

Measurement of Carbon–Proton Dipolar Couplings in Liquid Crystals by Local Dipolar Field NMR Spectroscopy

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Received: July 8, 1996; In Final Form: September 13, 1996[⊗]

The performance of several different two-dimensional NMR methods for the measurement of carbon–proton dipolar couplings in liquid crystalline phases is analyzed. Proton-detected local field spectroscopy allows the measurements of short range C–H couplings, which correspond to directly bond pairs, by direct inspection of the spectra. Off magic angle (OMAS) spinning techniques can be applied to anisotropic phases that can be oriented mechanically at an angle to the magnetic field, such as nematic phases. The consequent scaling of the chemical shift anisotropy and dipolar couplings can be used to resolve otherwise overlapping resonances. Moreover, an estimate of the accuracy of the technique can be achieved by performing a series of OMAS experiments with different sample orientations.

I. Introduction

Liquid crystalline compounds constitute an important class of materials because of the variety of applications that are constantly being discovered for this intermediate state of matter.^{1,2} However, the mechanisms that govern their physical and chemical properties are still not completely understood. Nevertheless, some features of the detailed molecular structure of liquid crystals have been shown to determine the stability or the existence of mesophases.^{3,4} Nuclear magnetic resonance has been one of the tools of choice for the study of these systems, since it provides a probe of the material structure at the molecular level.⁵ In particular, magnetic dipolar couplings, which can in principle be measured by NMR, constitute a direct link to structure and dynamics.⁶

A major limitation of the applicability of NMR spectroscopy to the study of liquid crystals is the complexity of spectra dominated by dipolar couplings. This complexity arises from the persistence of the dipolar interaction over relatively long distances, which is both an advantage and a handicap. For example, it is a valuable property for the study of molecules that exist in multiple conformations. On the other hand, the spectral complexity increases exponentially with the size of the system of coupled nuclei. For example, in the case of protons, the spectrum is often too complex to be analyzed even in the case of small molecules. This is true even though there is averaging of the interactions by motion and simplification due to any molecular symmetry.

In contrast to proton NMR, high-resolution spectra of dilute species such as carbon-13 can be obtained for larger molecules in the presence of proton decoupling. However, such spectra contain correspondingly little information about internuclear distances. The contrast between carbon-13 and proton spectra is demonstrated in Figure 1.

Two-dimensional NMR spectroscopy has long been used to exploit the resolution of carbon spectra to separate and simplify dipolar spectra.^{7–9} Particularly high resolution has been achieved using a proton-detected local field (PDLF) experiment

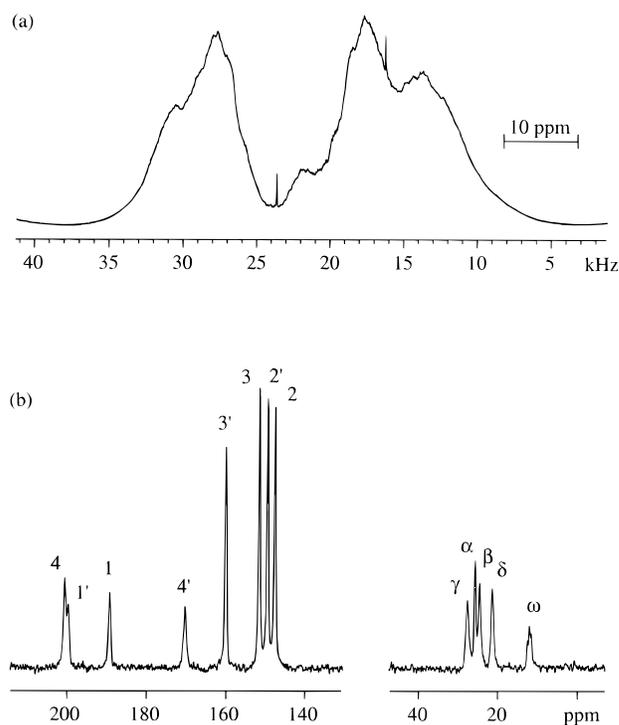


Figure 1. One-dimensional NMR spectra of the nematic liquid crystal 5CB (**1**) acquired at a proton frequency of 500 MHz: (a) proton spectrum obtained with a simple one-pulse–acquire sequence; (b) proton-decoupled carbon spectrum obtained with a cross-polarization sequence with no sample rotation. Thirteen carbon sites can be distinguished, whereas in the proton spectrum only two broad lines can be seen owing to the overlap of the large number of NMR transitions allowed for this system of 19 coupled protons (see text). Note that the two sharp peaks in the proton spectrum correspond to negligibly small amounts of impurity.

in the case of polycrystalline solids,⁹ membrane samples,¹⁰ or solutes in nematic phases.¹¹

In this paper we present the application to a real liquid crystalline system of the PDLF scheme alone and in combination with variable angle sample spinning. The experiments are conducted on a sample of 4-pentyl-4'-biphenylcarbonitrile (5CB), a well-characterized liquid crystalline compound,^{12–15}

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[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1996.

and the results in terms of reliability and resolution that can be achieved with and without spinning of the sample are discussed.

