Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

NMR in Liquid Crystals Spinning at and Near Magic Angle

K. V. Ramanathan [a] & C. L. Khetrapal [a] [b]

[a] Sophisticated Instruments Facility, Indian Institute of Science, Bangalore, 560 012, India

[b] National Institutes of Health, Bethesda, MD, 20892, USA

Version of record first published: 04 Oct 2006

To cite this article: K. V. Ramanathan & C. L. Khetrapal (1997): NMR in Liquid Crystals Spinning at and Near Magic Angle, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 303:1, 403-413

To link to this article: http://dx.doi.org/10.1080/10587259708039451

Mol. Cryst. Liq. Cryst., 1997, Vol. 303, pp. 403–413
Reprints available directly from the publisher
Photocopying permitted by license only

NMR IN LIQUID CRYSTALS SPINNING AT AND NEAR MAGIC ANGLE

K.V. RAMANATHAN* AND C.L. KHETRAPAL*†

*Sophisticated Instruments Facility, Indian Institute of Science,
Bangalore 560 012, India, † National Institutes of Health, Bethesda, MD
20892, USA

Abstract NMR spectra of liquid crystalline phases and the molecules dissolved therein, spinning at and near the magic angle provide information on the director dynamics and the order parameter. The studies on the dynamics of the liquid crystal director for sample spinning near magic angle in mesophases with positive and negative diamagnetic susceptibility anisotropies ($\Delta\chi$) and their mixtures with near-zero macroscopic diamagnetic susceptibility anisotropies have been reported. In systems with weakly positive $\Delta\chi$, the director has been observed to switch from an orientation parallel to the spinning axis at low rotational speeds to one perpendicular to the spinning axis at high rotational speeds, when the angle θ, the axis of rotation makes with the magnetic field is smaller than the magic angle θ_m. For systems with a small negative $\Delta\chi$, similar director behaviour has been observed for θ greater than θ_m. At magic angle, the spectra under slow spinning speeds exhibit a centre band and side bands at integral values of the spinning speeds. The intensities of the spinning side bands have been shown to contain information on the sign and the magnitude of the order parameter(s). The results are discussed with illustrative examples. Results on the orientation of the chemical shielding tensor obtained from a combination of the NMR studies in the solid and the liquid crystalline states, have been described.

INTRODUCTION

The director of a nematic liquid crystal of a static sample orients either parallel or perpendicular to an external magnetic field, depending on the sign of the diamagnetic susceptibility anisotropy ($\Delta\chi$) of the liquid crystal. This in turn produces orientational effects on the molecules dissolved therein resulting in a large number of interesting applications using NMR spectroscopy of oriented systems[1,2]. The director of a liquid crystal, which is spun in a magnetic field at a speed greater than a critical speed, orients along or perpendicular to the axis of spinning, depending on the angle this axis makes with the magnetic field[3,4]. Such studies provide information on the dynamics of the director under different conditions[5-9] and result in several applications [10-13]. The dynamics of the director in single and mixed liquid crystals of opposite $\Delta\chi$ spinning near the magic angle gives rise to interesting features[8] in the NMR spectra of such systems. The study of the spinning side band intensities in the ^2H NMR spectra of oriented molecules provides information on the director orientation and distribution as a function of the spinning speed[9]. The study of the side bands in magic angle spinning (MAS) NMR experiments provides a method for obtaining the sign of the order parameter[11-12]. Such studies lead to other applications also. For example, the ^{13}C spectrum of chloroform oriented in a liquid crystal can be used for setting the magic angle in MAS NMR experiments[10]. Use of the spinning side band intensities for the determination of the orientation of interaction tensors of relevance in NMR has also been suggested [13]. Some of these studies are described below.

