

NMR IN MIXED LIQUID CRYSTALS

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ABSTRACT

NMR studies in more than one and in mixed liquid crystals have led to novel applications of NMR and enhanced the scope of NMR spectroscopy of oriented systems in providing spectral, structural and conformational information which otherwise cannot be derived conveniently. The results are critically evaluated for the following types of experiments: (i) molecules dissolved in liquid crystals with different orientational behavior, (ii) solute molecules in mixed nematic-nematic materials of opposite diamagnetic anisotropies, (iii) dissolved molecules in mixed cholesteric-cholesteric and cholesteric-nematic liquid crystals and (iv) nematic-nematic liquid crystals themselves. Theoretical status of the experiments is described.

INTRODUCTION

NMR spectra of molecules oriented in more than one and in mixed liquid crystals (1, 2) lead to new applications of NMR. The studies have been undertaken in mixed nematic-nematic and nematic-cholesteric mixtures and the molecules dissolved therein with a view to enhance the scope of the NMR spectroscopy of oriented systems. For successfully employing the technique, it is essential to obtain precisely the spectral parameters

namely the direct dipolar couplings (D_{ij} 's) between the interacting nuclei i and j , the indirect spin-spin couplings (J_{ij} 's), the chemical shifts ($\nu_i - \nu_j$'s), the quadrupole coupling constants (QCC 's) and the anisotropies of the chemical shifts and the coupling tensors, from the spectra. To derive the relative internuclear distances from the dipolar couplings without assumptions, the number of independent D_{ij} 's must not be less than the sum of the geometrical parameters and the order parameters (S_{ij} 's) in the system. The use of more than one liquid crystal in NMR makes it possible to obtain the information which may not be possible from a single experiment. The use of mixed liquid crystals of opposite diamagnetic anisotropies leads to more interesting results. Some such experiments are critically reviewed in this paper. In addition, studies of mixed nematic-nematic liquid crystals of opposite diamagnetic anisotropies themselves have been undertaken in order to theoretically understand the underlying phenomena and to determine the ^{13}C -chemical shift anisotropies of the individual carbon atoms in liquid crystals. Results on mixed cholesteric-cholesteric and cholesteric-nematic liquid crystals are also presented (3, 4).

MOLECULES DISSOLVED IN
LIQUID CRYSTALS WITH DIFFERENT
ORIENTATIONAL BEHAVIOR

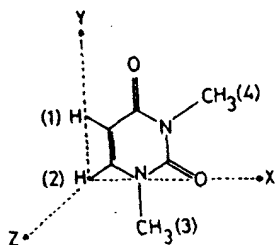
In a system where the number of derived dipolar couplings is less than the sum of the geometrical and order parameters to be derived, performing experiments under different orientation conditions such as using more than one liquid crystal is extremely useful. If the experiments are performed in two liquid crystals, the number of dipolar parameters derived becomes double but the number of geometrical parameters to be obtained remains unchanged neglecting the solvent effects on molecular geometry. The utility of the experiments can be demonstrated by the following examples:

(1) From NMR spectra of oriented AA'BB' and AA'BB'X systems where the dipolar couplings D_{AB} ($D_{A'B'}$) are much larger than the other coupling constants and where $D_{AA'}$, $D_{BB'}$, it is not possible to derive all the spectral parameters with acceptable precision. Such a situation is encountered in the spectra of p-disubstituted benzenes in general and p-substituted fluorobenzenes in particular. The spectra of the AA'BB'X types under such conditions are insensitive to the chemical shift ($\nu_A - \nu_B$), and the coupling parameters ($D_{AX} - D_{BX}$) and ($D_{AA'}$, $-D_{BB'}$). Thus one can only obtain D_{AB} ($D_{A'B'}$), $D_{AB'}$ ($D_{A'B}$), ($D_{AA'} + D_{BB'}$) and ($D_{AX} + D_{BX}$) instead of the individual coupling constants. Such a system needs two order parameters for the specification of molecular orientation and three relative internuclear distances for the fixation of relative nuclear positions. Consequently, a total

of five geometrical and order parameters are required to be determined, whereas the system in a single experiment provides only four dipolar parameters. If, however, the studies are carried out in two thermotropic solvents, the number of dipolar coupling parameters derived becomes eight and only two additional order parameters are required to be determined, assuming that the molecular geometry does not change with solvent. Such experiments thus permit the determination of molecular structure. The utility has actually been demonstrated for 2-(p-bromophenyl)-4,6-dichloropyrimidine (5). It must be emphasized that the method is more instructive if the order parameters in different experiments differ significantly.