II. Proton-Detected Local Field Spectroscopy

As mentioned in the Introduction, a general problem with the use of solid state NMR spectroscopy for structural studies is that the same interactions that provide geometrical information render the spectrum very complex. However, oriented phases present significantly simpler spectra than polycrystalline or amorphous solids. In a proton spectrum of a liquid crystalline compound, the intermolecular interactions are averaged to zero by molecular motion. The intramolecular interactions are also partially averaged by molecular motion, with the fine details of the averaging depending on the particular molecular motion and the nature of the phase. In a nematic phase, which is uniaxially oriented in a magnetic field, the intramolecular interactions are averaged to a single value for all the molecules in the sample. As a consequence, the NMR spectrum of a nematic is reminiscent of that of a single crystal and consists of sharp resonances instead of the broad powder patterns typical of a static solid. This simplification notwithstanding, the NMR spectrum rapidly becomes intractable. For a system of N spins $I = 1/2$ there are

$$n = \binom{2N}{N+1} \quad (1)$$

possible single quantum transitions (for a 10-spin system $n = 167\,960$).

A. Proton-Detected Local Field Experiment. The problem of spectral complexity can be avoided by using two-dimensional techniques that correlate the natural abundance carbon-13 spectrum with the dipolar spectrum. A high-resolution carbon-13 spectrum can be easily obtained in one dimension by applying heteronuclear decoupling to remove the effect of all the C-H (and consequently H-H) couplings. There are two basic methods by which one can measure the dipolar couplings in the other dimension of the experiment. In the original separated local field (SLF) experiment,^{7,8} the carbon-13 spectrum is measured in the presence of multiple-pulse homonuclear dipolar decoupling of the protons. In this case the removal of the H-H interactions yields a first-order carbon-13 spectrum where the dipolar spectrum of each carbon contains $n = 2^m$ lines, where m is the number of coupled protons. (If the carbon was connected to 10 protons, $n = 1024$.) In other words, the carbon-13 spectrum of an individual carbon consists of a "multiplet", the structure of which is a result of repeated splitting by the H-C couplings, analogous to the J multiplets observed for molecules in isotropic solutions.

A simpler spectrum is obtained if the proton signal is recorded in the dipolar dimension, once again in the presence of multiple-pulse homonuclear dipolar decoupling. In the absence of interactions with other protons each proton in a molecule containing one carbon-13 nucleus experiences only the local field due to that carbon, and thus, the spectrum of each proton is split into a doublet. At natural abundance only 1% of the other carbon atoms will be carbon-13 so that the proton dipolar spectrum correlated to a particular carbon-13 nucleus consists of a superposition of doublets arising from the coupling to each different proton. Thus, the dipolar spectrum contains $n = 2m$ lines (for $m = 10$, $n = 20$). This feature significantly simplifies the measurement of the coupling, since the splittings observed in the spectrum yield directly the motionally averaged heteronuclear H-C total couplings. This is the proton-detected local field experiment, which was only very recently applied to liquid crystalline systems, for example, a solute (benzene) in a nematic solvent.¹¹

Caution is required when scaling up the experiment from small solutes to more complex molecules, such as liquid-crystal-forming compounds. Firstly, larger molecules are likely to have a broader overall frequency distribution, which requires high-power decoupling, particularly for proton homonuclear decoupling. It has been suggested that temperature gradients resulting from high-power rf pulses leads to spectral broadening in liquid crystal samples.¹⁶ For this reason, a SLF experiment was proposed in which the dipolar Hamiltonian was scaled by fast rotation of the sample at an angle close to the magic angle.^{17,18}

