Natural Abundance ^{2}H NMR Spectra of Molecules Oriented in Liquid Crystals

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It has been demonstrated that the natural abundance ^{2}H NMR spectra of molecules dissolved in liquid crystals can be obtained easily with the help of present-day high-resolution FT NMR spectrometers. Such spectra obtained in the case of benzene and chloroform dissolved in liquid crystals are reported. These experiments could serve as valuable aids for the analysis of the complex proton NMR spectra of oriented molecules. © 1998 Academic Press

One of the major problems in the widespread applications of NMR spectroscopy of oriented molecules arises from the fact that the proton NMR spectra in normal thermotropic solvents are, in general, strongly coupled and they become rapidly complex with the increase in the number of interacting nuclei. Several techniques such as the use of isotopic substitution followed by heteronuclear decoupling (*1, 2*), multiple-quantum spectroscopy (*3–6*), near magic angle spinning (*7, 8*), and the use of liquid crystals with low-order parameters (*9, 10*) have been employed as aids in analyzing the complex proton spectra, but none of these techniques has been routinely employed due to practical difficulties. The use of natural abundance ^{2}H NMR of the molecules dissolved in liquid crystal solvents as a practical tool is suggested in this Communication. To our knowledge this is the first report on the natural abundance ^{2}H NMR spectra of molecules dissolved in liquid crystals, although the spectra of liquid crystals in pure form have been reported earlier (*11*).

The liquid crystal used in the present study is Merck ZLI-1114, *trans*-pentyl-(4-cyanophenyl)-cyclohexane. The ^{2}H NMR spectra of 4.5 wt% benzene and 4 wt% chloroform dissolved in the liquid crystal Merck ZLI-1114 were recorded on a Bruker AMX-400 NMR spectrometer at 303 K using a 10-mm-diameter sample tube. For the natural abundance ^{2}H NMR spectra nearly 64,000 and 140,000 free induction decays were accumulated with a delay of 1 s between scans requiring about 18 and 39 h for benzene and chloroform, respectively. In each case the corresponding proton spectra were also recorded under identical conditions. In the ^{2}H NMR spectra identification of the peaks arising from the solute has been made in the presence of the lines arising from the liquid crystal deuterons by comparison of spectra with and without the solute recorded under similar conditions and from the width of the lines. The solute lines were observed to be sharper than the lines from the solvent. Typical ^{2}H and ^{1}H NMR spectra of benzene under identical conditions are shown in Fig. 1.

The natural abundance ^{2}H NMR spectrum of benzene shows a quadrupole split doublet with a separation of 31.952 kHz. Using a value of 196.5 kHz (*12*) for the deuteron quadrupole coupling constant, this quadrupole split doublet corresponds to an order parameter of 0.1084 in the plane of the benzene ring. If one employs this value of the order parameter, the dipolar coupling between the *ortho* protons of benzene is −852.1 Hz. The proton spectrum of benzene under identical conditions of concentration, temperature, and solvent was separately analyzed by assigning 71 lines and using the *ortho, meta,* and *para* indirect spin–spin couplings as 7.5, 1.3, and 0.6 Hz, respectively. A root-mean-square error of 0.11 Hz was obtained between the observed and the calculated line positions with no line deviating by more than 0.4 Hz. A value of −852.1 Hz for the *ortho* H–H dipolar coupling in benzene was obtained by this procedure. Thus the value obtained by analysis of the proton NMR spectrum and that derived from knowledge of the order parameter obtained from the natural abundance ^{2}H NMR spectrum are found to be identical.

A quadrupole split doublet with a separation of 15.968 kHz was also observed in the natural abundance ^{2}H NMR spectrum of chloroform oriented in the nematic phase of ZLI-1114. Using a value of 180.0 kHz for the deuterium quadrupole coupling constant, an order parameter of 0.061 along the symmetry axis in chloroform is obtained. A study of the proton spectrum including ^{13}C satellites in chloroform also provides a value of 0.061 for the order parameter using $r_{CH} = 1.084$ Å.

