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MAGIC ANGLE SAMPLE SPINNING AND DIAMAGNETIC ANISOTROPY EFFECTS IN NMR SPECTRA OF ORIENTED SYSTEMS

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The use of Magic and Near Magic Angle Sample spinning in the NMR spectra of oriented systems is demonstrated to derive chemical information which otherwise cannot be obtained easily. A simple and straightforward procedure to precisely set the magic angle is described. New applications of high resolution NMR spectra of mixed liquid crystals of opposite diamagnetic anisotropies and the molecules dissolved therein are presented.

Key Words : Magic Angle; Liquid Crystal Director; Decoupling; Dipolar Coupling; Indirect Coupling; Chemical Shift Anisotropy

INTRODUCTION

NMR spectra of molecules oriented in liquid crystalline phases have found numerous applications particularly in the determination of molecular structure and conformation.[1] Though such spectra provide wealth of structural information which is otherwise difficult to obtain, they are in general quite complex due to the fact that they are mostly 'strongly' coupled and the concept of 'weak' coupling is essentially restricted to heteronuclei even at the highest magnetic fields currently available. In fact, working at high fields in such cases only helps to enhance the signal intensities in a given time. The increase of chemical shifts as a result of using high fields is not sufficient to make the spectra 'weakly' coupled. On the other hand, the chemical shifts which could be neglected for the preliminary spectral analysis at the lower fields can no more be ignored at the high fields. Thus, the use of high fields in general complicates the problem in oriented systems. The use of 2-dimensional NMR also in such cases generally does not find much applications except perhaps the multiple quantum spectroscopy—an area which is still not well explored. The use of very high fields in NMR may, however, help to orient the molecules without the use of liquid crystals but such experiments are not commonly employed. They have been reviewed in the literature.[2]

Attempts have, therefore, been made to discover new procedures which help the spectral analysis and provide additional information. Of the various methods, the use of mixed liquid crystals,[3] magic angle and near magic angle sample spinning[4–6] and high power decoupling[7] have shown significant promise to achieve the objectives. Some such results are described in the present paper.

Results and Discussion

The discussion of the results is restricted to the experiments : (1) mixed liquid crystals of opposite diamagnetic anisotropies; (2) precise setting of the Magic angle using NMR spectra of oriented systems; (3) liquid crystal director dynamics in near magic angle sample spinning experiments; and (4) a novel method for the assignment of spectral lines.

Mixed Liquid Crystals of Opposite Diamagnetic Anisotropies

NMR studies of molecules oriented in mixed liquid crystals of opposite diamagnetic anisotropies first reported in 1981[8,9] have led to several novel applications of NMR.[3] In such mixtures, the values of the dipolar couplings (D_{ij}'s) between nuclei i and j change gradually with relative concentrations of the two solvents until at critical concentration and temperature, they jump abruptly to twice or half with opposite signs depending upon the direction of approach of the critical point. A close examination of the results around the critical point reveals the coexistence of two types of spectra with dipolar couplings in one being twice with opposite sign to those in the other. They correspond to two types of orientations of the liquid crystal director, one being preferentially parallel and the other perpendicular to the magnetic field. Fig. 1 shows typical spectra demonstrating the 'coexistence' of the two orientations. Though the behaviour is theoretically well understood[10–12] the exact origin of the coexistence is still an open question.[13,14]

However, the following novel applications of NMR resulting from such experiments have been well exploited[15] : (*i*) determination of chemical shift anisotropy ($\Delta\sigma$) without the use of a reference compound or change of experimental conditions; (*ii*) separate determination of the indirect spin-spin and direct dipolar couplings between heteronuclei; (*iii*) determination of diamagnetic anisotropy of liquid crystals; (*iv*) precise determination of spectral parameters; (*v*) determination of the spectral parameters which otherwise cannot be obtained from the NMR spectra of oriented molecules; and (*vi*) the determination of molecular structure with minimal distortions. Though such applications for the molecules dissolved in liquid crystals are well known the work on the utility of such experiments to liquid crystals themselves is scarce.[7,16] Such applications are, therefore, discussed elsewhere in this paper.