(2) The proton NMR spectrum of N,N-dimethyl uracil (6) provides eight HH-dipolar couplings in a single experiment. In this case, three parameters are required for the specification of the molecular order and 8 geometrical parameters define the proton positions for specific modes of rotations of the methyl groups, under plausible assumptions (6). The 8 geometrical and the 3 orientational parameters cannot be derived from the 8 dipolar couplings obtained from a single experiment. If, however, the experiments are performed in two different liquid crystals, the total of six orientational parameters (3 for each experiment) and 8 geometrical parameters can be derived from the 16 dipolar couplings using a least-square-fit procedure. N, N-dimethyl uracil has been investigated in two different liquid crystal solvents, namely N-(p-methoxy benzylidene)-p'-n-butylaniline and p-n-butyl-p'-methoxyazoxy-benzene and

the geometrical parameters derived (6). It has been found that the preferred conformation of the molecule is that where one C-H bond of the methyl group (CH₃ (3)) (Structure 1)



(Structure 1)

is in the ring plane pointing towards the carbonyl group. The results were not sensitive to the mode of rotation of the methyl group (CH₃(4)) in line with the predictions of the bond polarization hypothesis (7).

MOLECULES DISSOLVED IN MIXED NEMATIC-NEMATIC LIQUID CRYSTALS

In a mixture of nematic liquid crystals with opposite diamagnetic anisotropies, the D_{ij} values change gradually with relative concentrations of the two solvents (8, 9) until at a critical concentration and temperature, they switch abruptly to twice or half with opposite signs, depending upon the direction of approach of the critical point. A close examination of the results in the vicinity of the critical point reveals the coexistence of two types of spectra at a particular temperature 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 optic axis, one being preferentially parallel and the other perpendicular to the magnetic field. The behavior is

theoretically well understood (10-12) in terms of the Landau theory. It is, however, not clear whether the two spectra near the critical point arise from certain inhomogeneities (e.g. temperature and concentration) or whether there is a "true" coexistence of the two phases like in other first order phase transitions. Though a report on the existence of the "Powder Pattern" is available (13), some further experiments are essential in order to conclusively establish the point. Nevertheless, the experiments lead to the following novel applications of NMR: (i) Determination of chemical shift anisotropy without the use of a reference compound or without the 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 spectral parameters, such as those in an oriented AB-System, which otherwise cannot be obtained from the line positions, (vi) determination of molecular structure with minimum distortions and (vii) precise determination of quadrupole coupling constants. Such applications have been extensively explored (14-20). Besides determining the vibrationally corrected r_{α} -structure, the chemical shift anisotropy and the sign and the magnitude of the indirect HP coupling in methyl dichlorophosphine (21), the abnormal orientation of the molecule has been interpreted in terms of the formation of a solvent-solute complex. Typical spectra are shown in Figure 1.

DISSOLVED MOLECULES IN MIXED
CHOLESTERIC-CHOLESTERIC AND
CHOLESTERIC-NEMATIC LIQUID
CRYSTALS

The objective to study NMR spectra in cholesteric liquid crystals is 3-fold:

(1) Such materials possess solubility properties which are different from those in other anisotropic media commonly used in NMR experiments and hence such investigations enhance the scope of the method. Acetonitrile is the only molecule studied so far where the r_α -structure has been derived in an optically compensated mixture of cholesteryl chloride and cholesteryl nonanoate (3). The r_α -value of the HCH bond angle determined is 109.2° which agrees well with the microwave value of 109.3° (22).

