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Determination of Long-Range Dipolar Couplings Using Mono-Deuterated Liquid Crystals

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A new approach is presented for the determination of long-range dipolar couplings in liquid crystals. The strategy is the use of monodeuterated compounds to observe $^2H-^{13}C$ splittings in the ^{13}C NMR spectra. As examples, the H−C dipolar coupling constants have been obtained from the spectra of 4′-cyanobiphenyl 2-deutero- and 6-deuterohexanoate over the whole nematic range. In addition, the ^2H NMR spectra of these compounds taken with $^1H-^1H$ dipolar decoupling show quadrupolar splitting and $^1H-^2H$ dipolar coupling. Besides the information obtained from the 1D spectra, one-bond and two-bond $^1H-^{13}C$ dipolar coupling constants of 4′-cyanobiphenyl hexanoate were determined using the method of proton encoded local field (PELF) spectroscopy in combination with off-magic-angle spinning (OMAS). The order parameters were calculated from the 2D spectra, and some of the coupling constants are compared with the H−C coupling constants obtained from the 1D experiments.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is an important experimental tool for the study of liquid crystals since it can give detailed information about molecular geometry, orientational ordering, and internal dynamics.[1] Natural abundance ^{13}C NMR provides a convenient method for the study of orientational ordering in liquid crystals because it can determine order parameters and motions of individual parts of liquid crystals. The 2D NMR method of separated local field (SLF) spectroscopy in combination with off-magic-angle spinning (OMAS) has been proven to be especially effective in studying the ordering of liquid crystals.[2] A recent improvement of this technique increased the resolution of the 2D spectra,[3] and is called PDLF (proton-detected local field)[3] or PELF (proton encoded local field) spectroscopy.[4] However, even with increased resolution, the 2D method can only provide one- and two-bond $^1H-^{13}C$ dipolar coupling constants.

The measurement of long-range dipolar coupling constants is important for conformational studies of liquid crystals. The earliest success was the determination of the $^1H-^1H$ dipolar couplings of the eight protons in the phenyl rings of 4-n-pentyl-4′-cyanobiphenyl (5CB) by Pines and co-workers,[5] who studied the multiple quantum ^1H spectra of chain-deuterated 5CB with ^2H decoupling. More recently, using 5CB-d15, in which the chain and its adjacent phenyl ring are deuterated, J. W. Emsley and co-workers were able to obtain some long-range $^1H-^1H$ dipolar coupling constants from single-quantum spectra.[6] From 2D double-quantum experiment,[7] Sandstrom and Levitt obtained 28 $^{13}C-^{13}C$ couplings between carbons in the cyanobiphenyl moiety of 5CB. Recently, L. Emsley and co-workers used a 3D version of the PELF method to obtain three- and four-bond H−C dipolar coupling constants in 5CB,[8] and a 2D method to obtain long distance $^2H-^{13}C$ dipolar coupling constants in perdeuterated 5CB.[9] Each method has its advantages and limitations, and these points will be discussed later. Here we present another approach to measure long-range dipolar coupling constants of liquid crystals. The strategy is the use of mono-deuterated compounds to observe $^2H-^{13}C$ splittings in the ^{13}C spectra with proton broadband decoupling. The method has been applied to determine long-range dipolar couplings in the nematic

liquid crystals 4′-cyanobiphenyl 2-deutero- and 6-deuterohexanoate over the whole nematic range. The use of a monodeuterated liquid crystal to observe $^2H-^{13}C$ couplings was first reported by Ernst and co-workers,[10] but the resolution was not very good, and couplings between the chain and the rigid core were not observed. Well-resolved long-range $^{19}F-^{13}C$ couplings in mono- and difluorinated liquid crystals have been reported more recently,[11,12] but fluorination leads to considerable changes in liquid crystalline properties. Thus, the present study on liquid crystals with monodeuteration in different positions of the chain enables us to obtain information not available previously. The ^2H NMR spectra of these compounds also provide the quadrupolar splittings of the deuterons and neighboring $^1H-^2H$ dipolar couplings in the nematic phase. In addition, the 2D PELF method has been used to obtain one- and two-bond $^1H-^{13}C$ dipolar coupling constants of 4′-cyanobiphenyl hexanoate, and the results are compared with those obtained from the 1D NMR study of the monodeuterated compounds.