Setting the Magic Angle using NMR Spectra of Oriented Molecules

It is well known that in high resolution NMR spectroscopy of solids, the angle (θ) which the spinning axis makes with the magnetic field direction should be as close to 54.7° (i·e. $\theta = \cos^{-1} 1/\sqrt{3}$, the magic angle) as possible since the imprecise settings of the angle lead to line-broadening. The commonly used methods for setting the magic angle involve measurements of the ^{13}C-NMR line-widths in standard samples and the use of quadrupole nuclei.[5] Since the measurements of line-widths and line-intensities are less precise than those of line

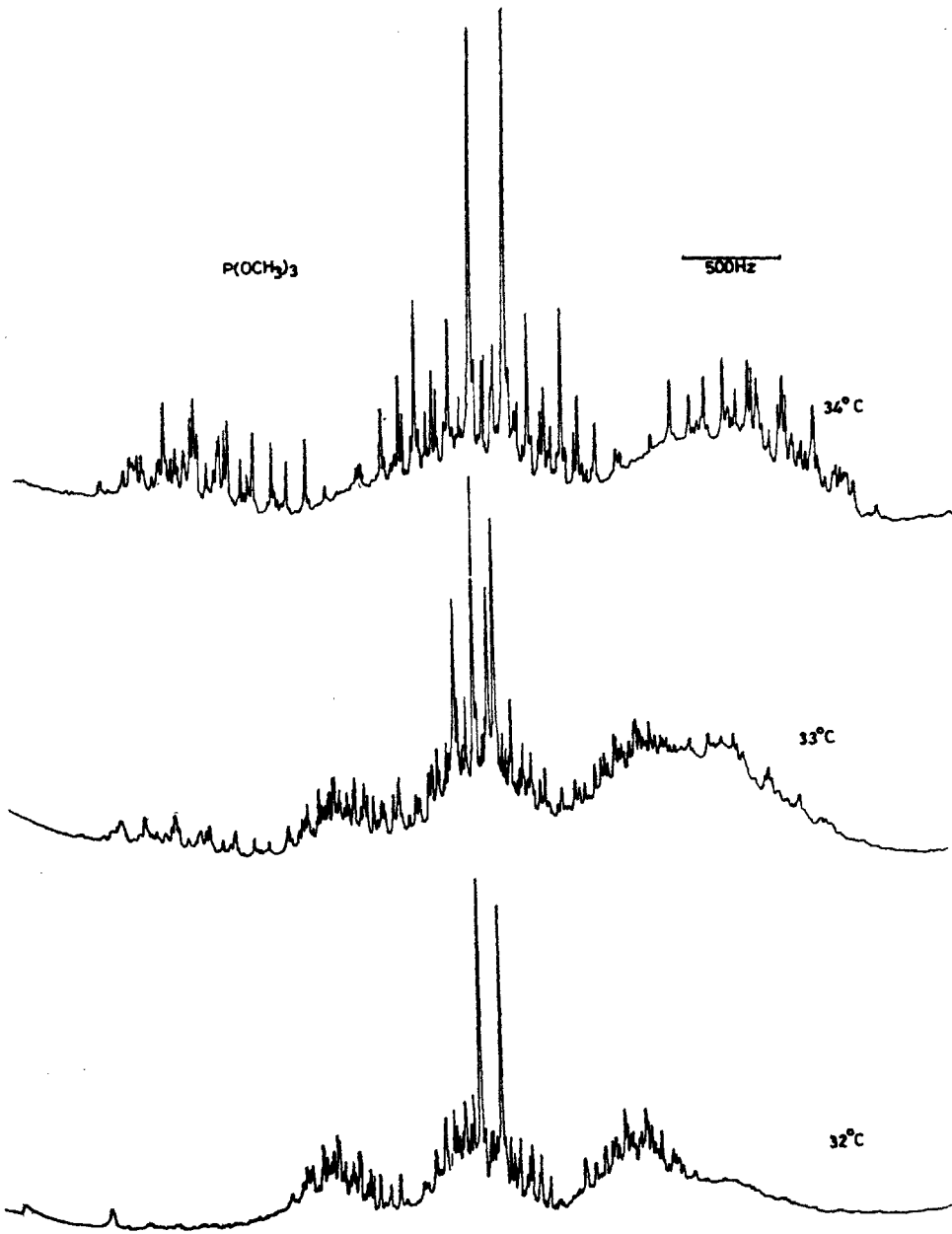


FIG 1 Proton NMR spectra of Trimethyl phosphite in 0.33 : 1.00 weight ratio of EBBA : ZLI-1167. Solute concentration, 3 weight %, temperatures, 32–34 °C as shown in the three traces; spectrometer frequency, 500MHz. Number of free induction decays accumulated, 100

