Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Canlet, C. and Fung, B. M.(2001) 'Determination of long range dipolar couplings in ferroelectric liquid crystals', Liquid Crystals, 28: 12, 1863 — 1872

To link to this Article: DOI: 10.1080/02678290110085597

URL: http://dx.doi.org/10.1080/02678290110085597

LIQUID CRYSTALS, 2001, VOL. 28, NO. 12, 1863–1872

Determination of long range dipolar couplings in ferroelectric liquid crystals

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(*Received 2 April 2001; accepted 25 June 2001*)

Long range dipolar coupling constants have been determined in three ferroelectric liquid crystals in their racemic forms using ^{13}C NMR. Two of these liquid crystals are esters of α-chloroacids and 4-octyloxy-4′-hydroxybiphenyl, and have a very large spontaneous polarization in the smectic C* phase. The strategy used in the present study is the observation and measurement of ^{2}H-^{13}C splittings in the ^{13}C spectra of monodeuterated compounds. The order parameters were calculated from the 1D spectra, and some of the coupling constants are compared with the ^{1}H-^{13}C coupling constants previously obtained from 2D experiments. In addition, the deuterium quadrupole splitting of these compounds was determined from their ^{2}H NMR spectra. The experiments were carried out over the whole mesomorphic ranges of the liquid crystals, covering the smectic A and smectic C phases.

1. Introduction

Ferroelectric liquid crystals (FLCs) have attracted considerable attention since their discovery in 1975 [1]. These materials form a chiral smectic C (SmC*) phase which exhibits spontaneous electrical polarization. Hence, considerable effort has been spent on the search for FLC molecules with large spontaneous polarization. An important class of FLCs is formed by the esters of optically active α-halocarboxylic acids with 4-alkoxy-4′-hydroxybiphenyls [2–4]. These compounds exhibit a chiral smectic C phase with very large spontaneous polarization $\mathbf{P}_S$ (up to 300 nC cm^{-2}).

A variety of techniques has been used to study molecular motion in liquid crystalline phases. Among them, NMR spectroscopy has been used very successfully to give detailed information on molecular geometry, orientational ordering and dynamics of molecular rotations [5]. Orientational ordering is one of the most fundamental characteristics of LC molecules. It has been shown that the 2D NMR method of separated local field (SLF) spectroscopy [6] and proton encoded local field (PELF) spectroscopy [7, 8], especially in combination with off-magic-angle spinning (OMAS), is very effective in studying the ordering of liquid crystals. The order parameters of several FLCs have been determined by the use of ^{13}C and ^{19}F NMR [9–13].

Molecular dynamics is perhaps the most powerful theoretical method for conformational studies of LCs. The criterion of its success is a comparison between the calculated order parameters of molecular segments and the corresponding experimental data. A more stringent test for the molecular dynamics calculations is a comparison between calculated and experimental long range dipolar coupling constants, which can be determined by using several different NMR techniques [14–19]. We have found that the use of monodeuterated LCs [14, 19] to observe ^{2}H-^{13}C splittings in the ^{13}C spectra gives very rich information [19]; the application of this approach to determine some long range dipolar coupling constants in three racemic ferroelectric liquid crystals is reported in this work. The compounds studied are 4′-(4-methyl-2-chloro-2-deuteropentanoyloxy)-4-octyloxybiphenyl (4M2C2DPOOB), 4′-(3-methyl-2-chloro-2-deuteropentanoyloxy)-4-octyloxybiphenyl (3M2C2DPOOB) and 4′-(4-hexylbenzoyloxy)-4-(1-methyl-1-deuteroheptyloxy)-biphenyl (HBO1M1DHOB). To simplify the spectral analysis, we also studied the protonated liquid crystals, 4′-(4-methyl-2-chloropentanoyloxy)-4-octyloxybiphenyl (4M2CPOOB), 4′-(3-methyl-2-chloropentanoyloxy)-4-octyloxybiphenyl (3M2CPOOB) and 4′-(4-hexylbenzoyloxy)-4-(1-methylheptyloxy)biphenyl (HBO1MHOB) by ^{13}C NMR. The ^{2}H NMR spectra of these compounds also provide the quadrupolar splittings of the deuterons. In addition, the one- and two-bond ^{1}H-^{13}C dipolar

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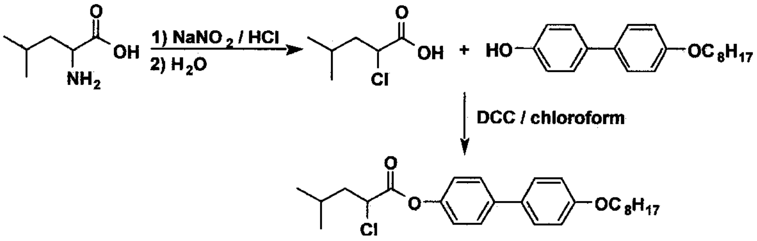
Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110085597



Scheme 1.