Experimental Section

4′-Cyanobiphenyl hexanoate was prepared by esterification of 4′-hydroxybiphenylcarbonitrile with hexanoyl chloride and pyridine in dry chloroform. The final product was recrystallized in hexane. Its nematic range is from 53.0 to 70.5 °C.

The monodeuterated liquid crystal, 4′-cyanobiphenyl 2-deuterohexanoate, was synthesized according to the Scheme 1. Its isomer, 4′-cyanobiphenyl 6-deuterohexanoate, was prepared similarly.

Methyl 2-deuterohexanoate was prepared by reduction of the methyl 2-bromohexanoate using $NaBD_4$ in dimethyl sulfoxide.[13] The ester was hydrolyzed with 2 equiv of KOH in methanol and then acidified. Finally, the acid was esterified with 4′-hydroxybiphenylcarbonitrile using dicyclohexylcarbodiimide (DCC) as dehydrating agent. The final product was recrystallized in hexane.

The 1D ^{13}C and ^2H NMR experiments were performed on 4′-cyanobiphenyl 2-deutero- and 6-deuterohexanoate using a Varian UNITY/INOVA 400 NMR spectrometer. The sample was placed in a standard 5 mm tube and spun slowly along the magnetic field so that the director was aligned parallel to the field. The temperature calibration was made by observing the
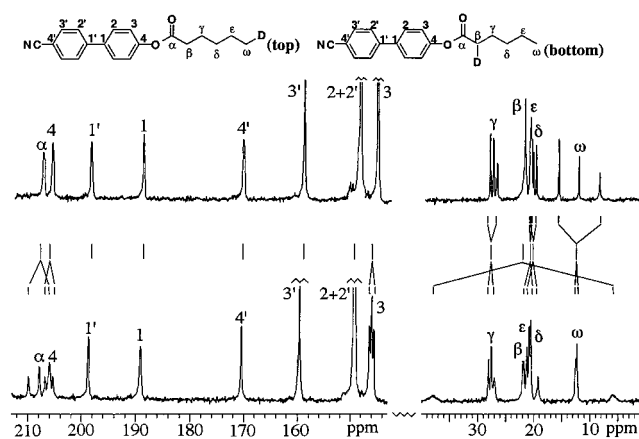
Figure 1. ^{13}C NMR spectra of 4′-cyanobiphenyl 2-deutero- and 6-deuterohexanoate at 100.58 MHz and 55 °C. The spectra were obtained with the SPINAL-64 broadband ^{1}H decoupling sequence with $\gamma B_2/2\pi = 18$ kHz. The long vertical bars in the middle show the peak positions of the nondeuterated homologue. The short vertical bars show the positions of the outer peaks for each resolvable triplet due to ^{2}H splitting.

SCHEME 1: Synthetic Scheme for 4′-Cyanobiphenyl 2-Deuterohexanoate
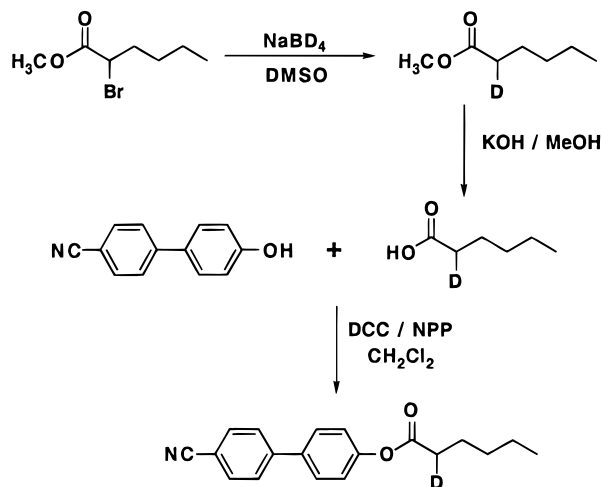
nematic to isotropic transition. The 2D PELF/OMAS C-13 NMR experiments[7] were performed on 4′-cyanobiphenyl hexanoate using a variable-angle spinning probe, with proton−carbon cross polarization and the BLEW-48 dipolar decoupling sequence.[14] The angle between the spinning axis and the magnetic field B_0, β, was determined by studying the deuterium quadrupole splittings of a solution of CDCl₃ in ZLI 1193; the ratio of the splittings obtained with and without spinning (spinning rate ∼1 kHz) is equal to $(3\cos^2\beta - 1)/2$.

