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Deuterium N.M.R. of liquid crystal solutions with proton–proton dipolar decoupling

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Deuterium N.M.R. of solute molecules in liquid crystal solutions with the removal of proton–proton dipolar coupling has been explored. The deuterium N.M.R. spectrum of a partially deuterated compound dissolved in a liquid crystal solvent is usually complex or unresolved because of proton–deuterium coupling and extensive proton–proton dipolar coupling. When the latter is removed by a special dipolar decoupling sequence, the deuterium N.M.R. spectrum becomes first order, and deuterium–proton dipolar coupling constants can be readily obtained from the spectrum. Results of monodeuterated hexanes and heptanes dissolved in ZLI 2142 are reported.

1. Introduction

Nuclear magnetic resonance (N.M.R.) is a powerful technique for studying the orientational ordering of liquid crystals at the molecular level [1]. Proton N.M.R. spectra of solute molecules dissolved in liquid crystal solvents usually consist of well-resolved peaks and can yield abundant information on molecular structure and ordering [2]. However, this kind of information is limited to very small molecules only, because the proton spectra of molecules having more than eight protons are usually very complicated and difficult to analyse. The study of carbon-13 N.M.R. of liquid crystals in natural abundance by using special pulse techniques and decoupling sequences has proved to be very useful, and has been applied to neat nematic liquid crystals [3–6] as well as liquid crystal solutions [7–10].

An alternate approach is to use specially labelled compounds. In particular, deuterium N.M.R. has been very successfully applied to study the orientational ordering [11–14], phase transitions [14–16], dynamic equilibrium [17, 18] and molecular motions [14, 19–21] in liquid crystals. The appreciable but not excessively large quadrupolar splitting (*c.* 1–100 kHz) and relaxation make deuterium N.M.R. a very effective technique for obtaining useful information on liquid crystal systems. The deuterium N.M.R. spectrum of a liquid crystal is dominated by quadrupolar splittings. In the nematic phase, there is macroscopic molecular ordering in a high magnetic field, and well-resolved pairs of deuterium peaks are usually observed. For neat nematic liquid crystals, deuterium–deuterium dipolar splittings are occasionally observed [11], but proton–deuterium splittings are generally not resolved because of line broadening caused by extensive proton–proton dipolar coupling. For the same reason, resolvable proton–deuterium splittings in the deuterium spectra of solute molecules in liquid crystal solutions are observed for only very simple compounds such as monodeuterobenzene [22]. In the latter case, the spectral pattern is complicated and the coupling constants have to be obtained by computer analysis of the deuterium spectrum. However, the spectrum can be simplified by applying a special decoupling sequence to remove proton–proton dipolar couplings [22]. The spectrum becomes first order and the splittings can be directly used to calculate the dipolar coupling constant without computer analysis [4, 22]. For more complex solute molecules, the completely coupled deuterium spectra are often unresolved and the signals appear as broad, featureless doublets showing quadrupolar splitting only. We report here on the application of proton–proton dipolar decoupling to study deuterium N.M.R. of monodeuterated hexanes and heptanes. The results demonstrate that first-order proton–deuterium coupling can be observed and dipolar couplings can be readily obtained. The latter supplement deuterium quadrupole couplings and offer additional information in the study of orientational ordering of molecules in liquid crystals.

2. Experimental

The liquid crystal solvent ZLI 2142 was purchased from EM Chemicals, Hawthorne, New York. 1-Bromohexane, 2-bromohexane, 3-bromohexane and 4-bromoheptane were purchased from Columbia Organic Chemical, Camden, South Carolina. 1-Bromoheptane was purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. A check on the purities of these compounds by proton N.M.R. indicated that each contained a small quantity of other isomers. Since the presence of other isomers does not affect the results of the deuterium N.M.R., no particular effort was made to separate them.

To prepare a monodeuterated alkane, a bromoalkane was reacted with magnesium in dry ether to form a Grignard reagent, which was then stirred for one hour with D_2O. The product was isolated by fractional distillation and identified by mass spectrometry.

All N.M.R. spectra were measured with a Varian XL-300 spectrometer with a VXR-4000 data system. The deuterium resonance frequency was 46 MHz. The BLEW-48 decoupling sequence [23] was programmed on a 2764 EPROM and applied asynchronously with data acquisition [24]. The proton decoupler power was calibrated by using an *in situ* method [25]. With an r.f. power of 20 W, $\gamma B_2/2\pi$ was 10·0 kHz. A 2 per cent duty cycle was used in all experiments, including the completely coupled ones, to ensure the same effect of r.f. heating.

