Measurement of Interproton, Nuclear Spin Dipolar Couplings in Liquid Crystalline Samples by Combining Variable Angle Sample Spinning, Isotope Dilution, and Deuterium Decoupling

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The proton NMR spectra of liquid crystalline samples can be simplified by selective, partial deuteration followed by deuterium decoupling. This leaves strong peaks from the protons at the undeuterated sites, but also weak resonances from the coupling of these protons to those at low abundance (2% in the present case) at the deuterated sites. The weak resonances can be separated from the strong by recording spectra while spinning the sample at a series of angles to the magnetic field. © 1997 Academic Press

Dipolar couplings, D_{ij}, between nuclei in molecules which are in liquid crystalline phases provide the key to unlocking the details of structure, orientational order, and conformational distributions (*1*). There is, however, a fundamental problem in obtaining dipolar couplings in that their presence often renders a NMR spectrum so complex as to be unresolved. This is particularly true for proton spectra of mesogenic molecules, or of solutes of similar structural complexity, and the standard approach is to simplify the spectra by replacing some of the protons by deuterium, followed by deuterium decoupling (*2, 3*). This has proved to be very successful, but there is a practical disadvantage in that the synthesis of molecules containing groups of protons surrounded by deuterons can be difficult, certainly costly, and usually very time-consuming. It is also necessary to synthesize several such specifically deuterated molecules in order to obtain a sufficiently large data set from which to obtain the required information. An attractive alternative to specific deuterium labeling is to use catalyzed H/D exchange reactions to produce molecules in which all the proton sites have been deuterated to a high, but not complete, extent. The few percent of remaining protons are then predominantly in groups of one, two, or three per molecule, and their spectra may be separated by multiple-quantum filtering (*4*). This experiment has been applied, for example, to obtain D_{ij}^{HH} values for *n*-alkanes dissolved in liquid crystalline solvents,

but it has not been used to study a mesogenic molecule since these are not easily fully deuterated catalytically (*5*). The method demonstrated here combines variable angle sample spinning to control the ratio of chemical shifts to dipolar couplings, with specific deuteration of one part of a molecule with random deuteration of another, a combination which is more easily achieved for compounds with different kinds of molecular subgroups, such as mesogens.

The sample used to demonstrate the technique is 4-*n*-pentyl-4′-cyanobiphenyl (5CB)-d_{15} which contains 98% of isotopomer **1** with the pattern of deuteration

1
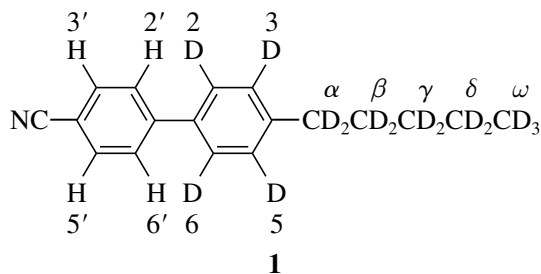
This sample was in fact used in the first demonstration of deuterium decoupling to obtain the proton spectrum of a mesogen, but the only spectral data obtained were the local order parameters for the primed ring (*6*). Figure 1 shows the ^{1}H–$\{^2$H$\}$ spectrum, and Fig. 2 the deuterium spectrum obtained on a static sample of 5CB-d_{15}. The quadrupolar splittings and interdeuteron dipolar couplings obtained from the deuterium spectrum are given in Table 1. The strong lines shown in Fig. 1a are from **1**, and iterative analysis on the line positions yielded the dipolar couplings $D_{2'3'}$, $D_{2'5'}$, and $(D_{2'6'} + D_{3'5'})$ and chemical shifts $\delta_{2'} = \delta_{6'}$ and $\delta_{3'} = \delta_{5'}$ given in Table 2. Figures 1b and 1c reveal that there are many extra lines of low intensity, which are from the seven isotopomers which contain one extra proton each.

