects is, however, not easy. Similarly, studies on tetrahedral molecules in mixed liquid crystals of opposite diamagnetic anisotropies lead to definite evidence for the existence of very large effects which are not yet understood. Some such anomalies are demonstrated in the present communication together with an unambiguous demonstration of the existence of the isotopic effects on the NMR splittings observed in tetramethylsilane.

2. EXPERIMENTAL

The proton NMR spectra of acetonitrile, benzene,

methanol and tetremethylsilane in single and mixed liquid crystals of positive and negative diamagnetic anisotropies were recorded on a Bruker WH-270 FT-NMR spectrometer equipped with a BNC-12 computer with a core memory of 20K. The liquid crystal of positive diamagnetic anisotropy was N-(p'-ethoxybenzylidene)-p-n-butylaniline (EBBA) and the one with negative diamagnetic anisotropy was Merck ZLI-1167 (a ternary eutectic mixture of propyl-pentyl-, and heptyl-bicyclohexyl carbonitrile). Nearly 0.3 : 1.0 mixture of EBBA and ZLI-1167 by weight, provided a critical mixture in all the cases where spectra due to both the orientations namely those corresponding to the alignment of the liquid crystal optic axis along and orthogonal to the magnetic field were observed at different temperatures depending upon the solute concentrations and the nature of the solute molecules. Typical spectra of benzene, acetonitrile and methanol have been discussed elsewhere[7] along with the experimental conditions. The spectra of tetremethylsilane at and near the critical point are shown in figure 1.

3. RESULTS AND DISCUSSION

3.1 Benzene and acetonitrile

The proton chemical shift anisotropies of benzene and acetonitrile were determined both by the NEMIX and the GRADIENT methods.

In the NEMIX method, the separation ($\Delta\delta$) between the centres of the two spectra at the critical point and the order parameters (S_c) of the symmetry axes were used to determine the proton chemical shift anisotropies ($\Delta\sigma_H$)

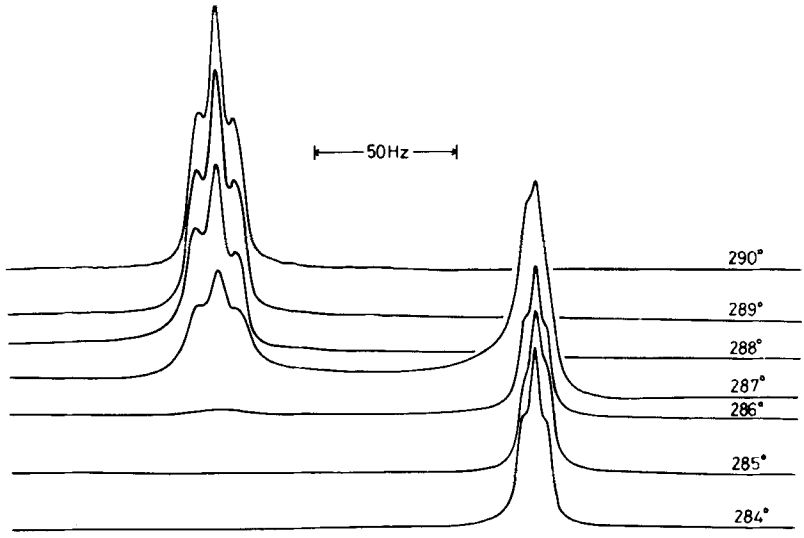

FIGURE 1 Proton magnetic resonance spectra of tetramethylsilane at various temperature in 0.3 : 1.0 mixture (by weight) of EBBA : ZLI-1167; solute concentration: 3% (by weight); spectrometer frequency: 270 MHz; No. of scans: 240.

with the help of relation(1):

$$\Delta\sigma_H = \Delta\delta / S_c \qquad (1)$$

The values thus obtained for benzene and acetonitrile are -1.49 ± 0.01 and -2.01 ± 0.01 ppm respectively.