3. Results and discussion

To study the deuterium N.M.R. of monodeuterated hexane, equal volumes of 1-deuterohexane, 2-deuterohexane and 3-deuterohexane were mixed and dissolved in ZLI 2142. Since the isomeric purity of each compound was not the same, the sample contained approximately, but not exactly, equal molar concentration of each isomer. The use of the solution of a mixture instead of three different solutions ensured that each of the three kinds of molecules had the same order parameter. The deuterium N.M.R. spectra of the mixture are shown in figure 1. The spectrum with broadband decoupling (figure 1 (*a*)) consists of three pairs of sharp peaks due to different deuterium quadrupole couplings for each compound. These peaks are sharper than those of perdeuterated hexane [26] because the latter are slightly broadened by deuterium–deuterium dipolar interactions. The two halves of the deuterium spectrum do not have equal heights due to differences in line widths, and the outer peaks are broader. These differences are not likely due to insufficient proton decoupling, because the proton spectral width was about 6 kHz and $\gamma B_2/2\pi$ was 10 kHz in our experiment. It may be due to a differential of proton–deuterium dipolar relaxation on the two transitions $|1, 1\rangle \rightarrow |1, 0\rangle$ and $|1, 0\rangle \rightarrow |1, -1\rangle$ between the deuterium

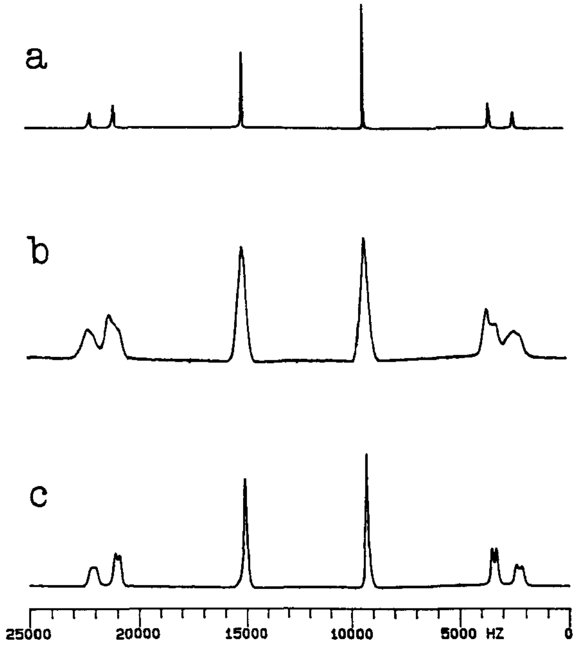

Figure 1. Deuterium N.M.R. spectra of a mixture of 1-deuterohexane, 2-deuterohexane and 3-deuterohexane (8 per cent by weight in ZLI 2142). (*a*) Broad band decoupled, (*b*) proton coupled, (*c*) proton–proton dipolar decoupled with BLEW-48. The resonance frequency was 46 MHz and the temperature was 298 K.

energy levels. A slightly inhomogeneous magnetic field and a temperature gradient in the sample due to r.f. heating (even with a cycle as small as 2 per cent) could also contribute to the difference. Since the relaxation effect is not our major concern, it has not been further investigated.

Without proton decoupling, the deuterium peaks for 1-deuterohexane and 3-deuterohexane become very broad, and those due to 2-deuterohexane split into asymmetrical doublets (figure 1 (*b*)). The line broadening and asymmetrical splitting are due to proton–deuterium dipolar splittings, which are in turn affected by extensive proton–proton dipolar couplings. Because of the complexity of the spin systems and the lack of spectral resolution, it is practically impossible to extract dipolar coupling constants from the spectrum.

When proton–proton dipolar coupling was removed by a special decoupling sequence (BLEW-48 [23] in this case), the peaks of 2-deuterohexane and 3-deuterohexane in the deuterium N.M.R. spectrum split into symmetrical doublets (figure 1 (*c*)). The splitting is due to deuterium–proton coupling of each deuterium with its geminal proton. Long-range couplings were not resolved. For non-spinning samples or samples spun along an axis parallel to B_0, the splitting is given by

$$\Delta\nu = f(2D + J), \qquad (1)$$

where f is a scaling factor for the decoupling sequence, D is the proton–deuterium dipolar coupling constant and J is the proton–deuterium scalar coupling constant. For 1-deuterohexane, the splittings were too small to be resolved, and they only contributed to line broadening (figure 1 (*c*)).

The compound 4-deuteroheptane contained about 17 per cent of 3-deuteroheptane, 3 per cent of 2-deuteroheptane and a trace amount of 1-deuteroheptane. The deuterium N.M.R. spectra of this mixture in ZLI 2142 are shown in figure 2. Like the case of monodeuterohexanes, rather narrow pairs of peaks were observed with complete proton decoupling (figure 2 (*a*)); the peaks were substantially broadened without proton decoupling (figure 2 (*b*)); peaks due to 4-deuteroheptane and 3-deuteroheptane were each split into a doublet with BLEW-48 decoupling (figure 2 (*c*)). Again, the first-order splitting in the latter is due to coupling with the geminal hydrogen without complication from proton–proton dipolar coupling.