separations, a method using the line-separations in the NMR spectra of oriented molecules has been proposed.[5] The method involves the use of the ^{13}C-NMR spectrum of chloroform (in the natural abundance of ^{13}C) oriented in the nematic phase of the liquid crystal solvent such as a ternary eutectic mixture of propyl-, pentyl- and heptyl-bicyclohexyl carbonitrile (ZLI-1167). The spectra show doublets with separations equal to $| J_{^{13}CH} + 2D_{^{13}CH} |$ where $J_{^{13}CH}$ and $D_{^{13}CH}$ are the indirect and the direct dipolar ^{13}C-H couplings respectively. The doublet separation changes with the angle θ and it can be interpreted in terms of the dynamics of the nematic director when the sample is spun around an axis making an angle with the magnetic field. For spinning speeds above a critical value (ω_c), the director aligns parallel or perpendicular to the spinning axis depending upon the sign of the diamagnetic susceptibility anisotropy of the liquid crystal and the angle θ, the anisotropic interactions being all scaled by a factor $\Delta = 1/2\ (3\cos^2\theta - 1)$ or $-1/2\ \Delta$ respectively.[17]

At the exact magic angle, $D_{^{13}CH}$ vanishes and hence the doublet separation corresponds to $J_{^{13}CH}$. The value of $J_{^{13}CH}$ can either be determined separately from studies of the NMR spectrum in an isotropic medium or by using mixed liquid crystals of opposite diamagnetic anisotropies, around the critical point where two spectra due to two different orientations of the liquid crystal directors corresponding to the director alignments along and orthogonal to the magnetic field coexist.[9] A value of 210 Hz for $J_{^{13}CH}$ was thus obtained for chloroform. It was also found that $J_{^{13}CH}$ and $D_{^{13}CH}$ should have opposite signs in ZLI-1167.[5]

The experiment, therefore, involves the determination of the doublet separation as a function of the angle θ. The separation equal to $J_{^{13}CH}$ (210Hz in this case) corresponds either to the exact magic angle or to the angle which corresponds to $D_{^{13}CH} = -J_{^{13}CH}$ (since the sign of the splitting is not known). The two possibilities can be conveniently distinguished since a slight increase or decrease of the angle decreases the splitting if the angle corresponds to the magic angle whereas the splitting increases in one direction and decreases in the other for the situation $D_{^{13}CH} = -J_{^{13}CH}$.

Liquid Crystal Director Dynamics in 'Near Magic Angle' Sample Spinning Experiments

The director of a nematic liquid crystal of a static sample orients either parallel or perpendicular to the external magnetic field, depending on the sign of the diamagnetic susceptibility anisotropy ($\Delta\chi$). The discovery that the director of a liquid crystal, when spun in a magnetic field at an angle other than 0° or 90° with respect to the magnetic field at a speed higher than a critical value (ω_c), can be made to orient along or perpendicular to the spinning axis, has opened up other interesting possibilities of applications.[18] NMR investigations on a quadrupolar nucleus (^{2}H in deuterated chloroform) in single as well as in mixtures of liquid crystals spinning at angles close to the magic angle have led to interesting results.[6] The liquid crystals used were trans-4-pentyl-4 (4-cyanophenyl)-cyclohexane (S-1114) with $\Delta\chi > 0$ and (ZLI-1167) with $\Delta\chi < 0$. The experiments at different

spinning speeds in mixtures of liquid crystals demonstrate that the director can switch orientation with the spinning speed when the axis of sample rotation makes an angle θ less than the magic angle (θ_m) for systems with $\Delta\chi$ weakly positive and when θ is greater than θ_m for systems with $\Delta\chi$ weakly negative.

It is found that for a single liquid crystal system such as S-1114 with positive $\Delta\chi$, the director orientation remains parallel to the spinning axis at different spinning speeds above a critical value, for $\theta < \theta_m$. But for a system with $\Delta\chi$ nearly zero and positive, for $\theta < \theta_m$, the director switches from an orientation along the spinning axis at low speeds to one perpendicular to it, at high speeds. A similar behaviour has been observed for the "critical" mixture with ZLI-1167 slightly in excess ($\Delta\chi < 0$) except that for $\theta < \theta_m$, no change in director orientation is observed when the spinning speed changes, and for $\theta > \theta_m$, the director switches orientation when spinning speed changes. In a "critical" mixture $\Delta\chi \simeq 0$), away from the "critical" temperature $\Delta\chi$ is weakly positive or negative and it has been possible to observe a similar behaviour in the director orientations as a function of the spinning speed.

The experiments confirm that the director orientation depends on $\Delta\chi$, the spinning speed and the angle the spinning axis makes with the magnetic field. By suitably adjusting these three parameters, it is possible to orient the director either parallel or perpendicular to the axis of sample rotation.