(2) Distinct NMR spectra for \underline{d} and \underline{l} enantiomers have been observed for optically active molecules dissolved in compensated cholesteric liquid crystals (23, 24). This is due to the fact that the degree of order of the solute molecules differs for the \underline{d} and \underline{l} geometry. The results have been demonstrated for racemic 3,3,3-trichloro propylene oxide dissolved in a mixture of cholesteryl chloride and cholesteryl myristate. The experiments demonstrate the use of cholesteric liquid crystals for the study of optically active compounds in order to obtain separate information on the \underline{d} and the \underline{l} forms. Such an information cannot be obtained from nematic and lyotropic mesophases normally used in NMR experiments. The potentials of such experiments have to be explored since no other report is available to the best of our knowledge.

(3) The cholesteric liquid crystals derived from cholesterol derivatives have negative diamagnetic anisotropy. It is, therefore, interesting to examine the orientational behavior of such materials when mixed with positive diamagnetic anisotropy nematic liquid crystals. Deuteron NMR spectra of molecules such as C_6D_6 , CD_3CN and $CDCl_3$ dissolved in such mixtures have been investigated. The influence of the addition of the nematic liquid crystals such as N-(p-methoxy benzylidene-p'-n-butylaniline (MBBA), trans-4-pentyl-4 (4-cyano-phenyl)-cyclohexane (S-1114) and a ternary eutectic mixture of propyl-, pentyl- and heptyl-bicyclohexyl carbobonitrile (ZLI-1167) on the deuteron NMR spectra of the molecules listed above dissolved in the compensated mixtures of 1: 0.74 weight ratio of cholesteryl chloride to cholesteryl nonanoate has been examined. Up to about 30 weight percent of MBBA, only one quadrupole split doublet of the dissolved probe molecule is observed. Around 30 weight percent and above, two quadrupole split doublets start appearing. Though the doubling of the quadrupole doublets is also observed in mixtures with S-1114 beyond a certain concentration, no such effect was observed for ZLI-1167. However, addition of ZLI-1167 to the mixture containing compensated cholesteryl mixture and MBBA sharpens both the doublets. The results indicate two domains in the mixtures beyond about 30% of MBBA (Figure 2).