NEAR MAGIC ANGLE SAMPLE SPINNING STUDIES

The director dynamics in near magic angle spinning has been studied by monitoring the deuterium NMR spectra of an 8% solution of deuterochloroform ($CDCl_3$) dissolved in the liquid crystals trans-p-pentyl-4-(cyanophenyl)-cyclohexane (S-1114) which has $\Delta\chi>0$ and a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile (ZLI-1167) which has $\Delta\chi < 0$ and in 1:1 mixture of these two liquid crystals which has the macroscopic $\Delta\chi \approx 0$. To such a mixture S-1114 or ZLI-1167 was added slightly in excess to make the macroscopic $\Delta\chi$ either weakly positive or negative respectively. The results of the experiments carried out on a Bruker MSL-300 FTNMR spectrometer at a resonance frequency of 46.07 MHz and at sample spinning speeds varying from 200 to 1600 Hz are shown in Figures 1 and 2. The angle θ, which the axis of sample rotation makes with the magnetic field was varied by 4-5° on either side of the "magic angle" (θ_m= 54.7°). Figures 1a and 1b show ^2H NMR spectra of $CDCl_3$ in S-1114 spun at two different speeds, the angle θ the rotor axis makes with the magnetic field being 53° ($\theta<\theta_m$). The spectra for θ = 56.5° ($\theta > \theta_m$) are shown in Figures 1c and 1d. The spectrum of the static sample is also shown in Figure 1e for comparison. For $\theta < \theta_m$, the director aligns parallel to the spinning axis[3] and the spectrum consists of a doublet scaled by a factor $\Delta=(3\cos^2\theta-1)/2$ as compared to the static sample. For $\theta = 53°$ the separation is 598 Hz at a spinning speed of 1660 Hz. For a different spinning speed (1070 Hz) the spectrum is similar with the splitting remaining nearly the same. For $\theta > \theta_m$ the director orients in a plane perpendicular to the spinning axis[3]. Since the spinning speeds employed are smaller than the quadrupolar splitting of 15405 Hz for the static sample (Figure 1e), the spectrum splits into side bands, each side band being a doublet with separation proportional to $-\Delta/2$. If the director is oriented exactly perpendicular to the spinning axis only even-order side bands are expected. The appearance of the weak odd-order side bands in the experimental spectra, particularly at lower spinning speeds (Figure 1d), indicates that the director orients in other directions also and this aspect has been examined in detail[9].

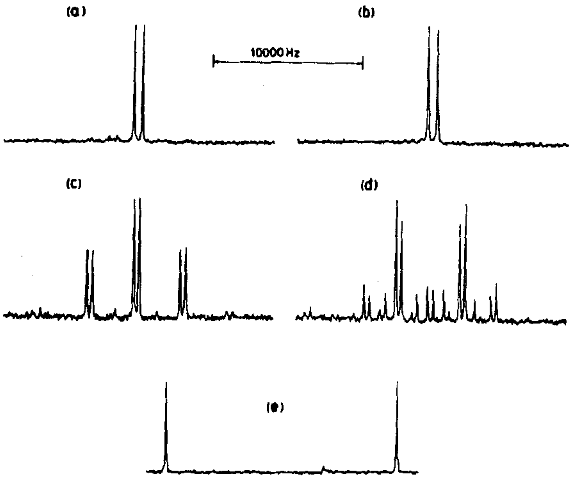

FIGURE 1 ^{2}H-NMR spectra of deuterochloroform oriented in the nematic phase of S-1114 for two different orientations (θ) of the axis of rotation with reference to the magnetic field and for two different spinning speeds (RO). DS refers to the doublet splitting. Solute concentration = 8 wt%, temperature = 292 K, spectrometer frequency = 46.07 MHz. (a) $\theta = 53°$, RO=1660 Hz, DS=598 Hz; (b) $\theta = 53°$, RO=1070 Hz, DS=610 Hz; (c) $\theta = 56.5°$, RO=1565 Hz, DS=354 Hz; (d) $\theta = 56.5°$, RO=1060 Hz, DS=366 Hz; (e) static sample (Ref.8).

For $CDCl_3$ dissolved in ZLI-1167 ($\Delta\chi < 0$), behaviour similar to that mentioned above is observed with the difference that for $\theta > \theta_m$ the director orients parallel to the spinning axis and for $\theta < \theta_m$, the average orientation of the director is perpendicular to the spinning axis.