A Novel Method for the Assignment of Spectral Lines

As mentioned earlier, one of the most important applications of NMR spectra of molecules oriented in mixed liquid crystals of opposite diamagnetic anisotropies is the determination of the chemical shift anisotropy without the change of experimental conditions or the use of a reference compound. The separation ($\Delta\delta$) of the lines due to two orientations for a particular nucleus is related to the chemical shift anisotropy ($\Delta\sigma$) and the order parameter (S) (corresponding to the liquid crystal director orientation along the magnetic field direction) of the symmetry axis, in a uniaxial liquid crystal by equation (1).

$$\Delta\delta = \Delta\sigma . S. \qquad \ldots(1)$$

The equation permits the evaluation of $\Delta\sigma$ in a straight forward manner if one measures $\Delta\delta$ and S. The method provides particularly satisfactory results for nuclei other than protons where the values of $\Delta\sigma$ are large compared to the "local" or "medium" effects.[13,14] Before $\Delta\sigma$ can be determined for the individual carbon atoms in the liquid crystals, it is necessary to assign lines to each type of orientation and to individual carbons and to determine the order parameter in the proton-decoupled ^{13}C-spectra.

The determination of the chemical-shift anisotropies in the cases reported herein was restricted to the aromatic, cyano, and olefinic (–CH = N–) carbon in N–(*p'*-methoxy benzylidine-*p*-*n*-butylaniline (MBBA), (S-1114) and ZLI-1167 since they provide well-separated lines. Since the spectra of the aliphatic side

chain carbons overlap, no attempt was made to determine $\Delta\sigma$ for them, and assignments of the spectral lines were not attempted for such carbons.

The assignment of lines corresponding to the orientations of the liquid crystal director along or orthogonal to the magnetic field direction can be made by comparing the three spectra above, below and at the critical point.

Assignment of lines to individual carbons was achieved as follows. For the purpose of assignments of lines in the liquid crystal-line media, it was essential to first assign the lines in the spectra in the isotropic media. This was achieved by "off-resonance"-decoupled and two-dimensional $^{13}C/^{1}H$ hetero-COSY spectra as discussed in the literature.[7]

The chemical shifts in the nematic phase for a nucleus i in the liquid crystal director oriented parallel and perpendicular to the magnetic field [$(\sigma_a)_\parallel$ and $(\sigma_a)_\perp$ respectively] are related to the isotropic chemical shift (σ_i), the order parameter (S), and the chemical-shift anisotropy ($\Delta\sigma$) by the equations :

$$(\sigma_a)_\parallel = \sigma_i + (2/3)\ \Delta\sigma\ .S \qquad \ldots(2)$$

and

$$(\sigma_a)_\perp = \sigma_i - (1/3)\,\Delta\sigma\ .S, \qquad \ldots(3)$$

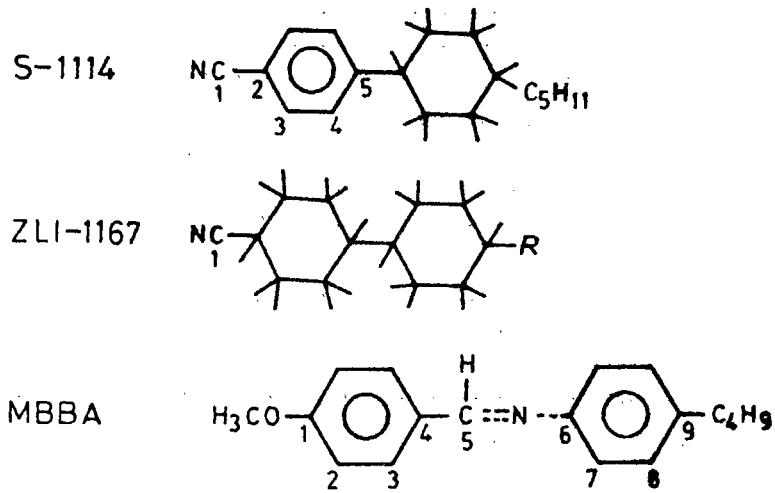
Equation (3) implies that the order parameter in the perpendicular orientation is $(-1/2)$ S at the critical concentration where both the orientations coexist. The equations further suggest that the separations between the lines in the isotropic phase and the parallel orientation is twice with opposite sign to that between the isotropic phase and the perpendicular orientation. Thus, the line pairs in the parallel and prependicular orientations for the same nucleus can be assigned using the positions in the spectra in the isotropic media. This led to an unambiguous assignment of the lines. Using the assignments of the lines thus made, isotropic chemical shifts were computed and it was found that they differ from those obtained from the spectra in the isotropic media by about 140 ± 35Hz for MBBA and 170 ± 20Hz for S-1114 solutions for all the positions. This is attributed to the medium effects.