The lines from the isotopomers with the extra proton in the unprimed ring, i.e., at positions 2 or 6, and 3 or 5, are

a

b

c

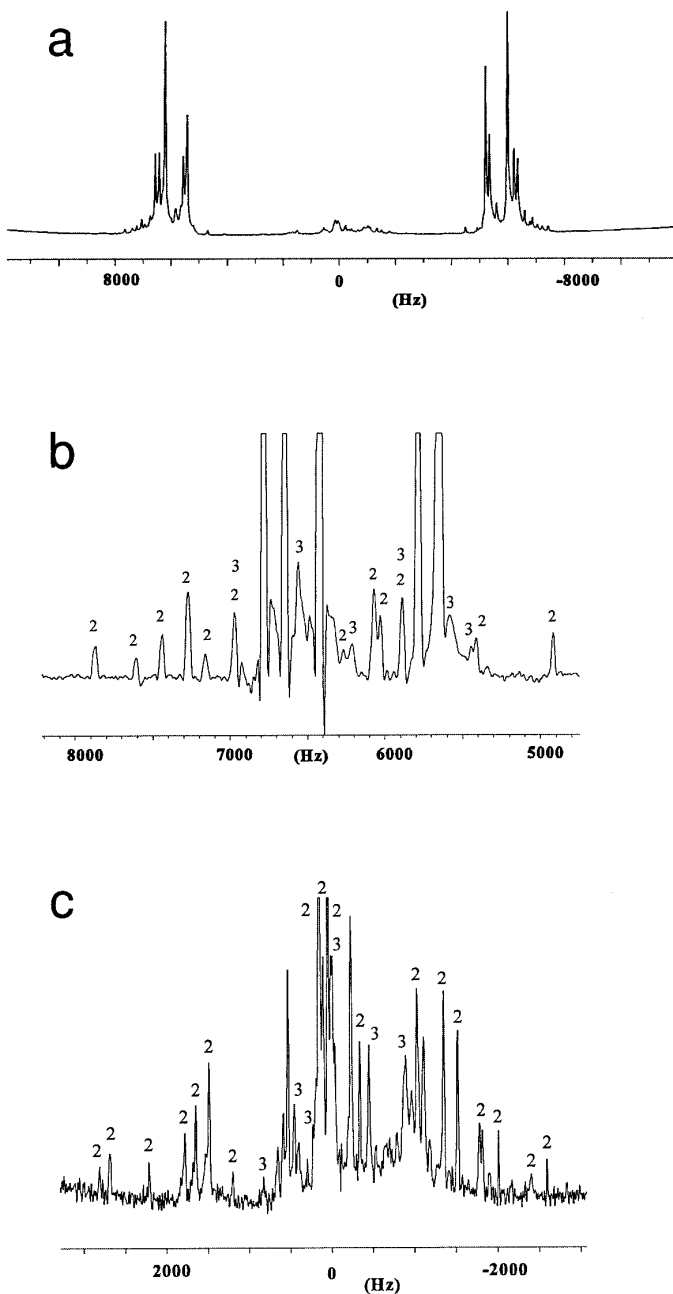**FIG. 1.** 200-MHz ^{1}H–{^{2}H} spectrum of a static sample of 4-n-pentyl-4′-cyanobiphenyl-d_{15} at 300 K. The spectral width used was 23,810 Hz accumulated into 4K of computer memory. Deuterium decoupling was achieved by irradiating at the center of the deuterium spectrum with approximately 11 W of RF power into the double-tuned solenoid coil of a Bruker probe type HP WB 73A. The deuterium irradiation was applied continuously throughout the acquisition time of 86 ms, and was switched off for a delay between pulses of 20 s. The spectrum is the result of applying a Gaussian–Lorentzian window function to the average of 40 free induction decays. (a) The complete spectrum, (b) expansion of the left outer part, and (c) expansion of the center. The peaks are labeled with the site of the fifth proton in the isotopomer.
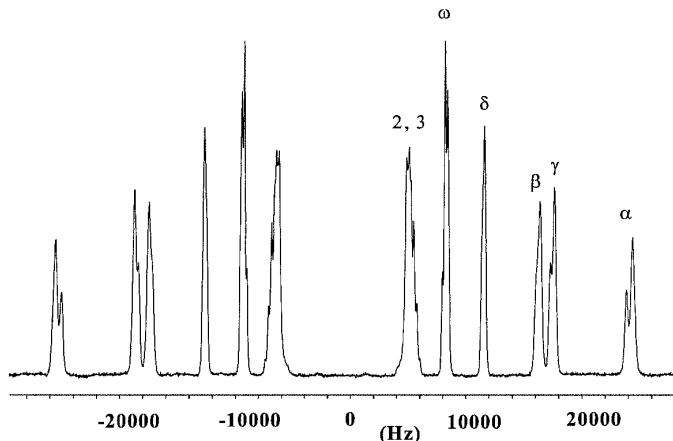