^2H NMR spectra of $CDCl_3$ in a "critical" mixture[14] of S-1114 and ZLI-1167 to which a slight excess of S-1114 has been added to make the macroscopic $\Delta\chi$ small and positive are shown in Figure 2. Traces A and B show spectra for $\theta > \theta_m$ at two different spinning speeds. The changes observed in the side band pattern in the two cases are due to the appearance of the spinning side bands at the respective spinning frequencies, the doublet separation being the same in the two cases. For $\theta < \theta_m$ the spectral pattern shows significant changes when the spinning speed is varied. Figure 2C corresponds to an orientation of the director perpendicular to the spinning axis, whereas Figure 2D corresponds to a parallel orientation. This can be seen from the presence of spinning

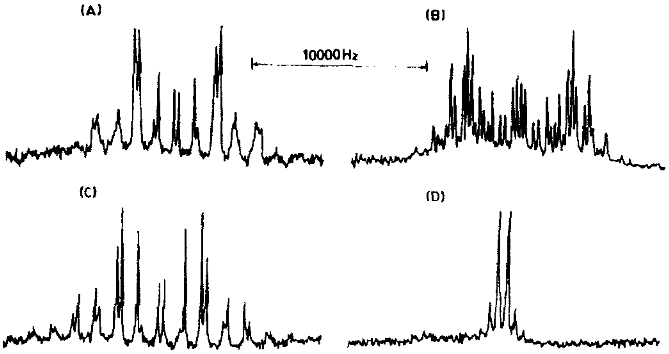

FIGURE 2 ^2H-NMR spectra of deuterochloroform in a near "critical" mixture of S-1114 and ZLI-1167 with a slight excess of S-1114 such that the macroscopic diamagnetic susceptibility anisotropy is positive but close to zero. The orientations (θ) of the axis of rotation with reference to the magnetic field, the spinning speed (RO) and the doublet splitting (DS) are: (A) $\theta = 56°$, RO=1150 Hz, DS=269 Hz; (B) $\theta = 56°$, RO=480 Hz, DS=269 Hz; (C) $\theta = 53°$, RO=1200 Hz, DS=293 Hz; (D) $\theta = 53°$, RO=470 Hz, DS=598 Hz (Ref.8).

side bands over a significantly large range of frequencies for a rotor speed of 1200 Hz (Figure 2C). Further the splitting of the central doublet in this case is 293 Hz in comparison to the splitting of 598 Hz observed at the lower spinning speed of 470 Hz (Figure 2D), which corresponds to a scaling factor of about 1/2 arising from a switch over of the director orientation by 90°.

Thus in the case of the single liquid crystal with positive $\Delta\chi$ the director orientation remains parallel to the spinning axis at different spinning speeds for a given value of $\theta < \theta_m$. But for a system with $\Delta\chi$ nearly zero and positive, the director switches from an orientation along the spinning axis at low speeds to one perpendicular to it at high speeds. A similar switch over of director orientation as spinning speed is varied has been observed in a "critical" mixture with ZLI-1167 slightly in excess ($\Delta\chi < 0$) for $\theta > \theta_m$.

In a "critical" mixture ($\Delta\chi \approx 0$), away from the "critical" temperature $\Delta\chi$ is weakly positive or negative. In this case also a similar behaviour of the director orientation as a function of the spinning speed has been observed.

SIGN OF THE ORDER PARAMETER FROM MAS SPECTRA OF ORIENTED MOLECULES

The order parameters of oriented systems can be obtained from the NMR spectra of the oriented molecules[1,2]. For example the deuteron magnetic resonance spectra of specifically deuterated oriented molecules show broad quadrupole split doublets [15,16] if the dipolar couplings are unresolved. The doublet separations provide the order parameters of the C-D bond axes from the known values of the deuteron quadrupole coupling constants. Analogous experiments have been widely used for the study of the mobility of the fatty acid chains in deuterated lipid and model membrane systems[17-19]. In interpreting such spectra, signs of the quadrupole splittings and hence those of the order parameters have not been taken into account since it has not been possible to derive them from the reported experiments. Since the sign of the order parameters provides information on the actual ordering along the particular axis of interest, a method to determine the sign is of importance for the study of the mobility of fatty acid chains. One of the methods suggested for this purpose utilises the relative intensities of the side bands observed in the magic angle spinning NMR spectra of oriented samples[11-12] and is described here.