B. Off Magic Angle Spinning Experiments. Fung and co-workers have pioneered the combination of carbon-detected local field experiments and sample spinning for liquid crystalline samples.^{17,18} The magnitude of the average dipolar coupling in a liquid crystal is a function of the angle formed by the main axis of symmetry (director) with the external magnetic field.^{6,19,20} In the case of a single crystal, this orientation can be set at will. Liquid crystalline samples, on the other hand, tend to be oriented by a magnetic torque either parallel or perpendicular to the direction of the field depending on the sign of the anisotropy of the magnetic susceptibility. However, the magnetic torque can be overcome in some cases by fast mechanical spinning of the sample.^{19,20} In this case, the main axis of symmetry of the phase (director) is aligned with the spinning axis, with consequent scaling of all couplings according to the relation:

$$d \propto \frac{1}{2}(3 \cos^2 \theta - 1) \quad (2)$$

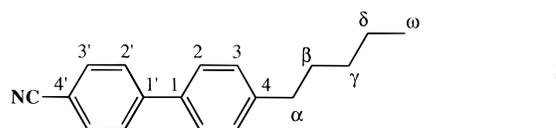
where d is the observed splitting and θ is the angle subtended between the axis of sample rotation and the magnetic field.

The advantage of scaling the couplings by sample spinning is that milder conditions for both heteronuclear and homonuclear decoupling can be used, although it is not obvious that this gain compensates for the loss of resolution due to the smaller splittings. However, it has been suggested¹⁶ that the high rf power required for a satisfactory removal of proton-proton couplings by means of MREV-8^{21,22} or similar sequences may result in an overall increase of the temperature in the sample, which would affect the orientational order of the liquid-crystalline compounds. The minimum power required for hetero- and homonuclear decoupling is determined by the size of the coupling to be averaged out, which can be controlled by off magic angle spinning of the sample.

C. Variable Angle Spinning Experiments. In this article we investigate the applications of proton-detected local field spectroscopy to liquid crystals on samples both in static and *variable* angle spinning conditions. We propose that reliable data can be obtained from a series of PDLF experiments recorded at different spinning angles. Instead of being measured from each individual spectrum, the dipolar couplings can then be measured from a linear regression to eq 2.

III. Experimental Section

All the spectra in this article were obtained for a sample of 5CB (4-*n*-pentyl-4'-cyanobiphenyl) (**1**) with the pulse sequence shown in Figure 2.



The ¹H magnetization is excited by the first 90° pulse and then immediately tilted by a 45° pulse into a frame perpendicular

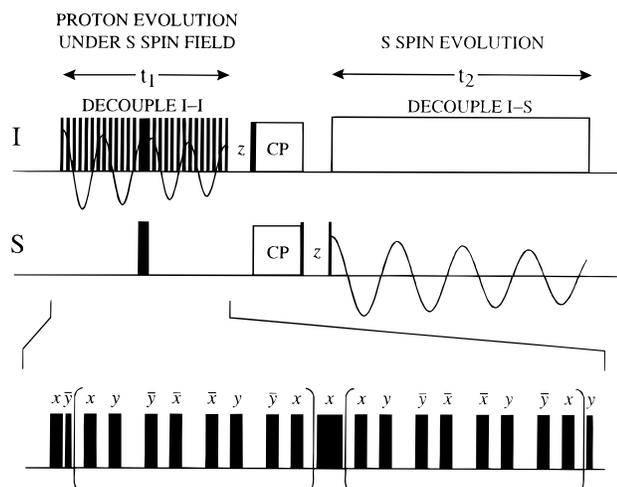


Figure 2. Pulse sequence appropriate for proton-detected local field spectroscopy. Proton magnetization is allowed to evolve under the carbon–proton heteronuclear couplings during the first evolution time (t_1). The MREV-8 multiple-pulse sequence removes the effects of the homonuclear dipolar Hamiltonian, while the simultaneous π -pulses applied to both proton and carbon remove the proton chemical shift while preserving the carbon–proton coupling interaction. Magnetization is then transferred to carbon via cross-polarization, and a carbon spectrum is acquired under broad-band proton decoupling.

to the effective field of the multiple-pulse sequence MREV-8. The multiple pulse train is applied during the evolution time t_1 to suppress the effect of proton homonuclear couplings. The chemical shifts of the protons are refocused. The simultaneous application of 180° pulses to proton and carbon at the center of t_1 refocuses the chemical shifts and ensures that proton magnetization evolves in this dimension only under the C–H dipolar and scalar interaction. The magnetization is then tilted back into the rotating frame by another 45° pulse. This can be followed by an optional z filter, during which spin diffusion among the protons could yield an equalization of the amplitudes, and then by the cross polarization sequence, which transfers the proton coherence to carbon. The carbon signal is then detected during t_2 in the presence of CW decoupling of the protons. This sequence leads to a two-dimensional correlation spectrum in which carbon chemical shifts in ω_2 are correlated to carbon–proton couplings in ω_1 .