The GRADIENT method was also employed in both the cases (namely benzene and acetonitrile) by changing the temperature above and below the critical point. The order parameters of the symmetry axes (S_{c_3} for acetonitrile and S_{c_6} for benzene) were plotted against the chemical shift in the nematic phase (σ_{aniso}) with respect tetra-

methylsilane used as the internal reference. The plots are shown in figure 2 and 3 for benzene and acetonitrile respectively. Figures 2 and 3 show that the plots are straight lines in each case for each type of orientation. However, though the extrapolation of the straight lines from both the sides of the critical point to zero order parameter meet at the same point in benzene, there are significant deviations in acetonitrile. This clearly demonstrates that the isotropic chemical shift deter-

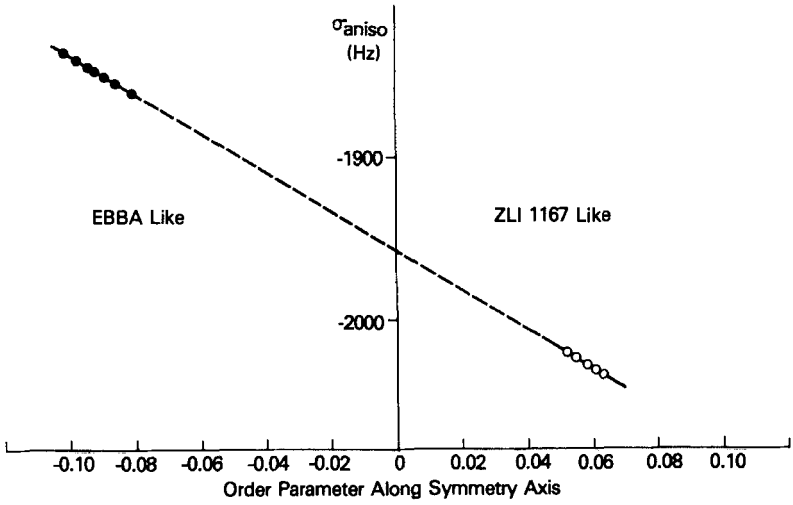

FIGURE 2 A plot of chemical shift in the nematic phase with reference to tetramethylsilane as an internal standard vs. the order parameter of the 6-fold symmetry axis in benzene dissolved in a 0.3 : 1 (by weight) mixture of EBBA : ZLI-1167. The change in the order parameter was achieved by variation of the temperature around critical point (16°C). Solute concentration: 3 weight per cent; spectrometer frequency: 270 MHz.

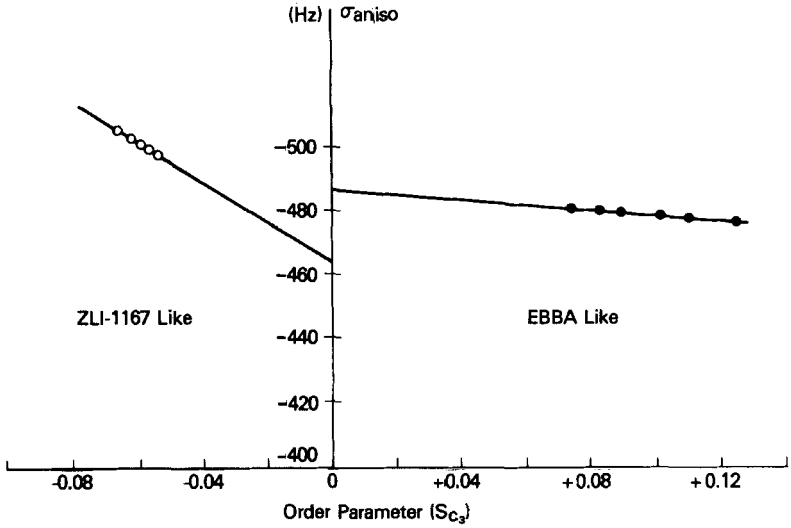

FIGURE 3 A plot of σ_{aniso} vs. the order parameter of the 3-fold symmetry axis in acetonitrile. Other details are the same as those for fig. 2 except that the critical temperature was 21°C

mined by the GRADIENT method certainly contains contributions from the solvent effects which are different for different orientations at least in acetonitrile. Such corrections must be estimated before deriving the 'true' isotropic chemical shifts. In benzene, on the other hand the isotropic chemical shift derived by the GRADIENT method is the same as the isotropic phase value. The chemical shift anisotropy value ($\Delta\sigma_H$) derived by the GRADIENT method is, however, -3.34 ppm. against the value determined by the NEMIX method as -1.49 ppm. The $\Delta\sigma_H$ values for acetonitrile determined by the GRADIENT method are 0.42 and 3.48 ppm depending upon whether they are derived from EBBA or ZLI-1167 type of orientations. They

differ drastically from the value obtained by the NEMIX method (-2.01 ppm). An estimate of local effects is, therefore, very essential in order to obtain results consistent with both the methods.