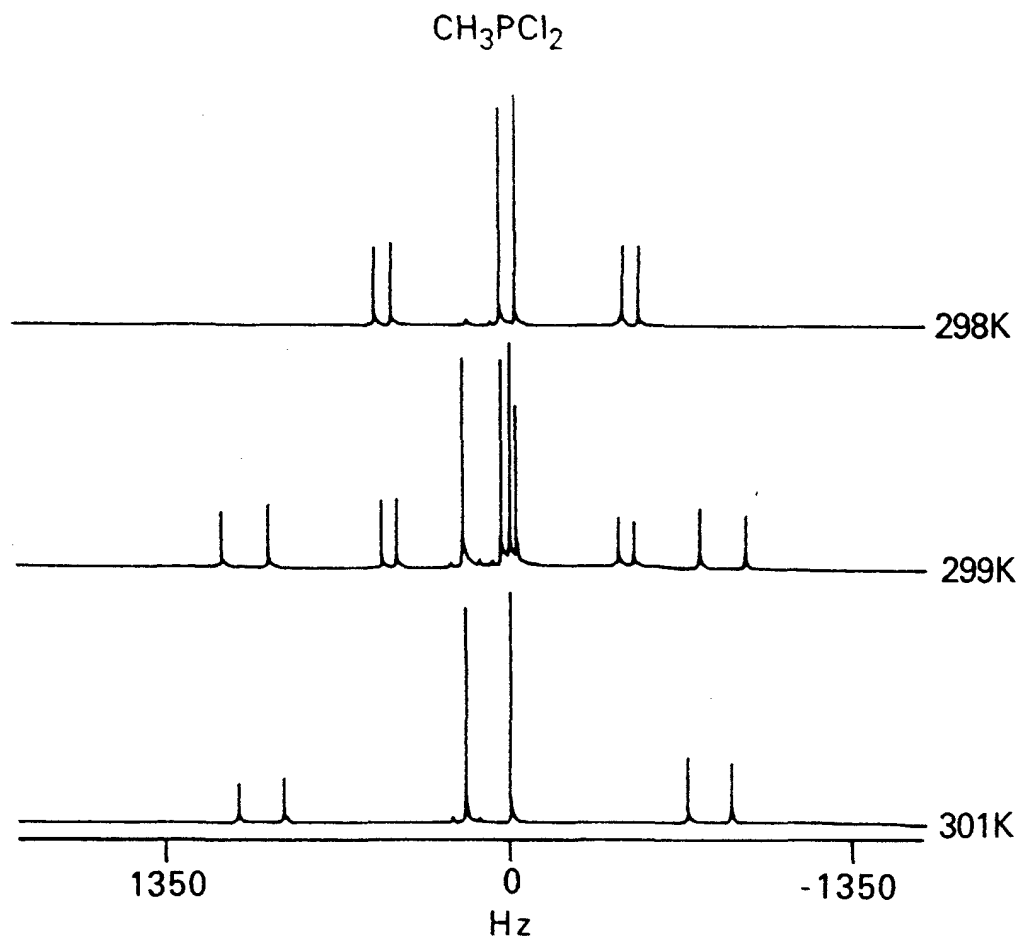


Figure 1: Proton NMR spectra of 7 weight percent solution of CH_3PCl_2 oriented in a 1 : 1 weight percent of S-1114 and ZLI-1167

Spectrometer Frequency: 270 MHz
 Temperature: as indicated in the figure
 Number of Scans: 1500



41.44 MHz deuteron NMR spectrum of C_6D_6 in a mixture of cholesteryl chloride : cholesteryl nonanoate : MBBA in the weight ratio of 1.0 : 0.73 : 0.73.

Solute Concentration: 2.7 weight percent
 Temperature : 17°C

41.44 MHz deuteron NMR spectrum of CDCl_3 in a mixture of ZLI-1167, cholesteryl chloride, cholesteryl nonanoate and MBBA in weight ratio of 1.0 : 0.075 : 0.055 : 0.43.

Solute Concentration : 4.6 weight percent
 Temperature : 20°C.

Figure 2

SPECTRA OF NEMATIC-NEMATIC LIQUID CRYSTALS THEMSELVES

The objective of such studies is 2-fold:

(1) The Landau theory developed (10-12) for the behavior of mixed liquid crystals of opposite-diamagnetic anisotropies is based on the study of the orientational behavior of the liquid crystals and was tested by experimental results from studies of the dissolved molecules assuming that the solute orientation follows the solvent orientation. In order to test the assumptions, ^2H -NMR study of MBBA- d_2 and ZLI-1167 mixtures without a dissolved molecule was undertaken (25). The results show two quadrupole-split doublets at the "critical" point where both the orientations "coexist". The experiments were performed on a JEOL FX-100 spectrometer operating at 15.35 MHz for deuterons and using a conventional electromagnet. A spinning of the sample around the axis orthogonal to the magnetic field resulted in the disappearance of the doublet corresponding to the orientation where the liquid crystal director is preferentially aligned along the direction of the magnetic field (Figure 3). The assumption that the solute molecules follow the orientation of the liquid crystal is, therefore, justified as established by this experiment.