Results and Discussion

1D ^{13}C NMR Study of Monodeuterated Liquid Crystals. Recently, we have developed a very efficient broadband decoupling sequence for liquid crystals, which uses only moderate decoupler power ($\gamma B_2/2\pi < 20$ kHz) to remove all [1]H−[13]C couplings to yield sharp ^{13}C peaks.[15] The ^{13}C spectra of the monodeuterated liquid crystals 4′-cyanobiphenyl 2-deutero- and 6-deuterohexanoate obtained by the use of this decoupling sequence (SPINAL-64) are shown in Figure 1. The spectra were obtained with [1]H−[13]C cross polarization, and the −CN peak is too broad and weak to be observed. Single pulse without cross polarization can also be used.

For 4′-cyanobiphenyl 2-deuterohexanoate, the coupling of the ^{2}H nucleus with eight types of carbons (the carbonyl, the 3-

and 4-carbons of the nearby phenyl ring, and the five carbons of the aliphatic chain) can be observed. These carbon atoms are separated from the deuterium atom by one to five bonds in both directions. For 4′-cyanobiphenyl 6-deuterohexanoate, only four sets of [2]H−[13]C splittings are observed. This is because the deuterium atom is much farther away from the phenyl rings, and the rapid rotation of the −CH₂D group about the C(ϵ)−C(ω) bond reduces the average [2]H−[13]C dipolar coupling constants. These coupling constants (D) are related to the observed splittings $\Delta\nu$ by

$$\Delta\nu = 2D + J \tag{1}$$

where J is the scalar coupling constant. The signs of $\Delta\nu$ cannot be determined and are assumed to be positive based on geometric considerations. The J values were determined from spectra in the isotropic phase, and only the directly bonded pairs were nonzero. For peaks with small overlapping, the $\Delta\nu$ values were obtained by simple spectral deconvolution. A complete analysis of the results obtained for these compounds over the entire nematic range has been made. For comparison with other data, the [2]H−[13]C dipolar coupling constants are converted to [1]H−[13]C dipolar coupling constants using the equation:

$$D_{CH} = (\gamma_H/\gamma_D)D_{CD} = 6.5142 D_{CD} \tag{2}$$

where γ_H and γ_D are the gyromagnetic ratios of proton and deuterium, respectively. The data are summarized in Table 1.

^{2}H NMR Spectra. For the monodeuterated compounds, the deuterium quadrupole coupling constants can be determined from the ^{2}H NMR spectra directly. Furthermore, when a good [1]H−[1]H dipolar decoupling sequence (BLEW-48)[14] is used, neighboring [1]H−[2]H splittings can be observed (Figure 2) and the bond order parameters calculated.