FIG. 2. 30.7-MHz ^{2}H spectrum of a static sample of 5CB-d_{15} at 300 K recorded with the same probe as the proton spectrum in Fig. 1. The spectral width used was 71,429 Hz accumulated into 8K of computer memory.

readily identified in Figs. 1b and 1c. Iteration on these lines, keeping the dipolar couplings between the protons within the primed ring, and their chemical shifts, constant at the values in Table 2, yielded the dipolar couplings and chemical shifts also shown in Table 2.

The spectra from isotopomers with the extra proton in one of the alkyl chain positions could not be separately identified in the spectrum given by the static sample. The technique of variable angle sample spinning (VASS) has been used in order to locate the spectra from the chain-protonated isotopomers (7). The sample has a positive anisotropy, $\Delta\chi$, in the magnetic susceptibility, and on rotation about an axis inclined at an angle θ to the magnetic field, B_0, the mesophase uniformly aligns along the rotation axis, provided that $0° \leq \theta < 54.7°$ and that the rotation speed exceeds a threshold frequency, which for 5CB is <200 Hz. The effect of the director alignment is to reduce all the second-rank, anisotropic interactions by a factor of $R(\theta) = (3 \cos^2\theta - 1)/2$. Thus, the dipolar couplings, which are completely anisotropic, become

$$D_{ij}(\theta) = R(\theta)D_{ij}(0°), \qquad [1]$$

TABLE 1

Quadrupolar Splittings, $\Delta\nu_i$, and Dipolar Couplings, D_{ij}, Obtained from the Deuterium Spectrum of a Static Sample of 4-n-Pentyl-4′-cyanobiphenyl-d_{15} at 300 K

i	$\Delta\nu_i$/Hz	D_{ii}/Hz
α	$50{,}056 \pm 10$	123 ± 6
β	$36{,}479 \pm 10$	84 ± 6
γ	$33{,}984 \pm 10$	75 ± 6
δ	$24{,}375 \pm 10$	50 ± 6
ω	$17{,}597 \pm 10$	55 ± 6

TABLE 2

Dipolar Couplings, D_{ij} (Hz), and Chemical Shifts, δ_i (Hz), for Protons in 4-*n*-Pentyl-4′-cyanobiphenyl-d_{15} Obtained from the Static and Spinning Samples with the Program ARCANA (*18*)

			VASS spectra			
R	$D_{2'3'}$	$D_{2'5'}$	$D_{2'6'}$	$D_{2'\alpha} + D_{3'\alpha}$	$D_{2'\beta} + D_{3'\beta}$	$D_{2'\omega} + D_{3'\omega}$
0.075	-295 ± 1	1 ± 2	28 ± 2	-17 ± 1	-17 ± 1	
0.10	-372 ± 1	4 ± 1	33 ± 1	-22 ± 1	-21 ± 1	
0.18	-708 ± 1	5 ± 2	64 ± 1			-13 ± 1
0.27	-1067 ± 1	11 ± 1	91 ± 1			-19 ± 1