The proton-coupled ^{13}C MAS spectrum of ^{13}C-enriched chloroform dissolved in ZLI-1167 is shown in Figure 3a. The splittings observed for the centre band (A_o, B_o) and the side band of order N (A_N, B_N) are due to the isotropic J (^{13}C-^{1}H) coupling. Using the known value of the carbon chemical shift anisotropy $\Delta\sigma$ and the value of the constant $K^{C\text{-}H}$ defined as $K^{C\text{-}H} = \gamma_H \gamma_C / r^3_{C\text{-}H}$ to be -22.55 KHz corresponding to a proton-carbon distance ($r_{C\text{-}H}$) of 1.1A°, the spectra of chloroform for positive and negative signs

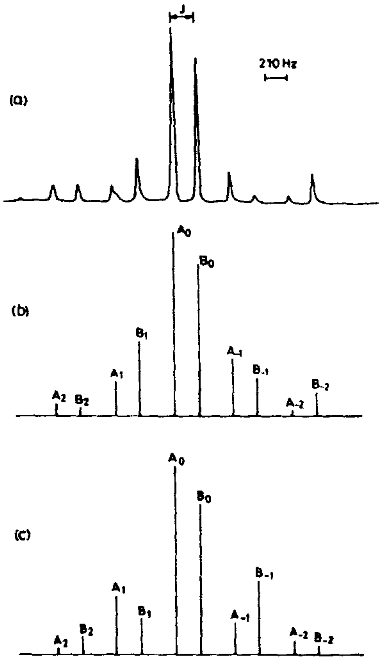

FIGURE 3 (a) Proton-coupled ^{13}C MAS NMR spectrum of an approximately 8 wt % solution of chloroform in the nematic phase of ZLI-1167 obtained at 75 MHz and at 290 K. Sample rotation frequency was 500 Hz. (b,c) ^{13}C spectra simulated for the same experimental conditions as in (a) with $\Delta\sigma = -40$ ppm, carbon - proton dipolar coupling $K^{C\text{-}H} = -22.55$ kHz and $S_{zz} = +0.025$ (b) and $S_{zz} = -0.025$ (c) (Ref.11).

of the order parameter S_{ZZ} of the symmetry axis are calculated and are shown in Figure 3 along with the experimental spectrum. γ_H and γ_C are the magnetogyric ratios of ^1H and ^{13}C respectively. The calculated spectra indicate that the intensities of the positive and negative side bands are interchanged when the sign of the order parameter is reversed. Figure 3b which corresponds to a positive sign of S_{ZZ} corresponds to the experimental spectrum in agreement with previous reports[1].

It is also possible to obtain the sign of the order parameter when only the chemical shift anisotropy interaction is present. The ^{13}C MAS spectra of benzene and chloroform dissolved in ZLI-1167 with proton decoupling are shown in Figures 4a and 5a respectively. The spectra simulated with positive and negative values of the order

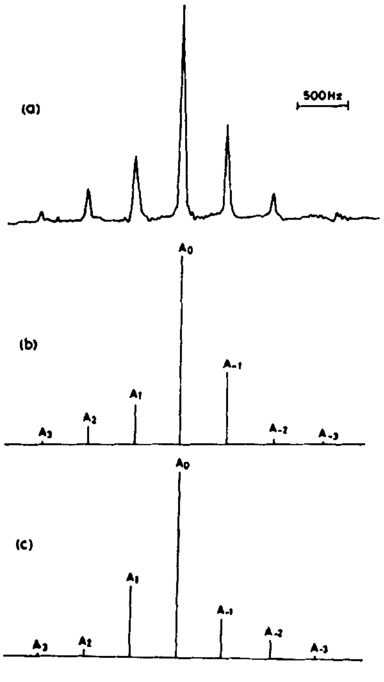

FIGURE 4 (a) ^{13}C MAS NMR spectrum of an approximately 8 wt % solution of benzene in the nematic phase of ZLI-1167 obtained at 75 MHz and at 290 K with high-power proton decoupling. Sample rotation frequency was 465 Hz. (b,c) ^{13}C spectra simulated for the same experimental conditions as in (a) with $\Delta\sigma$= 190 ppm, and S_{zz} = + 0.048(b) and S_{zz} = - 0.048 (c) (Ref.11).

parameters of the symmetry axes are shown in Figures 4b and 4c for benzene and Figures 5b and 5c for chloroform respectively. From a comparison of the experimental and theoretical spectra positive signs for the order parameters S_{ZZ} of the symmetry axe of both benzene and chloroform are obtained in agreement with those reported in literature[20,21].