The “static” PDLF spectrum shown in Figure 3 was obtained on a 500 MHz Varian Unity+ spectrometer using a double tuned 5 mm MAS probe, built by APS rotor consultants, without spinning the sample. For the MREV sequence a ω_1 field of 55 kHz was used, which was reduced to ~ 30 kHz during the acquisition period for heteronuclear decoupling. The reduced field during acquisition was chosen to minimize sample heating effects while still being compatible with good decoupling (note that the ω carbon is therefore slightly broadened in ω_2). The variable angle spinning spectra (an example is shown in Figure 4) were obtained on a home-built spectrometer operating at a proton resonance frequency of 301.2 MHz with a Tecmag acquisition system and a home-built variable angle spinning probe head.²³ The ω_1 fields were constant throughout the experiment and depended on the spinning angle. They ranged from 30 to 35 kHz. Note that these fields are less than those used in the MREV sequences in the static experiment.

The scale shown for the ω_1 dimension in both cases (proton–carbon coupling) is already corrected for the MREV-8 scaling factor, which is taken to be the theoretical value of 0.47. The OMAS spectra are symmetric about zero frequency in ω_1 , since only the cosine-modulated component of the carbon–proton coupling was acquired in t_1 . The static spectra were recorded with sign discrimination in ω_1 using the States method.¹⁰

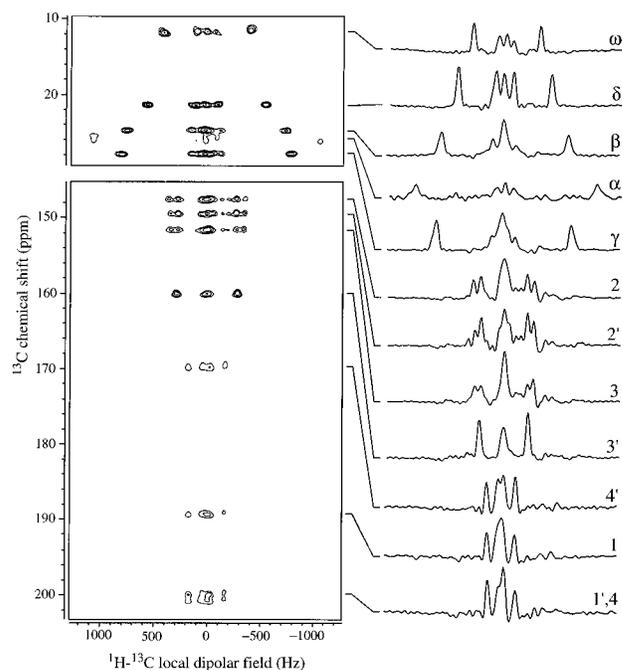


Figure 3. Contour plot of the proton-detected local field spectrum of 5CB (1) recorded with the pulse sequence in Figure 2 under “static” conditions. The traces taken parallel to ω_1 for each carbon site show clearly distinct doublets that are directly related to individual C–H couplings. The spectrum was acquired with 64 points in t_1 and an MREV-8 cycle time of $66 \mu\text{s}$ using $4.5 \mu\text{s}$ 90° pulses. Sixty-four scans were acquired per increment with a 6 s recycle delay to avoid sample heating.

IV. Results and Discussion

The PDLF spectrum of 5CB recorded under “static” conditions is shown in Figure 3. The dipolar cross sections are shown for each individual carbon resonance, and it can be remarked that in every case the largest coupling (corresponding usually to directly bonded pairs) can be measured by direct inspection of the spectrum. The OMAS spectra (Figure 4) are, not surprisingly, very similar to the static spectra, apart from the scaling factor of the splittings. Note that the carbon chemical shifts are also dependent on the spinning angle, since there is an anisotropic contribution to the resonance position,²⁴ and that this can provide a method to disentangle resonances that overlap at any one angle. The resolution obtained for the two spectra recorded under these particular experimental conditions is very similar, confirming the hypothesis that the loss of resolution due to scaling is compensated for by an improved performance of the multiple-pulse sequence.

Note that, as predicted above, the PDLF spectrum does indeed provide a simple image of the coupling network. In fact the PDLF multiplet will often be even simpler than predicted by the statistical arguments above. This is illustrated by considering the spectrum of the ω carbon in 5CB (shown schematically in Figure 5b). A large splitting is expected for the three methyl protons and a second smaller splitting for the two equivalent δ protons. Under the best conditions of resolution and optimized polarization transfer, a long-range coupling to the γ protons might also be detected, yielding a total of six lines. In the carbon-detected experiment one would expect the carbons to be split into a quartet with a large splitting by the methyl protons, which would further separate into a smaller triplet by splitting due to the δ protons, which may be eventually split into another triplet by the γ protons, yielding a total of 36 lines.