The deuterium NMR spectrum of 4′-cyanobiphenyl 2-deuterohexanoate is a doublet of doublets. The larger doublet separation is due to quadrupole splitting of the deuterium and the smaller doublet separation due to dipolar coupling to the neighboring proton. For 4′-cyanobiphenyl 6-deuterohexanoate, a doublet of triplets was observed. The smaller triplet separation is due to dipolar couplings to the two neighboring protons. The exact splitting of the overlapping peaks were determined by spectral deconvolution. The quadrupolar splitting is related to the order parameter tensor components of the C−D bond by

$$\Delta\nu = (3e^2qQ/2h)[S_{aa} + \eta(S_{bb} - S_{cc})] \tag{3}$$

If it is assumed that the deuterium quadrupole coupling constant $e^2qQ/h = 168$ kHz and the asymmetry parameter $\eta = 0$ in eq 3, S_{aa} is the order parameter of the C−D bond, S_{CD}. It can be readily calculated while $\Delta\nu$ is taken to be negative from geometric considerations.
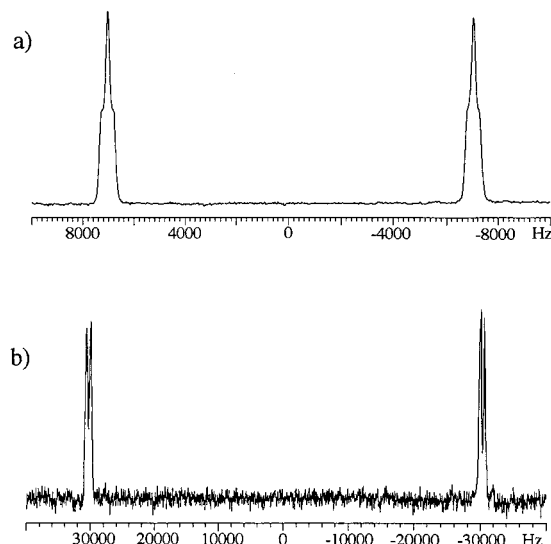
For the [1]H−[2]H dipolar splittings, $\Delta\nu$ is assumed to be negative based on geometric considerations. The dipolar coupling constants can be calculated by using eq 1. The order parameters of each H−D bond, S_{HD}, is related to the corresponding H−D dipolar coupling constant by

$$S_{HD} = -(4\pi^2 r^3/\gamma_H\gamma_D h)D_{HD} = -3.163 \times 10^{-4} D_{HD} \tag{4}$$

where h is the Planck's constant and r is the distance between the hydrogen atom and the deuterium atom. The values of the order parameters S_{CD} and S_{HD} are summarized in Table 2. For comparison, S_{CD} values calculated from [2]H−[13]C dipolar coupling constants (Table 1) are also listed. The small systematic

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TABLE 1: ^{1}H–^{13}C Dipolar Coupling Constants for 4′-Cyanobiphenyl Hexanoate at Several Temperatures

T (°C)	β–α	β–β	β–γ	β–δ	β–ε	β–ω	β–3	β–4	ω–γ	ω–δ	ω–ε	ω–ω
55	645	5285	173	459	114	68	127	235	208	111	339	1167
57	635	5138	163	446	111	65	124	231	202	104	322	1121
59	619	4962	156	430	107	62	121	228	192	101	309	1072
61	593	4773	140	417	104	59	114	208	182	98	293	1023
63	560	4519	137	394	91		114	176	173	91	277	962
65	508	4242	127	368	88				160	85	270	893
67	625	3819	114	329	78				147	65	238	808
69		3024		254					124	52	198	678

a)

b)

Figure 2. ^{2}H NMR spectrum of (a) 4′-cyanobiphenyl 6-deuterohexanoate and (b) 4′-cyanobiphenyl 2-deuterohexanoate at 61.395 MHz and 55 °C. The spectra were obtained with BLEW-48 ^{1}H–^{1}H dipolar decoupling, with $\gamma B_2/2\pi = 16$ kHz.