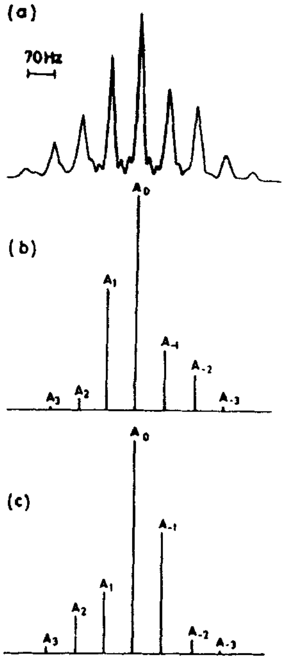

FIGURE 5 (a) ^{13}C MAS NMR spectrum of an approximately 8 wt % solution of chloroform in the nematic phase of ZLI-1167 obtained at 75 MHz and at 290 K with high-power proton decoupling. Sample rotation frequency was 70 Hz. (b,c) ^{13}C spectra simulated for the same experimental conditions as in (a) with $\Delta\sigma = -40$ ppm, and $S_{zz} = +0.04$ (b) and $S_{zz} = -0.04$ (c)(Ref.11).

ORIENTATIONS OF CARBON CHEMICAL SHIFT TENSORS FROM THE MAS SPECTRA OF SAMPLES ORIENTED IN LIQUID CRYSTALS

A combination of the results obtained from the NMR studies of the neat samples in the solid state and of the samples oriented in the nematic phases of liquid crystals spinning at the magic angle are relatively recent and provide information on the orientation of the chemical shift tensor[13]. MAS NMR spectra in the solid state give the magnitudes of the components of the chemical shift tensor. In order to obtain the orientation of this tensor, the MAS spectrum of the sample oriented in the liquid crystal has been used and the results have been illustrated in the case of the molecule cis, cis-mucononitrile (Figure 6a). The elements of the order parameter tensor for the molecular fixed frame of mucononitrile oriented in ZLI-1167 are known[22]. From the MAS NMR spectrum of the molecule in the solid state, the principal components of the chemical shift tensor δ_{11}, δ_{22} and δ_{33} were obtained. Assuming an orientation of the chemical shift tensor in the

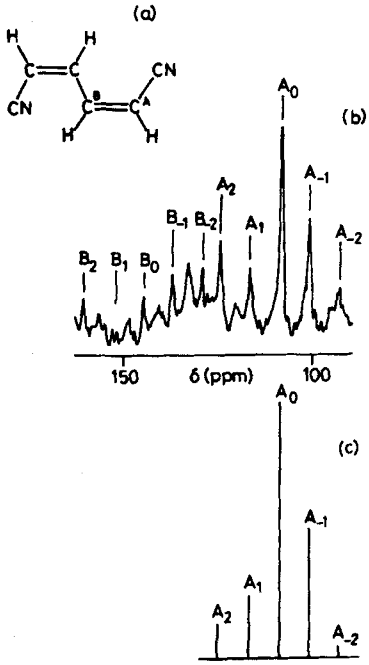

FIGURE 6 (a) Structure of cis, cis-mucononitrile. (b) Proton decoupled ^{13}C MAS NMR spectrum of approximately 8 weight percent solution of cis, cis-mucononitirle oriented in ZLI-1167 at 300 K and at 75 MHz. Sample rotation frequency was 593 Hz. A_N's and B_N's correspond to side bands due to carbons A and B respectively. (c) Simulated side band spectrum of carbon A for χ = 15° (Ref.13).

molecular fixed frame, an effective chemical shift tensor, δ_e, which is a function of the sum of the products of the chemical shift tensor components and the corresponding order parameters, was obtained and the intensities of the side bands were calculated. These were then compared with the experimental intensities (Figure 6b) to obtain the probable orientation of the chemical shift tensor in the molecule fixed frame. For the carbon A of cis, cis-muconontrile, with the assumption that the most shielded component namely δ_{33} is perpendicular to the plane of the molecule, the least shielded component δ_{11} was found to make an angle $\chi = 15° \pm 5°$ with respect to C-C bond under the assumption of undistorted bond angles corresponding to Sp^2- hybridisation of the olefinic carbons. The corresponding simulated spectrum is shown in Figure 6c.

