

NMR STUDIES OF MOLECULES DISSOLVED IN CHOLESTERIC LIQUID CRYSTALS

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ABSTRACT

The results obtained from NMR spectroscopy of molecules oriented in cholesteric liquid crystals are presented. The advantages, limitations and future prospects of using cholesteric materials as orienting media for NMR experiments have been discussed with emphasis on our own recent work.

I. INTRODUCTION

Though thermotropic nematic and lyotropic mesophases have been widely used as solvents in NMR experiments (1,2) comparatively much less work has been reported on cholesteric materials. On the other hand, since such materials exhibit remarkable unusual properties leading to novel technological applications, the interest in such studies has enhanced in recent times. One of the reasons for the scarce use of the cholesteric materials as orienting media particularly in the proton NMR experiments lies in the difficulty in orienting them and in obtaining sharp lines. However, the experiments demonstrating that suitable mixtures of cholesteric materials provide sharp lines in proton NMR spectroscopy (3-5) promise new applications.

Studies on orientation of optically active compounds, translational diffusion, deuteron magnetic resonance of deuterated molecules dissolved in cholesteric liquid crystals and their mixtures with nematics and the determination of molecular geometry have all been reported.

The purpose of this short review is to present a critical evaluation of the results and the prospects of the use of cholesteric materials as anisotropic media in NMR experiments. Though reports on the study of spin-lattice relaxation times T_1 and $T_{1\rho}$ and self diffusion studies (6), the induced cholesteryl lyotropic mesophases (7,8) and the orientational order in cholesteric liquid crystals (9-12) are available, they are not included here since the review is restricted to small molecules dissolved in cholesteric liquid crystals.

II. STUDY OF OPTICALLY ACTIVE COMPOUNDS

Distinct NMR spectra for \underline{d} and \underline{l} enantiomers have been observed for optically active molecules dissolved in optically active cholesteric liquid crystals (3). 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-trichloropropylene oxide dissolved in a mixture of cholesteryl chloride and cholesteryl myristate.

The experiments clearly demonstrate the use of cholesteric mesophases for the study of optically active compounds in order to obtain separate information on the \underline{d} and the \underline{l} forms. Such information cannot be had from nematic and lyotropic mesophases. The potentials of such experiments have yet to be exploited.

III. STUDY OF TRANSLATIONAL DIFFUSION

Translational diffusion coefficient of small molecules such as methane and dichloromethane dissolved in five cholesteric mixtures of alkyl cyanobicyclohexane and cholesteryl chloride have been measured in the temperature range of 25°C to 75°C using pulse gradient spin echo method (13). For cholesteric phases, it is expected that the diffusion coefficient along the pitch (D_{\parallel}) is different from that orthogonal to it (D_{\perp}). Further, NMR investigations in pure neat cholesterics indicate that D_{\parallel} is proportional to the square of the pitch (14-16); the relation has also been derived (17) using simple random walk model for cholesteric liquid crystals. The studies, therefore, provide a method for the determination of the pitch of the helix. NMR has also been used to determine the pitch in a cholesteric lyomesophase formed by adding \underline{l} -alanine to a solution of disodiumchromoglycate in water (18).

In mixture of the nematic liquid crystal ZLI-1167 (aternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonitrile) containing 20% cholesteryl chloride with a

pitch of 2.2 μ , $D_{\perp} / D_{\parallel} \approx 1.1$ for both methane and dichloromethane has been obtained. The Arrhenius activation energies for the diffusion constants are determined as 6-7 KCal/mole. The diffusion coefficients are found to be independent of the pitch i.e. the cholesteryl chloride concentration.

IV. DEUTERON MAGNETIC RESONANCE OF MOLECULES DISSOLVED IN CHOLESTERIC LIQUID CRYSTALS

Deuteron magnetic resonance is particularly a useful technique for the study of the orientation of the molecules dissolved in liquid crystals exhibiting cholesteric and blue mesomorphism (19,21). Both the line separations and the shapes of the quadrupole splittings have been interpreted. The features of the cholesteric phase spectra and of the molecules dissolved therein indicate that the ordering of the phase is incomplete. This is illustrated by the observations of the asymmetry of the quadrupole split doublet components of partially deuterated liquid crystals and the weak inner doublets in the spectra of the dissolved deuterated probe molecules such as benzene- d_6 . The blue phase spectra exhibit features which are distinctly different from those of cholesteric and isotropic phases. They are consistent with the fact that the phase consists of cholesteric-like chiral segments with elementary units arranged in cubic symmetry. The dimensions of the elementary units are of the order of the cholesteric phase pitch length. It may be mentioned that the studies of the blue phase have also been undertaken

using fluorine and proton NMR spectroscopies but due to lower magnetic fields used and the smaller anisotropic interactions of the ^{19}F and the ^1H , the blue phase spectra consisting of broad and isotropic-like signals were obtained (10).