Preliminary natural abundance ^{2}H NMR spectra of *o*-dibromobenzene of approximately 4 wt% dissolved in S-1114 at 303 K provide two quadrupole split doublets with separations of about 36 and 25 kHz, respectively. Using a value of 180 kHz for the quadrupole coupling constant, S values of 0.13 and 0.09 have been obtained for the C_2
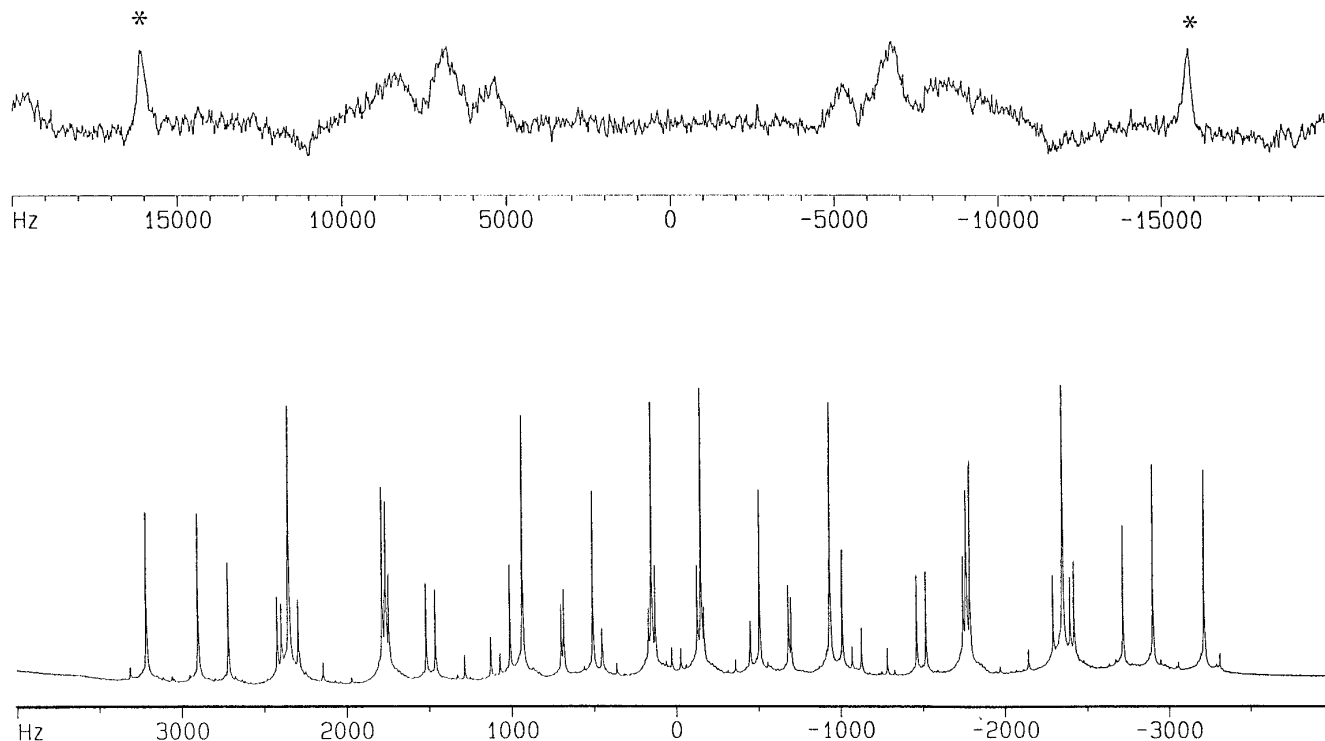
FIG. 1. Top trace: Natural abundance ^{2}H NMR spectrum of benzene (lines marked with *) oriented with liquid crystal ZLI-1114; solute concentration, 4.5 wt%; temperature, 303 K. Bottom trace: ^{1}H NMR spectra of the same sample under identical conditions; number of scans, 64,000 for ^{2}H and 40 for ^{1}H NMR spectra, respectively. Spectrometer frequency, 400 MHz for protons and 61.43 MHz for deuterons.

symmetry axis and the axis perpendicular to it in the plane of the ring, respectively. The corresponding values derived from the proton spectrum of the molecule under identical conditions are 0.14 and 0.08, respectively. The values are in agreement with each other within an experimental error of ± 0.01 in S values estimated by taking into account the width of ^{2}H NMR lines. Detailed studies of such complicated systems are in progress.

The results demonstrate that the natural abundance deuteron NMR spectra of molecules dissolved in liquid crystals can be obtained within reasonable time on the present-day spectrometer. The values of the order parameter thus obtained from the deuterium spectra can help to analyze the complex proton spectra. Such experiments may enhance the scope of the technique of NMR spectroscopy of oriented molecules, particularly when being applied to more complicated systems.

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