The order parameter in the proton-decoupled ^{13}C spectra was detemined as follows. Equation (1) implies that the relative chemical-shift anisotropies of the individual carbons in these systems can be determined without the knowledge of the order parameter (S). However, for the determination of the absolute values of the chemical-shift anisotropies, a knowledge of the order parameter is essential. It was determined for the MBBA/d_2/ZLI-1167 mixture by studying the deuteron NMR spectra of MBBA/d_2/ZLI-1167 mixture under identical conditions. A value of $S = 0.54 \pm 0.004$ was obtained.

The values of ($\Delta\sigma$) thus obtained using Eq. (1) are reported in Table I for the aromatic carbons, the olefinic carbon (—CH=N—) in MBBA, and the cyanide carbon in ZLI-1167. Using the value of $\Delta\sigma$ for the cyanide carbon in ZLI-1167, the order parameter for the parallel orientation in the S-1114/ZLI-1167 mixture was computed using Eq. (1) and the separation of the lines for the ZLI-1167

TABLE I

^{13}C chemical-shift anisotropies of MBBA, S-1114, and ZLI-1167



Order parameter in MBBA = 0.54; order parameter in S-1114 = 0.55; $\Delta\sigma$ for carbon I in ZLI-1167 = 352.2 ppm.

Carbon No.	Chemical-shift anisotropy (ppm)	
	in MBBA	in S-1114
1	157.4	347.2
2	76.7	159.7
3	57.1	77.9
4	145.3	70.4
5	127.2	175.9
6	155.3	—
7	67.1	—
8	64.1	—
9	139.4	—

cyanide carbons in the parallel and the perpendicular orientations. This was found to be 0.55. This was used for the computation of the other ($\Delta\sigma$) values included in Table I. The $\Delta\sigma$ values thus determined are in the normal ranges for those obtained by other methods for similar carbons.

CONCLUSION

The results reported, herein, demonstrate some novel applications of NMR spectroscopy of oriented molecules. The use of mixed liquid crystals of opposite diamagnetic anisotropies, the magic and the near magic angle sample spinning along with high power heteronuclear decoupling promise numerous new applications of NMR.

REFERENCES

1 P Diehl and C L Khetrapal *NMS-Basic Principles and Progress* **1** (*Eds* P Diehl E Fluck and R Kosfeld) Springer-Verlag Berlin (1969)
2 C L Khetrapal B S Arunkumar and S Raghothama *Specialists Periodical Report : NMR.* **17** The Royal Society of Chemistry England (1988)
3 C L Khetrapal *Bull Mag Res* **8** (1987) 158
4 J Courtieu D W Alderman D M Grant and J P Bayles *J chem Phys* **77** (1982) 723
5 C L Khetrapal B S Arunkumar K V Ramanathan and N Suryaprakash *J Mag Res* **73** (1987) 516 and the references therein
6 B S Arunkumar N Suryaprakash K V Ramanathan and C L Khetrapal *Chem Phys Lett* **136** (1987) 227
7 B S Arunkumar N Suryaprakash K V Ramanathan and C L Khetrapal *J Mag Res* **76** (1988) 256
8 C L Khetrapal and A C Kunwar *Mol Cryst Liq Cryst* **72** (1981) 13
9 C L Khetrapal and A C Kunwar *Chem Phys Lett* **82** (1981) 170
10 K P Sinha R Subburam and C L Khetrapal *Chem Phys Lett* **96** (1983) 472
11 K P Sinha R Subburam and C L Khetrapal *Mol Cryst Liq Cryst* **94** (1983) 375
12 K P Sinha R Subburam A C Kunwar and C L Khetrapal *Mol Cryst Liq Cryst* **101** (1983) 283
13 C L Khetrapal A C Kunwar and M R Lakshminarayana *Mol Cryst Liq Cryst* **111** (1984) 189
14 E E Burnell and C A de Lange *Chem Phys Lett* **136** (1987) 87
15 C L Khetrapal and A C Kunwar *Israel J Chem* **23** (1983) 299
16 C L Khetrapal H J Yeh and A Saupe *Mol Cryst Liq Cryst* **92** (1984) 243
17 T Vaananen J Jokisaari and M Selantaus *Chem Phys Lett* **129** (1986) 399
18 B M Fung and M Gangoda *J Chem Phys* **83** (1985) 3285