3.2 Methanol

As mentioned earlier[7], the chemical shift difference of the methyl protons in the two orientations is 166.4 Hz at 270 MHz such that the molecules with larger spread (EBBA-like orientation) 'appear' at lower field. Using a scaling distance of 1.80 Å between the methyl protons, a very unrealistic value of -104.3 ppm is obtained for $\Delta\sigma_H$ for the methyl protons in methanol. It can be interpreted in terms of the 'multiple site theory' and the 'local effects' as mentioned earlier.[7]

3.3 Tetramethylsilane

At the critical point, tetramethylsilane provides two spectra (essentially triplets) separated by 0.42 ppm (288 K) in figure 1 and the EBBA-like orientation appears at a lower field. Since it is a tetrahedral molecule, a small splitting (giving rise to essentially the triplet structure) attributed to distortions in the tetrahedral symmetry is usually observed in this case. Though various explanations have been given to understand the orientation of the tetrahedral and cubic molecules but none gives a fully satisfactory answer[1,2]. In the present case even if the entire triplet splitting is attributed to the normal orientational effects caused by distortions in symmetry, one can estimate an upper limit of the shift between the two groups at the critical point where the two spectra

coexist. Taking a value of 10^{-3} for S_{C_3} (corresponding to the entire splitting) and a very large value of the proton chemical shift anisotropy of 5.0 ppm for the methyl protons in tetramethylsilane, the upper limit of the shift ($\Delta\delta$) between the tetramethylsilane lines at coexistence turns out to be 2.0 Hz at 270 MHz (0.007 ppm) which is negligible compared to the observed value of 0.42 ppm. The results, therefore, indicate dominant 'local effects' even in tetrahedral molecules. Their theoretical estimate should throw light on the mechanism of orientation in tetrahedral molecules.

Another interesting feature in the proton spectrum of tetramethylsilane including ^{13}C-H satellites is the clear observation of the isotopic effects arising from a ^{13}C substitution in the natural abundance. The total triplet splitting (figure 4) due to ^{12}C tetramethylsilane is 14.9 Hz compared to a value of 16.7 Hz in the species containing a ^{13}C-nucleus. This difference of 1.8 Hz arises from the 'true' distortions in the molecular symmetry caused by a ^{13}C-substitution.

From the coexistence of the two ^{13}C-satellite spectra at the critical point, a value of $^{1}J_{C-H}$ in tetramethylsilane is determined as 118.4 Hz. This is the same as that determined from the spectrum in an isotropic phase. Values of the dipolar couplings $D_{^{13}C-H}$ and D_{HH} derived for the EBBA-like orientation at the critical point turn out to be -4.88 and -2.81 Hz respectively (i.e., $D_{^{13}C-H}/D_{HH} = 1.74$). For a tetrahedral value of the HCH bond angle, this ratio is 0.73. The results, therefore, clearly indicate that the mechanism of orientation of

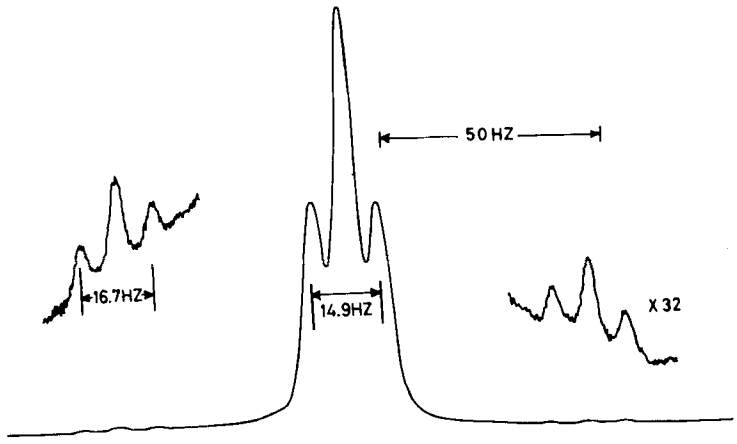

FIGURE 4 Proton NMR spectra including ^{13}C-satellites of tetramethylsilane at 20°C in EBBA; solute concentration: 3 weight per cent; spectrometer frequency: 270 MHz; No.of scans: 240.

tetrahedral molecules is more complex than attributing it to simple distortions in the tetrahedral symmetry.

4. CONCLUSIONS

The experiments discussed, herein, report interesting results derived from the spectra of molecules oriented in mixed liquid crystals of opposite diamagnetic anisotropies. They pose several theoretical questions in order to understand them fully. Though the 'coexistence' of the two types of spectra at the critical point gives rise to several new applications of NMR, it is still not clearly understood whether the spectra arise because of real 'coexistence' of the two phases or some sort of inhomogeneities give rise to their appearance. In any case,

the applications of the experiments are of great interest to chemists and their theoretical understanding poses interesting problems to physicists.

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