In practice the long-range couplings (of which there may be many) may not provide observable splittings and may lead to a broadening of the lines in the carbon-detected experiment and

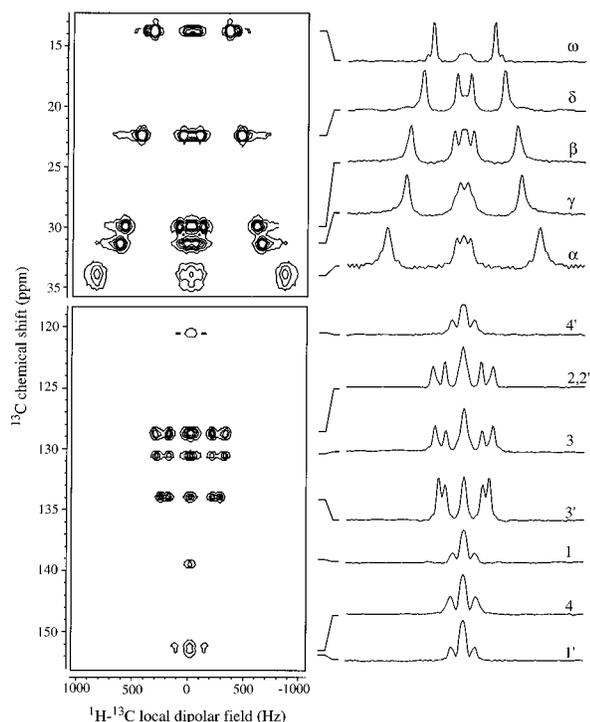


Figure 4. Contour plot of the OMAS–PDLF spectrum of 5CB recorded by spinning the sample at a rate of about 1.6 kHz at an angle of 48.2° with respect to the magnetic field. Note that the position and order of the carbon resonances differ from those in Figure 3 owing to the scaling of the chemical shift anisotropy. For example, in this experiment the signal from carbon 2 and 2' overlap.

subsequent loss of resolution. These small couplings are very sensitive to details of the structure, since they mirror interactions over many bonds. The PDLF scheme can potentially reveal the small couplings, since the short-range splittings are not broadened by long-range couplings. However, it is often not possible to distinguish and assign long-range couplings because the corresponding doublets will lead to a superposition of peaks at the center of the local field spectrum. In principle this nuisance can be attenuated by using short contact times in the cross-polarization step. To measure and assign long-range couplings, PDLF-type experiments with higher dimensionality^{25,26} are necessary to further disentangle the overlapping signals.

Figure 5 shows a simulation of the outcome of a PDLF and a SLF spectrum on two systems, benzene dissolved in a nematic liquid crystal and the ω -carbon of 5CB. Note that this comparison also highlights that the sensitivity of the PDLF spectrum will usually be much greater than that of the SLF spectrum, owing to the lower multiplicity of the spectrum. For the specific example shown in Figure 5, a 10-fold improvement in sensitivity is calculated.

A. Precision and Accuracy. As discussed above, in the original SLF experiment, dipolar couplings are measured by interpreting the multiplet generated by any $\{C, H_n\}$ -coupled spin system. This type of multiplet consists of combination lines arising from sums and differences of the different coupling constants. The *precision* of the measurement for the SLF method is limited by the ability to distinguish and assign the many signals that may overlap in the multiplet, given the maximum resolution attained with the multiple pulse sequence and the experimental signal-to-noise ratio. The *accuracy* of the measurement is limited by the validity of the assumption that the frequency scaling factor generated by the multiple-pulse decoupling sequence is uniform throughout the spectrum. Some of the multiple-pulse sequences available for removal of the