(2) The ^{13}C -NMR spectra of the liquid crystals MBBA, S-1114 and ZLI-1167 were studied in the natural abundance of ^{13}C with high power proton decoupling and cross polarization, on a Bruker MSL-300 spectrometer (26). The spectra near the "critical" point in the mixtures of liquid crystals of opposite-diamagnetic

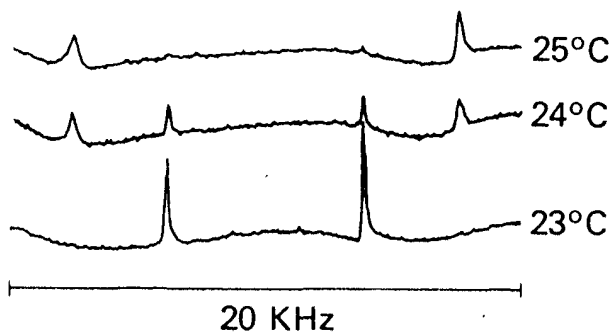
anisotropies were also investigated. The appearance of the two spectra (Figure 4) near the critical point permits the evaluation of the ^{13}C -Chemical shift anisotropy of the individual carbons in liquid crystals without the use of a reference compound or the change of experimental conditions as for the solute molecules. Though the experiments have been completed, assignments of the lines to the individual carbons has still to be made. Though the earlier work (27, 28) on the assignments of the ^{13}C -carbon lines may be helpful for the assignments when the liquid crystal director aligns preferentially along the magnetic field direction, the assignments for the alignment of the director orthogonal to the magnetic field has still to be made. The ^{13}C -resonance for the cyanide carbon has been unambiguously assigned and a value of 350 ppm for the ^{13}C -chemical shift anisotropy derived. More experiments leading to the assignments are in progress.

CONCLUSIONS

The results reported in this paper clearly demonstrate the potentials of using more than one liquid crystals or the mixed liquid crystals of opposite diamagnetic anisotropies leading to novel applications of NMR.

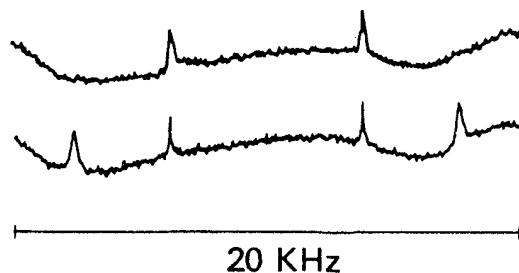
ACKNOWLEDGEMENT

I am grateful to Dr. E.D. Becker for critical discussions.



Proton decoupled deuteron NMR spectra of 0.3 : 1 weight ratio of MBBA- d_2 : ZLI-1167 at 23, 24 and 25°C.

Figure 3



Proton decoupled deuteron NMR spectra of 0.3 : 1 weight ratio of MBBA- d_2 : ZLI-1167 at 24°C in a conventional electromagnet. Upper trace is with sample spinning and the lower one is without spinning of the sample.

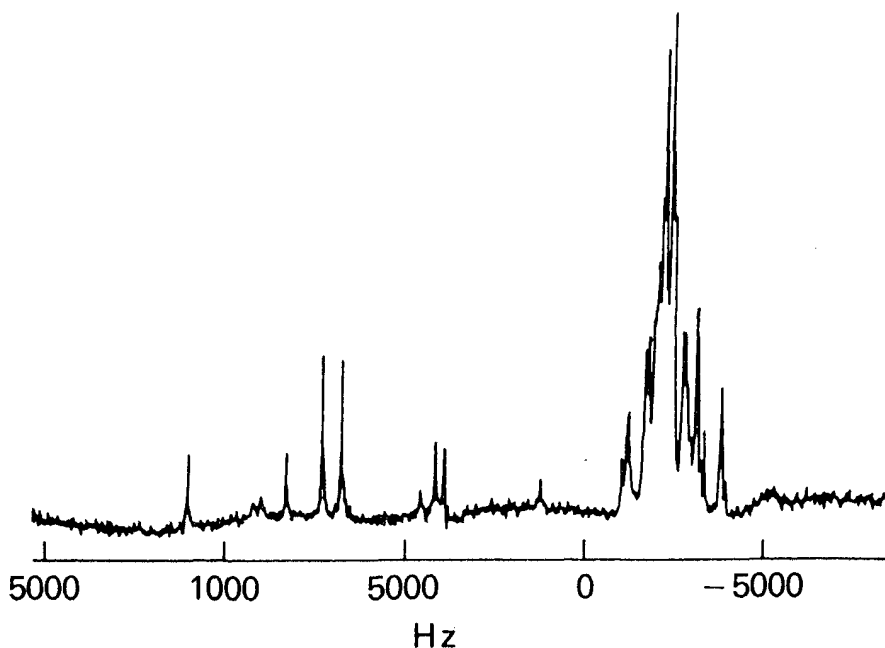


Figure 4:

^{13}C -NMR spectrum of a mixture of S-1114 and ZLI-1167 with broad band proton decoupling at 289.9K where the spectra due to two orientations of the liquid crystal "coexist."

REFERENCES

1. C.L. Khetrapal, Bull. Mag. Res. 5, 140 (1983).
2. C.L. Khetrapal, Proc. Ind. Acad. Sci. (Chem. Sci.) 95, 49 (1985).
3. C.L. Khetrapal and K.V. Ramanathan, Chem. Phys. Lett. 118, 589 (1985).
4. C.L. Khetrapal, K.V. Ramanathan and M.R. Lakshminarayana, Bull. Mag. Res. 7, 139 (1985).
5. C.L. Khetrapal, A.C. Kunwar and S. Arumugam, Org. Mag. Res. 22, 707 (1984).
6. C.L. Khetrapal and A.C. Kunwar, Proc. Ind. Acad. Sci. (Chem. Sci.) 93, 1215 (1984).
7. C.L. Khetrapal and E.D. Becker, J. Mag. Res. 43, 8 (1981).
8. C.L. Khetrapal and A.C. Kunwar, Mol. Cryst. Liq. Cryst., 72, 13 (1981).
9. C.L. Khetrapal and A.C. Kunwar, Chem. Phys. Lett. 82, 170 (1981).
10. K.P. Sinha, R. Subburam and C.L. Khetrapal, Chem. Phys. Lett. 96, 472 (1983).
11. K.P. Sinha, R. Subburam and C.L. Khetrapal, Mol. Cryst. Liq. Cryst. 94, 375 (1983).
12. K.P. Sinha, R. Subburam, A.C. Kunwar and C.L. Khetrapal, Mol. Cryst. Liq. Cryst. 101, 283 (1983).
13. J. Jokisaari and Y. Hiltunen, Chem. Phys. Lett. 115, 441 (1985).
14. J. Jokisaari and Y. Hiltunen, Mol. Phys. 50, 1013 (1983).
15. M.R. Lakshminarayana, A.C. Kunwar and C.L. Khetrapal, J. Mag. Res. 60, 184 (1984).
16. S. Raghothama, J. Mag. Res. 57, 294 (1984).
17. P. Diehl, J. Jokisaari and F. Moia, J. Mag. Res. 49, 498 (1982).
18. P. Diehl and J. Jokisaari, Chem. Phys. Lett. 87, 494 (1982).
19. J. Jokisaari and Y. Hiltunen, J. Mag. Res. 67, 319 (1986).
20. C.L. Khetrapal, G. Govil and H.J.C. Yeh, J. Mol. Struct. 116, 303 (1984).
21. C.L. Khetrapal, S. Raghothama and N. Suryaprakash J. Mag. Res. (In Press).
22. C.C. Costain, J. Chem. Phys. 29, 864 (1958).
23. E. Sackmann, S. Meiboom and L.C. Snyder, J. Am. Chem. Soc. 90, 2184 (1968).
24. E. Sackman, S. Meiboom and L.C. Snyder, J. Am. Chem. Soc. 89, 5981 (1967).
25. C.L. Khetrapal, H.J. Yeh and A. Saupe Mol. Cryst. Liq. Cryst. 92, 243 (1984).
26. C.L. Khetrapal, K.V. Ramanathan, N. Suryaprakash and Arun Kumar (To be published).
27. A. Pines and J.J. Chang, J. Am. Chem. Soc. 96, 5590 (1974).
28. A. Hohener, L. Muller and R.R. Ernst, Mol. Phys. 38, 909 (1979).