			Static spectrum			
$D_{2'3'}$	$D_{2'5'}$	$D_{2'6'}$	$D_{2'\alpha} + D_{3'\alpha}{}^a$	$D_{2'\beta} + D_{3'\beta}{}^a$	$D_{2'\omega} + D_{3'\omega}{}^a$	
-3919 ± 1	44 ± 1	332 ± 1	-223 ± 10	-218 ± 10	-72.4 ± 4	
$D_{2,2'}$	$D_{2,3'}$	$D_{3,2'}$	$D_{3,3'}$			
-1516 ± 4	-331 ± 5	-362 ± 9	-85 ± 8			

		Chemical shifts/ppm			
i	2′	3′	2	3	
δ_i	5.591 ± 0.005	6.685 ± 0.005	5.811 ± 0.020	5.516 ± 0.010	
i	α^a	β^a	γ^a	δ^a	ω^a
δ_i	2.3 ± 0.100	0.87 ± 0.03	1.0 ± 0.2	1.0 ± 0.2	0.0 ± 0.3

a Extrapolated from the VASS spectra.

and the chemical shifts, which have a scalar part, δ_i^0, as well as an anisotropic contribution, δ_i^{aniso}, change to

$$\delta_i(\theta) = \delta_i^0 + R(\theta)\delta_i^{\text{aniso}}. \qquad [2]$$

The deuterium spectrum of 5CB-d_{15} is dominated by quadrupolar splittings, $\Delta\nu_i$, which are also wholly anisotropic, and so these too are reduced by the alignment of the directors,

$$\Delta\nu_i(\theta) = R(\theta)\Delta\nu_i(0°). \qquad [3]$$

A deuterium (Fig. 3) and a deuterium-decoupled proton spectrum (Fig. 4) were recorded for each of several values of θ. The reduction factors are given alongside each spectrum. These are calculated by comparing the dipolar couplings which fit the lines from isotopomer **1** in the static (Fig. 1a) and VASS spectra. This reduction factor takes into account the slight difference in temperature at which the spectra were recorded, as well as the angular factor.

The most striking feature of the spectra in Fig. 4 is that as the spectrum from **1** narrows a stage is reached when lines from the isotopomers containing a proton in the alkyl chain positions become clearly visible at high field. The high-field region of the spectrum corresponding to θ close

to the magic angle ($R(\theta) = 0.018$) shows essentially single resonances from the five chain positions, but with Hγ and Hδ resonances overlapping. This is in agreement with a proton spectrum of this sample recorded in the isotropic phase. As
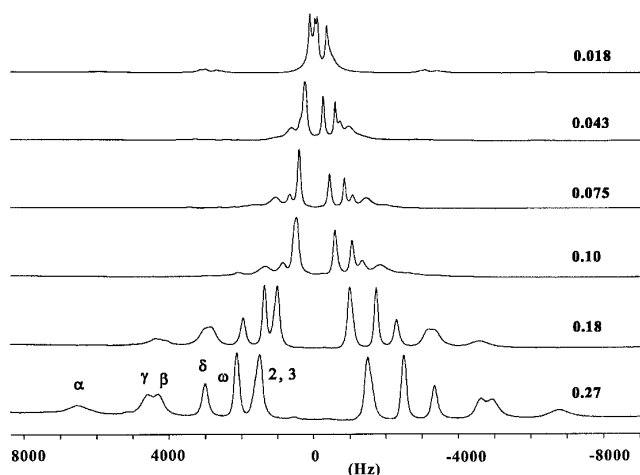