TABLE 2: Order Parameters S_{CD} and S_{HD} Calculated from Quadrupolar Splittings and Dipolar Coupling Constants for 4′-Cyanobiphenyl 2-Deutero- and 6-Deuterohexanoate at Several Temperatures

	β deuterium			ω deuterium		
T (°C)	S_{CD}^a	S_{CD}^a	S_{HD}	S_{CD}^a	S_{CD}^a	S_{HD}
55	−0.241	−0.233	0.108	−0.056	−0.051	0.038
57	−0.234	−0.226	0.106	−0.054	−0.049	0.037
59	−0.227	−0.219	0.102	−0.052	−0.047	0.036
61	−0.219	−0.210	0.100	−0.050	−0.045	0.034
63	−0.210	−0.199	0.096	−0.047	−0.042	0.032
65	−0.198	−0.187		−0.044	−0.039	0.030
67	−0.182	−0.168		−0.041	−0.036	
69	−0.159	−0.133		−0.036	−0.030	

^{a} Values in the first column were obtained from deuterium quadrupole coupling constants; values from the second column were obtained from ^{2}H–^{13}C dipolar coupling constants.

differences are likely due to the assumptions involved in the calculations ($e^2qQ = 168$ kHz, $\eta = 0$, and $r_{CD} = 0.110$ nm).

Because the mobility of the chain increases toward the end of the chain, the absolute values of the order parameters S_{CD} and S_{HD} decrease significantly (Table 1). For the long-range dipolar coupling constants (Table 1), there are no obvious trends because these values depend on the average of many conformations. Although it is difficult to use these dipolar coupling constants to extract order parameters, they serve as useful database for the study of conformational properties of liquid crystals and stingent criteria for judging the success of molecular dynamics simulations.

2D ^{13}C NMR Study of the Nondeuterated Compound. For a complete determination of all one-bond and some two-bond dipolar coupling constants, we used the 2D PELF/OMAS
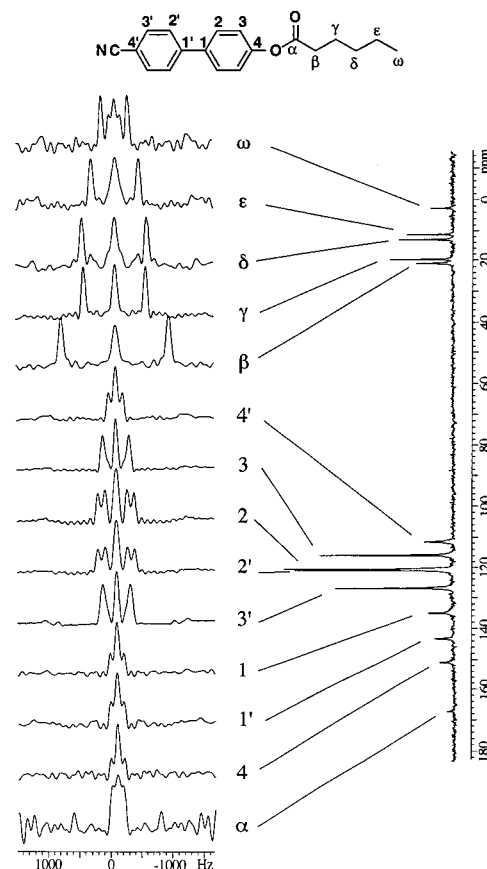
Figure 3. ^{13}C NMR spectrum of 4′-cyanobiphenyl hexanoate at 55 °C (right) with sample spinning at a rate of 1.310 kHz along an axis forming an angle of 47.33° with respect to B_0. Traces in the ω_1 dimension in a 2D PELF experiment are shown on the left.

TABLE 3: Comparison of One-Bond ^{1}H–^{13}C Dipolar Couplings (Hz) Obtained from Two Kinds of Experiments

	β carbon from		ω carbon from	
T (°C)	^{2}H–^{13}C	PELF	^{2}H–^{13}C	PELF
55	5285	5227	1167	1145
59	4962	5004	1072	1011
63	4519	4536	962	932
67	3819	3873	808	841

method[3,4] to study the protonated compound 4′-cyanobiphenyl hexanoate. For OMAS, the sample was spun rapidly (~1 kHz) at an angle β with respect to the magnetic field B_0 to reduce the dipolar coupling and obtain sharp ^{13}C peaks, and the value of β was chosen to be 47.33° in this experiment. For the 2D PELF experiment, the local ^{1}H–^{13}C dipolar field is studied quantitatively: in the evolution period, the BLEW-48 decoupling sequence[14] is used to remove ^{1}H–^{1}H dipolar couplings, and then the encoded proton–carbon dipolar coupling information is transferred to carbons by cross polarization; in the detection period, the SPINAL-64 broadband decoupling sequence[15] was used to obtain normal proton-decoupled ^{13}C spectrum in the