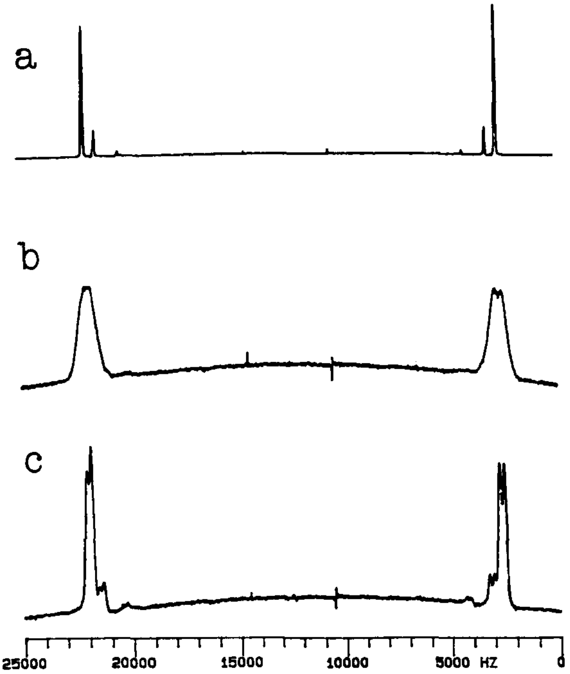

Figure 2. Deuterium N.M.R. of 4-deuteroheptane, with 17 per cent 3-deuteroheptane and 3 per cent 2-deuteroheptane (10 per cent by total weight in ZLI 2142). (*a*) Broad band decoupled, (*b*) proton coupled, (*c*) proton–proton dipolar decoupled with BLEW-48. The resonance frequency was 46 MHz and the temperature was 298 K.

It is straightforward to use equation (1) to calculate the dipolar coupling constant D from the first order splitting $\Delta\nu$. It has been shown that the 'windowless' BLEW-48 sequence is the most efficient decoupling sequence for removing proton–proton dipolar coupling in liquid crystals [22]. Its scaling factor is $f = 0{\cdot}420$. We could not determine the geminal J_{DH} experimentally from either proton or deuterium N.M.R. of the neat, isotropic monodeuterated alkanes, because the spectra were broadened by other J(D–H) couplings. However, the value of $-2{\cdot}0$ Hz determined for other compounds [27] can be used, and it is not expected to have any appreciable anisotropy [2].

The results of the proton–deuterium dipolar couplings calculated according to equation (1) and the deuterium quadrupole couplings ($q_{\mathrm{D}} = 2\Delta\nu_Q/3$) for the monodeuterated alkanes are listed in the table. It should be pointed out that the signs of the H–D dipolar coupling constants cannot be determined from our experiment.

Deuterium quadrupole couplings (q_D) and geminal proton–deuterium dipolar couplings (D_{HD}) of monodeuteroalkanes in ZLI 2142. The experimental uncertainties for q_D are about 2 per cent and those for D_{HD} are about 5 per cent.

	q_D/kHz	D_{HD}/kHz
	Deuterohexanes (8 per cent)	
1-	3·05	–
2-	9·35	0·20
3-	10·53	0·20
	Deuteroheptanes (10 per cent)	
1-	2·67	–
2-	10·97	≈0·25
3-	12·20	0·28
4-	12·87	0·27

Since the H–D splittings are small (~200 Hz) due to the small magnetogyric ratio of deuterium and the deuterium peaks are broad due to quadrupole relaxation, long-range couplings are not resolved and the accuracies of the geminal couplings are not very high (*c.* 5 per cent error). In the case of hexane, more information with higher accuracy can be obtained by studying proton multiple-quantum transitions of partially deuterated compounds [28, 29]. The present results serve to demonstrate an alternative technique for deuterium N.M.R. It may be useful for the study of other partially deuterated, more complicated molecules [30], for which a proton multiple quantum transition study would be less straightforward. The application of this technique to tritium N.M.R. [31] of liquid crystals may also be of interest, because only monotritiated compounds are practical and the large magnetogyric ratio of tritium is likely to make long-range splittings resolvable.

In summary, we have shown that first-order proton–deuterium splittings can be observed in the deuterium N.M.R. spectra of monodeuterated hexanes and heptanes in liquid crystal solutions by applying a decoupling sequence which removes proton–proton dipolar couplings. Values of dipolar coupling constants were obtained for geminal H–D pairs.

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