FIG. 3. 30.7-MHz ^{2}H spectra of a sample of 5CB-d_{15} at 300 K and rotating with a frequency of 3000 Hz about an axis inclined so as to give the reduction factors $R(\theta)$ shown against each spectrum.
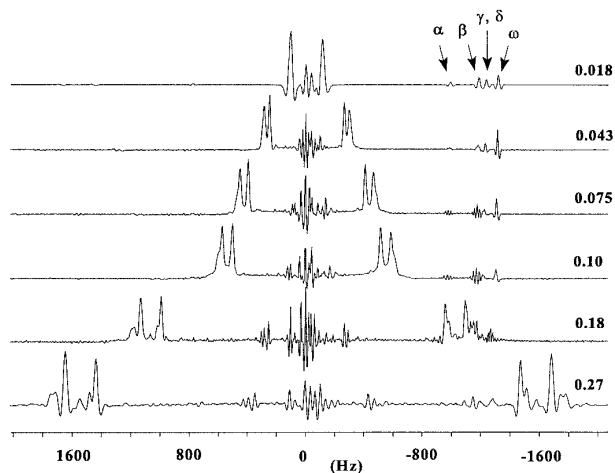
FIG. 4. 200-MHz ^{1}H–{^{2}H} spectra of a sample of 5CB-d_{15} at 300 K and rotating at a frequency of 3000 Hz. The reduction factors, $R(\theta)$, of each spectrum relative to the static spectrum shown in Fig. 1 are given against each spectrum. In each case the conditions used to record the spectra were identical to those for the static spectrum.

θ is decreased from the magic angle the high-field peaks develop structure. For example, when $R(\theta) = 0.075$, the resonances from Hα and Hβ can be clearly seen to be split, which together with the positions of the lines from the four abundant protons is sufficient to yield values of $D_{2'3'}(\theta)$, $D_{2'5'}(\theta)$, $(D_{2'6'}(\theta) + D_{3'5'}(\theta))$, and $(D_{i2'}(\theta) + D_{i3'}(\theta))$, where i is α or β. The resonance from a single proton in the methyl group does not begin to split until it is almost overlapped by the strong lines from **1**, but these lines are resolved in the VASS spectrum corresponding to $R(\theta) = 0.18$. The values obtained for $D_{ij}(\theta)$ were then used together with the values of $R(\theta)$ to give the couplings appropriate to a static sample which are shown in Table 2.

This is the first example of using the VASS NMR technique to obtain dipolar couplings between the protons in a liquid crystalline sample. It demonstrates that very useful information can be obtained, but only in combination with deuteration and deuterium decoupling in order to observe the proton spectra of isotopomers in which the presence of a large scalar contribution to the chemical shift leads to improved resolution in the VASS spectrum.

The data in Table 2 can be used to investigate the following aspects of the structure and orientational order in this benchmark mesogen. The interring D_{ij} are dependent on the rotational potential about the interring bond. This has been investigated previously from D_{ij} values obtained for the molecule with a fully deuterated chain (8, 9). The couplings from the ring to Hα can be used to study the nature of the rotational potential about the C4–Cα bond, which has been investigated previously by obtaining D_{ij} values for the compound fully deuterated everywhere except for the unprimed

ring and the CαH$_2$ group (10). The nature of the conformations generated by rotations about the C–C bonds in the alkyl chain, and the effect of this conformational distribution, has been investigated previously via the quadrupolar splittings obtained on the compound studied here (11). The complete data set in Tables 1 and 2, particularly with the inclusion of the dipolar couplings from the ring to Hα, Hβ, and Hω, will now provide a much more critical test of the theoretical models used in investigations of this and other mesogens.

It is also possible to obtain dipolar couplings without resorting to deuteration to simplify spectra. Thus, Sandstrom and Levitt (12) have obtained 28 ^{13}C–^{13}C couplings for 5CB by the 2D double-quantum experiment. These couplings were between carbons in the cyanobiphenyl group. Fung et al. (13, 14) pioneered the detection of ^{13}C–^{1}H dipolar couplings using separated local field spectroscopy combined with VASS. This experiment has been significantly improved recently by incorporating inverse proton detection (15, 16), and reached a pinnacle of sophistication by extension to 3D (17). These experiments obtain one-bond D_{CH} values and the 3D version also obtains some longer range values, and in particular between the ring and chain, and within the chain. These experiments, together with those described here, show that NMR spectroscopy can now obtain sufficiently large sets of data so that the most intimate secrets of mesogens can be revealed.

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