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TABLE 4: Semiempirical Parameters for the Aromatic Carbons of 4′-Cyanobiphenyl Hexanoate Obtained by Fitting the Experimental Data to Eq 7

C	1	2	3	4	1′	2′	3′	4′
a	83.93	31.87	35.62	87.08	89.18	33.13	42.27	98.81
b	5.50	3.94	4.00	6.18	4.07	2.56	3.45	−3.82
correlation coeff	0.992	0.992	0.992	0.992	0.995	0.995	0.995	0.995

TABLE 5: Semiempirical Parameters for the Aliphatic Carbons of 4′-Cyanobiphenyl Hexanoate Obtained by Fitting the Experimental Data to Eq 7

C	β	γ	δ	ϵ	ω
a	47.78	28.38	27.21	28.63	42.05
b	−1.11	0.09	−0.01	0.84	0.18
correlation coeff	0.990	0.993	0.983	0.993	0.996

ω_2 dimension; one-bond and some two-bond couplings can be observed in the ω_1 slices.

The 2D PELF/OMAS spectra of 4′-cyanobiphenyl hexanoate at 55 °C are shown in Figure 3. In the spectra in the ω_1 dimension, all one-bond C−H coupling and some two-bond couplings can be observed. Each type of proton gives a doublet, and the central peaks are due to overlapping of unresolved long-range couplings. Each splitting $\Delta\nu$ is related to the $^1\text{H}-^{13}\text{C}$ dipolar coupling constant by

$$\Delta\nu = f[(3\cos^2\beta - 1)D + J] \qquad (5)$$

where f is a scaling factor determined by the $^1\text{H}-^1\text{H}$ dipolar decoupling sequence in the evolution period ($f = 0.414$ for the BLEW-48).[4] For the aliphatic chain, the bond order parameter is[2]

$$S_{\text{CH}} = -4.407 \times 10^{-5} D_{\text{CH}} \qquad (6)$$

Two of the dipolar coupling constants thus obtained can be directly compared with those calculated from the 1D spectra of the monodeuterated compounds, and the results are shown in Table 3. The data obtained from the two types of experiments agree with each other very well, which is reassuring. Actually, because the $^1\text{H}-^{13}\text{C}$ dipolar coupling constants obtained by the PELF/OMAS method depend on the accuracies of the scaling factor f and the angle β, the $^2\text{H}-^{13}\text{C}$ dipolar coupling constants obtained from the 1D spectra are more accurate.

The method for calculating the order parameters of the phenyl rings is the same as the SLF/VAS method[2] and will not be repeated here. For the phenyl ring containing the aliphatic chain, the averaged values of the bond angles are as follows: H2−C2−C3 = 119.4° ± 0.4°, and C2−C3−H3 = 119.6° ± 0.4°. For the phenyl ring directly bearing the cyano group, the corresponding angles are H2′−C2′−C3′ = 118.9° ± 0.4°, and C2′−C3′−H3′ = 119.8° ± 0.4°.