CONCLUSION

The spectra of molecules oriented in liquid crystalline phases and spinning at and near magic angle provide information on the dynamics of the director. These were studied both for single liquid crystals and for mixtures of liquid crystals having macroscopic diamagnetic susceptibility anisotropy $\Delta\chi$ nearly zero. For certain range of angles which the axis of spinning makes with the magnetic field, the systems with weakly positive or negative $\Delta\chi$ show a switch over of director orientation from one which is parallel to the spinning axis at low rotational speeds to the one which is perpendicular the spinning axis at high rotational speeds. The spinning side bands observed in the MAS spectra of oriented samples provide information on the sign of the order parameter. Information about other interaction tensor parameters could also be obtained from such studies.

ACKNOWLEDGEMENT

The authors would like to acknowledge Dr. Edwin D. Becker for helpful discussions.

REFERENCES

1. P. Diehl and C.L. Khetrapal, NMR Basic Principles and Progress, 1, 1-95 (1969).
2. J.W.Emsley and J.C. Lindon, NMR spectroscopy using liquid crystal solvents (Pergamon Press, New York, 1975).

3. J. Courtieu, D.W. Alderman, D.M. Grant and J.P. Bayles, J. Chem. Phys., 77, 723 (1983).
4. R. Teeaar, M. Alla and E. Lippmaa, Org. Magn. Reson., 19, 134 (1982).
5. T. Vaananen, J. Jokisaari, M. Selantaus, Chem. Phys. Lett., 129, 399 (1986).
6. J.P. Bayle, A. Khandar-Shahabad and J. Courtieu, Liq. Cryst., 1, 189 (1986).
7. J.P. Bayle, A.Khandar-Shahabad, J. Courtieu and S.K. Khan, Liq. Cryst., 1, 371 (1986).
8. B.S. Arun Kumar, N. Suryaprakash, K.V. Ramanathan and C.L. Khetrapal, Chem. Phys. Lett., 136, 227 (1987).
9. B.S. Arun Kumar, K.V. Ramanathan and C.L. Khetrapal, Chem. Phys. Lett., 149, 306 (1988).
10. C.L. Khetrapal, B.S. Arun Kumar, K.V. Ramanathan and N. Suryaprakash, J.Magn. Reson.,73, 516 (1987).
11. B.S.Arun Kumar, K.V. Ramanathan, C.L. Khetrapal, S.J. Opella and Edwin D. Becker, J. Magn. Reson., 86, 516 (1990).
12. K.V. Ramanathan, N. Suryaprakash, C.L. Khetrapal and Edwin D. Becker, Proc. National Acad. Sci. (India), (In Press).
13. K.V. Ramanathan, N. Suryaprakash, C.L. Khetrapal, Edwin D. Becker, Klaus Eichele and Roderick E. Wasylishen,(to be published).
14. C.L. Khetrapal and A.C. Kunwar, Chem. Phys. Lett., 82, 170 (1981).
15. J.C.Rowell, W.D. Philips, L.R. Melby and M. Panar, J. Chem. Phys. 43, 3442 (1965).
16. P. Diehl and C.L Khetrapal, Can. J. Chem. 47, 1411 (1969).
17. J. Charvolin, P. Manneville and B. Deloche, Chem. Phys. Lett. 23, 343 (1973).
18. J. Seelig and W. Niederberger, Biochemistry 13, 1585 (1974); J. Am. Chem. Soc. 96, 2069 (1974).
19. G.W. Stockton, C.F. Polnaszek, L.C. Leitch, A.P. Tullock and I.C.P. Smith, Biochem. Biophys. Res. Commun., 60, 844 (1974).
20. P.K. Battacharyya and B.P. Dailey, J. Magn. Reson. 12, 36 (1973).
21. G. Englert, Z. Naturforsch. A27, 715 (1972).
22. R. Christy Rani Grace, N. Suryaprakash, Anil Kumar and C.L. Khetrapal, J. Magn. Reson. A107, 79 (1994).