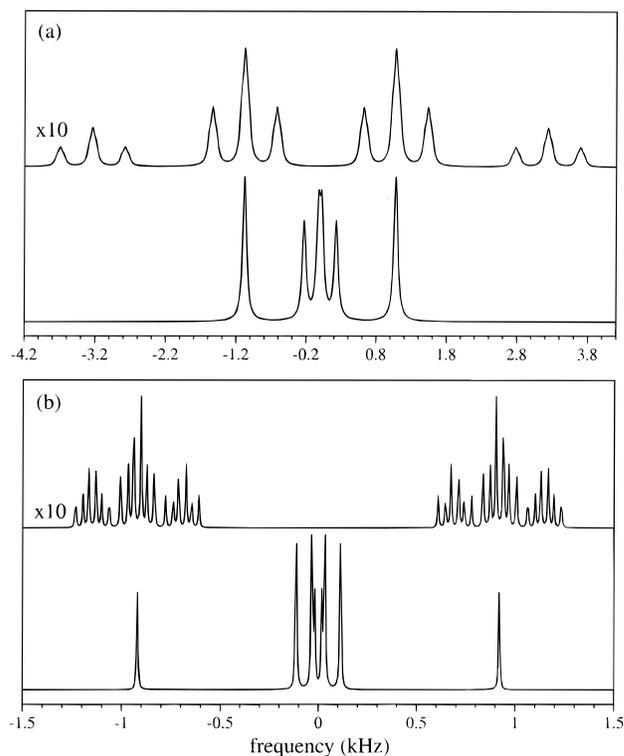


Figure 5. Simulation of the relative performance of SLF and PDLF spectroscopy. Part a shows the expected for the case of benzene dissolved in a nematic liquid crystal. Note that the SLF spectrum (top trace) has a higher multiplicity and is reduced in amplitude by about a factor 10 with respect to the PDLF spectrum. Part b shows the expected spectra for the ω carbon in 5CB (1). Note how, once again, the PDLF experiment (lower trace) is associated with a 10-fold gain in sensitivity. The smaller couplings broaden the SLF lines but merely contribute to the zero frequency peak in the PDLF experiment.

homonuclear proton couplings are more tolerant than others to irradiation offset and variations in the coupling size, and then they provide a uniform scaling factor.²⁷ Nevertheless, even in the most favorable case there is likely a variation of at least 1% of the scaling factor. Therefore, the accuracy and the precision in a SLF experiment are of about the same magnitude.

In a PDLF experiment, the variation of the scaling factor is the largest source of systematic error. The precision of the measurement is intrinsically high, since the couplings can be obtained from a simple difference of two peak maxima, which results in an uncertainty of potentially less than 0.1%. This uncertainty for the splittings cannot reflect the accuracy of the measured couplings, which we expect to be at least 1 order of magnitude larger. The accuracy of the experiment can be evaluated instead by exploiting the dependence of the dipolar couplings on the rotor orientation in an OMAS experiment. The effect of variation of the spinning angle on the dipolar couplings is represented in eq 2. However, owing to the particular geometry of the radio frequency coil in the probe head used for this experiment, the radio frequency field amplitude is also modulated as a function of the spinning angle. Consequently, the rf field used for decoupling will diminish accordingly with the scaling factor so that the ratio between dipolar couplings and the rf field does not exceed the range of angles we have used ($42\text{--}52^\circ$). However, measurements performed at different angles will then produce a difference in the scaling factor for a given frequency (i.e., carbon–proton pair) of the same order as one could expect for the range of frequencies observed. Therefore, the dipolar couplings obtained from a linear regression of a set of OMAS measurements to eq 2 (shown in Figure 6) are expected to be sensitive to this source of systematic error. Correspondingly, the calculated error margin better represents