Temperature Dependence. To study the temperature dependence of the order parameters over a wide temperature range, one can combine the PELF/OMAS results with ^{13}C chemical shift data, which are readily obtained from one-dimensional NMR experiments. Thus, the 2D PELF/OMAS experiments were performed at four temperatures to obtain the order parameters, which can be related to the ^{13}C chemical shifts through a semiempirical equation[16,17] for the both phenyl rings and C−H bonds in the aliphatic chains:

$$\Delta\delta = aS + b \qquad (7)$$

where $\Delta\delta = \delta_{\text{LC}} - \delta_{\text{iso}}$, and a and b are constants. The values of a and b obtained from linear least-squares fitting of the experimental data are listed in Tables 4 and 5.
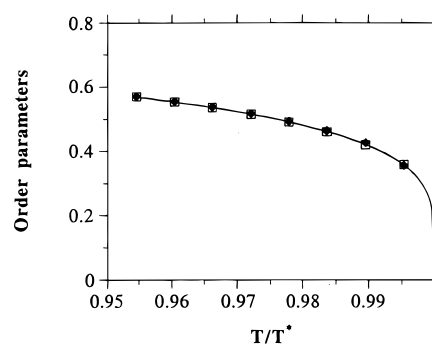
Figure 4. Plot of order parameters of the aromatic rings of 4′-cyanobiphenyl hexanoate against T/T^*, with $T^* = 343.6$ K. The open squares are for the nonprimed ring; the filled circles are for the primed ring. The solid line was calculated from eq 8.
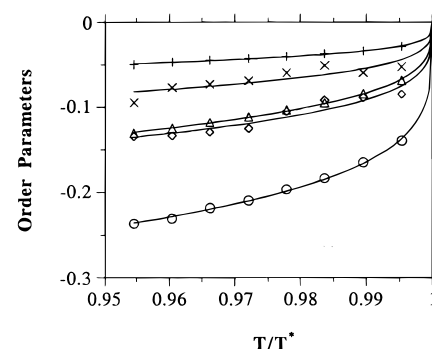
Figure 5. Plot of C−H order parameters of the aliphatic carbons of 4′-cyanobiphenyl hexanoate against T/T^*, with $T^* = 343.6$ K. The symbols are (○) β, (△) γ, (◇) δ, (×) ϵ, and (+) ω. The solid lines were calculated from eq 8.

TABLE 6: Values of S_0 and F Obtained by Fitting the Calculated Order Parameters to Eq 8

C	ring 1	ring 2	β	γ	δ	ϵ	ω
S_0	1.08	1.06	−0.494	−0.315	−0.330	−0.190	−0.104
F	0.21	0.20	0.24	0.25	0.26	0.27	0.25

After the constants a and b in eq 7 have been determined from the experimental PELF/OMAS data at four temperatures, the ^{13}C chemical shifts were measured at more temperatures in a wider range; the corresponding order parameters were then calculated using eq 7. The data for the aromatic rings and for the aliphatic carbons are presented in Figures 4 and 5. They are fitted to the Haller equation:[18−21]

$$S(T) = S_0(1 - T/T^*)^F \qquad (8)$$

where S_0 and F are empirical constants and T^* is a temperature at which the order parameter becomes zero.

The values of S_0 anf F obtained by fitting the order parameters calculated from chemical shifts to eq 8 are listed in Table 6, where ring 1 refers to the phenyl ring containing the chain. T^* was initially treated as a variable parameter for fitting each curve; then, the average value of 343.6 K was used as a fixed parameter for all final fittings. The order parameters of the two phenyl rings in this compound are equal within experimental error, implying that the two rings can be treated together as a

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TABLE 7: Values of D_0 and F Obtained by Fitting the $^1H-^{13}C$ Dipolar Coupling Constants to Eq 9

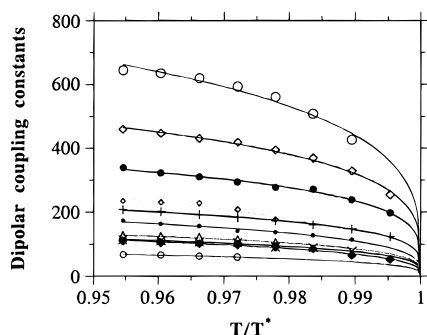|	$\beta-\alpha$	$\beta-\gamma$	$\beta-\delta$	$\beta-\epsilon$	$\beta-\omega$	$\beta-3$	$\beta-4$	$\omega-\gamma$	$\omega-\delta$	$\omega-\epsilon$
D_0	1529	412	995	258	168	249	769	423	305	677
F	0.27	0.28	0.25	0.26	0.28	0.26	0.28	0.23	0.22	0.23