The deuterium NMR spectra of deuterated molecules dissolved in mixtures of opposite handed chirality have also attracted attention (20,21). The NMR spectra of such compensated cholesteric mixtures providing media with very large pitch exhibit sharp lines characteristic of high ordering without any contribution due to randomly oriented domains. The spectra of benzene- d_6 , acetonitrile- d_3 and chloroform- d have thus been studied. The influence of the addition of the nematic liquid crystals such as MBBA [N-(p-methoxybenzylidene)-p'-n-butylaniline], S-1114 [trans-4-pentyl-4(4-cyanophenyl)-cyclohexane] and ZLI-1167 on the deuterium NMR spectra of the deuterated molecules (C_6D_6 , CD_3CN , CDCl_3) dissolved in the compensated cholesteric mixtures consisting of 1:0.74 weight ratio of cholesteryl chloride to cholesteryl nonanoate has also been examined. Upto 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 (Fig.1) start appearing. Though a doubling of the quadrupole doublet is also observed in mixtures with S-1114 beyond a certain concentration, no such effect

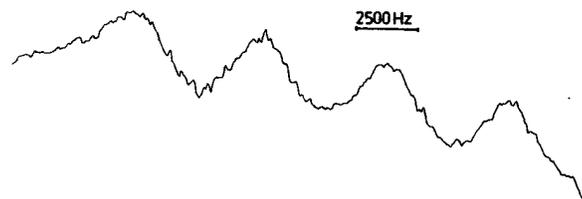


Fig.1. 41.44 MHz Deuterium NMR spectrum of C_6D_6 dissolved in a mixture of cholesteryl chloride : cholesteryl nonanoate : MBBA in the weight ratio of 1:0.73:0.73.

Solute Concentration : 2.7 weight percent

Temperature : 17°C

No. of Scans : 32,000

is noticeable in mixtures with ZLI-1167. However, addition of ZLI-1167 to the mixture containing the compensated cholesteric mixture and MBBA sharpens both the doublets (Fig.2). The

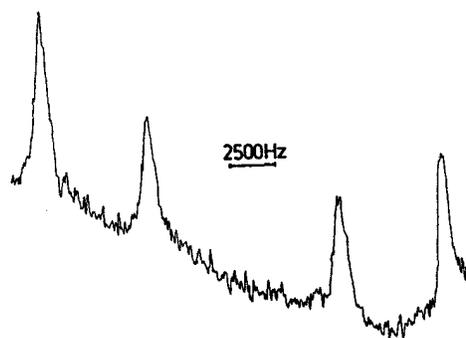


Fig.2. 41.44 MHz Deuterium NMR spectrum of CDCl_3 dissolved in mixture of ZLI-1167, cholesteryl chloride, Cholesteryl nonanoate and

MBBA in the weight ratio of 1:0.075:0.055:0.43.

Solute Concentration : 4.6 weight percent

Temperature : 20°C

No. of Scans : 1,28,000

exact explanation and the possible applications of such experiments are being explored.

V. DETERMINATION OF GEOMETRY OF MOLECULES DISSOLVED IN CHOLESTERIC LIQUID CRYSTALS

The only compound studied in a cholesteric liquid crystal solution for the determination of molecular structure is acetonitrile (5). The proton NMR spectrum of ^1_3C -acetonitrile including the ^{13}C -satellites in the natural abundance of ^{13}C has been investigated in a 1:0.74 weight ratio of cholesteryl chloride to cholesteryl nonanoate. The spectrum with a linewidth at half height of 4 Hz (Fig.3) was obtained. The r_α -structure

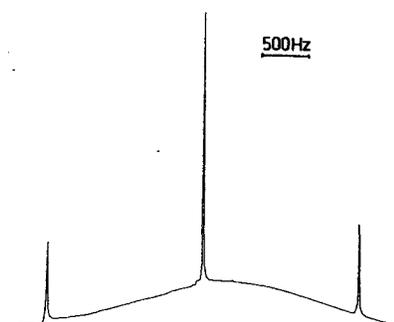


Fig.3. 270 MHz proton NMR spectrum of CH_3CN dissolved in a mixture of cholesteryl chloride and cholesteryl nonanoate in the weight ratio of 1:0.74.

Solute Concentration : 5 weight percent

Temperature : 34°C

No. of Scans : 28

of acetonitrile has thus been determined. The r_α value of the HCH bond angle has been obtained as 109.2°. This agrees well with the microwave value of 109.3° (22).

It has thus been concluded that the cholesteric liquid crystals can be used as convenient solvents in NMR spectroscopy. They provide sharp lines with widths comparable to those in normal thermotropic nematic solvents. Due to the different solubility properties of the cholesteric and the nematic liquid crystals, the results certainly promise the enhancement of the scope of the NMR spectroscopy of oriented systems. The study of a variety of optically active compounds in such solvents may be of future interest. Though the solvent effects on the structure of molecules dissolved in such mesophases have yet to be explored, the indication from the first reported study are that the effects may be of the same order of magnitude as in the case of normal nematics.

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