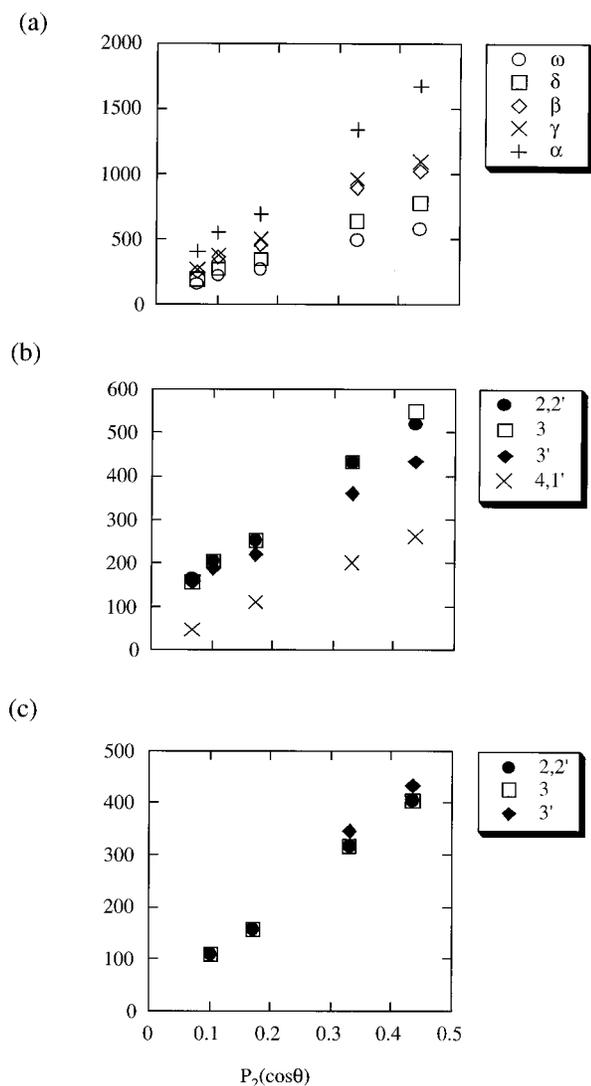


Figure 6. Dipolar splittings from OMAS–PDLF spectra recorded at different sample spinning angles: (a) aliphatic resonances, largest splitting; (b) aromatic resonances, largest splitting; (c) aromatic resonances, long-range couplings.

TABLE 1: Carbon–Proton Dipolar Couplings from PDLF Spectra

nuclei	OMAS ^a D/Hz	static D/Hz
Aliphatic Carbons		
α	3473 ± 150	4656
β	2154 ± 152	3223
γ	2327 ± 160	3472
δ	1603 ± 68	2366
ω	1153 ± 63	1676
Aromatic Carbons ^b		
2, 2'	977 ± 35	1449, 1394
	895 ± 26	1229, 1229
3	1052 ± 35	1388
	908 ± 25	1229
3'	756 ± 32	1126
	991 ± 45	1290
4/1'	583 ± 3	748

^a Values obtained from a fit to five data sets obtained at different angles. See text. ^b The first entry refers to directly bonded protons; the second entry to long range interactions.

the accuracy of the PDLF measurement. (Note that this argument is also applicable to SLF measurements as a method for determining the accuracy.) The couplings measured by this method are given in Table 1 and have an uncertainty of about 4–5%.

B. Data Analysis. As discussed in the Introduction, the magnetic dipolar couplings measured by NMR in liquid crystals are motionally averaged quantities. This property together with their sensitive dependence on internuclear distances provides the opportunity for studying not only the structural features but also the overall dynamics of the anisotropic phase. Indeed, dipolar couplings have been used as constraints for testing detailed models of dynamics.^{15,28–31} To test the meaningfulness of the couplings produced by the PDLF methods (Table 1), we now compare the description of the average orientation of the molecule of 5CB in the nematic phase as constrained by PDLF data with results from previous investigations.^{15,17,18,28–31}

The average dipolar coupling for a rigid molecule in a liquid crystal is commonly described in terms of the Saupe ordering matrix, $S_{\alpha\beta}$:

$$D = -\frac{\gamma^2 h}{4\pi^2} \frac{1}{2r^2} \langle (3 \cos^2 \theta - 1) \rangle = \sum_{\alpha,\beta=x,y,z} S_{\alpha\beta} D_{\alpha\beta} \quad (3)$$

where r is the internuclear distance, γ is the gyromagnetic ratio, and θ is the angle subtended by the internuclear vector with the magnetic field. The $D_{\alpha\beta} = [K/(2r^3)](3 \cos \theta \cos \theta_\beta - \delta_{\alpha\beta})$ are the components of the dipolar coupling tensor, expressed in a molecular fixed axis system. The terms $S_{\alpha\beta}$, usually referred to as order parameters, describe the molecular orientation with respect to the director in terms of the direction cosines of the internuclear vector:

$$S_{\alpha\beta} = \langle 3 \cos \theta_\alpha \cos \theta_\beta - \delta_{\alpha\beta} \rangle / 2 \quad (4)$$

For a molecule with internal degrees of freedom eq 3 is not strictly valid not only because the motion could change the internuclear distances but also because each allowed conformer could experience different orientational forces and therefore be associated with a different set of order parameters. Couplings that are sensitive to the internal dynamics, for example, between nuclei in which the distance varies significantly in different conformers, can only be reproduced by a model that takes into account a description of the interdependence of molecular shape and anisotropic properties. For example, the dynamics and orientation of the aliphatic chain of 5CB have been thoroughly analyzed using NMR constraints.¹⁴ Such an analysis is outside the scope of this article. On the other hand, the two phenyl rings can be treated as “rigid” subunits and the couplings relative to each ring can be analyzed independently using the formalism of eq 3. The number of order parameters necessary to describe each ring subunit can be evaluated on the basis of symmetry arguments,³² and if quasi-hexagonal symmetry is assumed for the rings, then only two order parameters are necessary to completely describe the molecular orientation. This assumption has been shown to be strictly valid for the ring carrying the aliphatic chain, while a small deviation from the symmetrical geometry was calculated for the second ring, where the two protons next to the CN group are slightly tilted back to form a C–C–H angle of about 121°. Table 2 shows the phenyl ring order parameters calculated by fitting the experimental dipolar couplings to eq 3 using the assumed ring geometry and standard values for the bond lengths ($r_{C-H} = 1.09 \text{ \AA}$, $r_{C-C} = 1.40 \text{ \AA}$).