Figure 6. Plot of long-range dipolar coupling constants of the carbons of 4′-cyanobiphenyl 2-deutero- and 6-deuterohexanoate against T/T^*, with $T^* = 343.6$ K. The symbols are (○) $\beta-\alpha$, (●) $\beta-\gamma$, (◇) $\beta-\delta$, (×) $\beta-\epsilon$, (○) $\beta-\omega$, (△) β-3, (◇) β-4, (+) $\omega-\gamma$, (◆) $\omega-\delta$, and (●) $\omega-\epsilon$. The solid lines were calculated from eq 9.

rigid core. It has been suggested that the numerical values of S_0 for the rigid core should be close to unity.[18−21] Although a variety of experimental techniques utilized in the determinations of order parameters indicated that this is not always true,[22] the values of S_0 for both phenyl rings in 4′-cyanobiphenylhexanoate are close to unity (Table 6). For a perfectly aligned all-trans conformation of the aliphatic chain, S_0 for each C−H bond should be close to −0.333 (i.e., [3 cos^{2}109° 28′ − 1]/2). The values listed in Table 6 for two carbon atoms (γ and δ) agree with this estimation reasonably well, but that for the β carbon is more negative because it is connected to a carboxy segment. In general, the mobility toward the end of the aliphatic chain increases and the order parameter decreases; therefore, the two outer carbons atom (ϵ and ω) have S_0 values less negative than the other carbons. The exponent F is roughly a parameter to judge how fast the motion decreases with temperature, and has a value of about 0.2 for many liquid crystals.[18−21] It is also the case for the rigid core in the present compound (Table 6). The F values for the C−H bonds in the chain are slightly larger, reflecting the larger temperature dependence of the chain motion.

Although the long-range dipolar coupling constants cannot be used directly to calculate the order parameters, they are also determined by the orientational ordering of the liquid crystal molecules and may obey a relation similar to the Haller equation (eq 8). Therefore, we tried to fit the data listed in Table 1 to the following equation:

$$D(T) = D_0(1 - T/T^*)^F \qquad (9)$$

where D_0 and F are empirical constants and T^* is a temperature at which the dipolar coupling constants become zero. The results are presented in Figure 6, and the values of D_0 and F are listed in Table 7. The values of F are relatively constant, but the physical significance is not clear.

Conclusion

Long-range dipolar coupling constants are important in the investigation of detailed chain motions and rapid rotations or jumps of the rings. In this report, we have presented the first example of using one-dimensional ^{13}C NMR to obtain long-range H−C dipolar couplings for the chain, and compared the results with those obtained from the 2D PELF/OMAS method.

Additional data for the two monodeuterated isomers of 4′-cyanobiphenyl hexanoate were obtained from 1D ^{2}H NMR.

Finally, it is appropriate to compare our approach with other methods for the determination of long-range dipolar coupling constants. Compared with other 1D methods, the syntheses of monodeuterated liquid crystals are considerably simpler and less expensive than polydeuterated liquid crystals,[5,6] and the analysis of the ^{13}C spectra is much more straightforward than the analysis of the ^{1}H spectra. A 2D ^{2}H−^{13}C method for the study of perdeuterated 5CB[9] yields information similar to those presented here, but the resolution is not as good. The 2D ^{13}C−^{13}C double quantum method[7] and the 3D PELF method[8] do not require special syntheses, but take up extensive spectrometer time. Furthermore, the assignment of the ^{13}C−^{13}C couplings is not straightforward[7] and the 3D method requires resolved ^{1}H peaks, has low resolution, and does not yield information on nonprotonated carbons.[8] Therefore, the approach of using monodeuterated compounds complements other NMR methods nicely for the determination of long-range dipolar coupling constants in liquid crystals.

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