The main order parameter, S_{zz} , is the most sensitive to temperature, since it describes the global order of the phase. The difference in the calculated values of S_{zz} for the “static” and for VAS PDLF experiments (about 0.52 and 0.41, respectively) can be ascribed to the 4° difference in room temperature between the two laboratories where the experiments were performed.¹⁵ In each data set, the value of the order parameter

TABLE 2: Order Parameters^b

ring	static PDLF			OMAS-PDLF			SLF ^a		
	rms/Hz	S_{zz}	ΔS	rms/Hz	S_{zz}	ΔS	rms/Hz	S_{zz}	ΔS
1	27	0.51	0.03	27	0.40	0.02	29	0.50	0.05
2	36	0.52	0.03	33	0.42	0.03	27	0.50	0.05

^a From ref 18. ^b We indicate the ring carrying the aliphatic chain as ring 1 and the one carrying the CN group as ring 2. The errors on the order parameters can be estimated to be of the same order as those on the measured couplings, that is, about 5%.

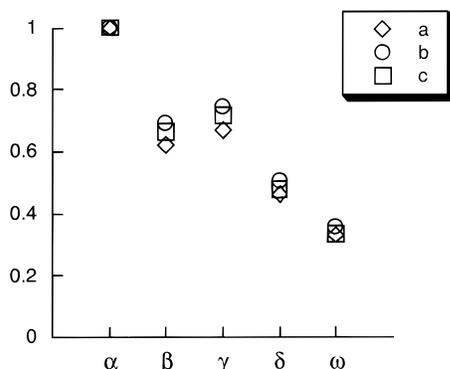


Figure 7. Comparison of the measured carbon-proton dipolar couplings for the aliphatic chain in 5CB as determined by different separated local field methods, and all couplings are scaled to the largest in the set: (a) VAS-PDLF; (b) "static" PDLF; (c) SLF.

is found to be slightly larger in the ring carrying the CN group, as has been observed previously.

The term that represents the biaxiality, $S_{xx} - S_{yy}$, is found to be 0.03. A similar value was proposed on the basis of the analysis of multiple-quantum NMR of protons¹³ in the case where the geometrical difference between the two rings would make them distinguishable (D_2 symmetry). The value of 0.069 calculated for the biaxiality via proton dipolar couplings¹⁵ is not directly comparable to our result, since inclusion of vibrational motion, which is expected to raise this order parameter, was not taken into account in this study. A slightly higher value for the uncorrected biaxiality ($S_{xx} - S_{yy} = 0.05$) was calculated in a previous study,¹⁸ using C-H couplings measured via SLF experiments.

A simple analysis of the type used for the aromatic coupling is not adequate to describe the complex dynamics of the aliphatic chain. However, it is observed that the couplings measured here follow the same trend along the chain as results from a previous study¹⁸ (Figure 7).

VI. Conclusions

We have shown that techniques based on the principle of proton-detected local field (PDLF) spectroscopy are suitable for the determination of carbon-proton dipolar couplings in liquid crystals. The technique gives rise to high-resolution spectra, which consist of a sum of doublets corresponding to distinct C-H pairs. The method offers substantial gains both in resolution (and thus in the precision of the measurement of dipolar couplings) and in sensitivity. The measurement of the couplings is performed straightforwardly from the spectrum with high precision.

For liquid crystals that can be oriented mechanically by fast spinning of the sample, we have demonstrated that OMAS PDLF experiments can be carried out under mild conditions of rf irradiation. The "static" and OMAS PDLF experiments produce similar resolution and can be seen as complimentary techniques. The additional degree of freedom provided by the orientation of the sample with respect to the magnetic field allows for partial scaling of dipolar couplings and chemical shift anisotropy. This property can be used to resolve sites that are

occasionally overlapping and, perhaps more importantly, to assess the accuracy of measured dipolar couplings from a series of independent experiments performed at different spinning angles.

Acknowledgment. We are grateful to Dr. Anne Lesage (ENS-Lyon) for help recording the static PDLF spectra. Professor Klaus Schmidt-Rohr (University of Massachusetts, Amherst) is acknowledged for his support and many fruitful discussions. This investigation was supported, in part, by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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