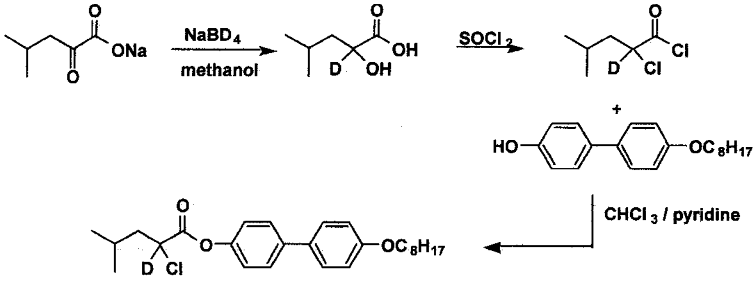
coupling constants of 3M2CPOOB are compared with those previously determined in this laboratory using the 2D SLF method [9].

2. Experimental

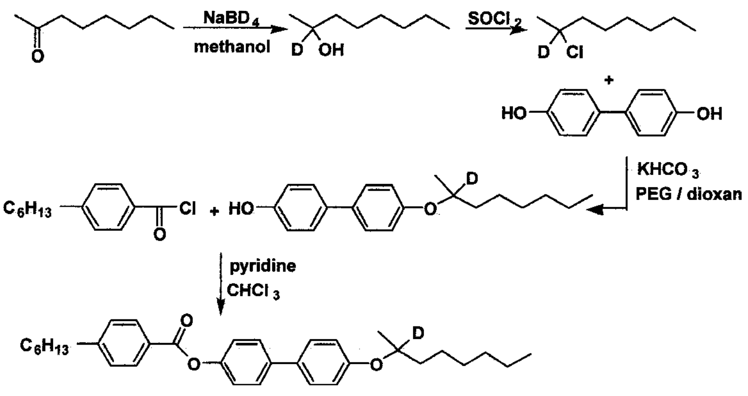
3M2CPOOB was synthesized according to scheme 1 as described in the literature [2, 3]. Its isomer 4M2CPOOB was prepared similarly. The transition temperatures of the purified 3M2CPOOB are: 63.5°C from isotropic liquid to SmA phase, 46.5°C from SmA to SmC phase, 30.0°C from SmC to SmG phase and 20.0°C from SmG to solid. The transition temperatures of the purified 4M2CPOOB are: 68.6°C from isotropic liquid to SmA, 56.5°C from SmA to SmC and 52.5°C from SmC to solid.

The monodeuterated liquid crystal 3M2C2DPOOB was synthesized according to scheme 2. 2-Deutero-2-hydroxy-3-methylpentanoic acid was prepared by reduction of the corresponding ketone using $NaBD_4$ in methanol. Then, the acid chloride was obtained by action of thionyl chloride on the acid. Finally, the acid chloride was esterified with 4-octyloxy-4′-hydroxybiphenyl and pyridine in dry chloroform. The final compound was recrystallized from hexane. Its isomer 4M2C2DPOOB was prepared similarly.

The monodeuterated liquid crystal HBO1M1DHOB was synthesized according to scheme 3. 2-Octanone was reduced with $NaBD_4$ in methanol to give the corresponding alcohol. This alcohol was then transformed to the chloride compound with thionyl chloride. The next step was the mono-alkylation of the chloride with 4,4′-biphenol using $NaHCO_3$ as base in a mixture of dioxan/PEG (polyethylene glycol) as solvent. Finally, the phenol was esterified with 4′-hexylbenzoyl chloride in pyridine and dry chloroform. The final compound was recrystallized from ethanol. The protonated analogue was prepared similarly. The transition temperatures of the purified HBO1M1DHOB are: 85°C from isotropic liquid to nematic (N) phase, 51.8°C from N to SmC phase and 40°C from SmC to solid.



Scheme 2.



Scheme 3.

The 1D ^{13}C and ^{2}H NMR experiments were performed using a Varian UNITY/INOVA 400 NMR spectrometer. The sample was placed in a standard 5 mm tube and rotated slowly along the magnetic field so that the director aligned parallel to the field. The temperature calibration was made by observing the nematic to isotropic transition for the compounds studied.

3. Results and discussion

3.1. ^{13}C *NMR study of monodeuterated liquid crystals*

In an early ^{13}C NMR study of a monodeuterated liquid crystal, long range ^{2}H-^{13}C splittings were not well resolved because of inefficient ^{1}H decoupling [14]. For our recent work [19] and the present study, we used a very efficient broadband decoupling sequence for liquid crystals developed in our laboratory [20], which removes all ^{1}H-^{13}C couplings to yield sharp ^{13}C peaks and requires only moderate decoupler power ($\gamma B_2/2\pi < 20$ kHz). The ^{13}C spectra of the monodeuterated liquid crystals 4M2C2DPOOB, 3M2C2DPOOB, and HOB1M1DHOB and their protonated analogues obtained by the use of this decoupling sequence (SPINAL-64) are shown in figures 1, 2, and 3, respectively.

For 4M2C2DPOOB, the coupling of the ^{2}H nucleus with five types of carbon (the carbonyl, the 3′- and 4′-carbons of the nearby phenyl ring, and the carbons α′ and β′ of the aliphatic chain) is resolvable (figure 1).

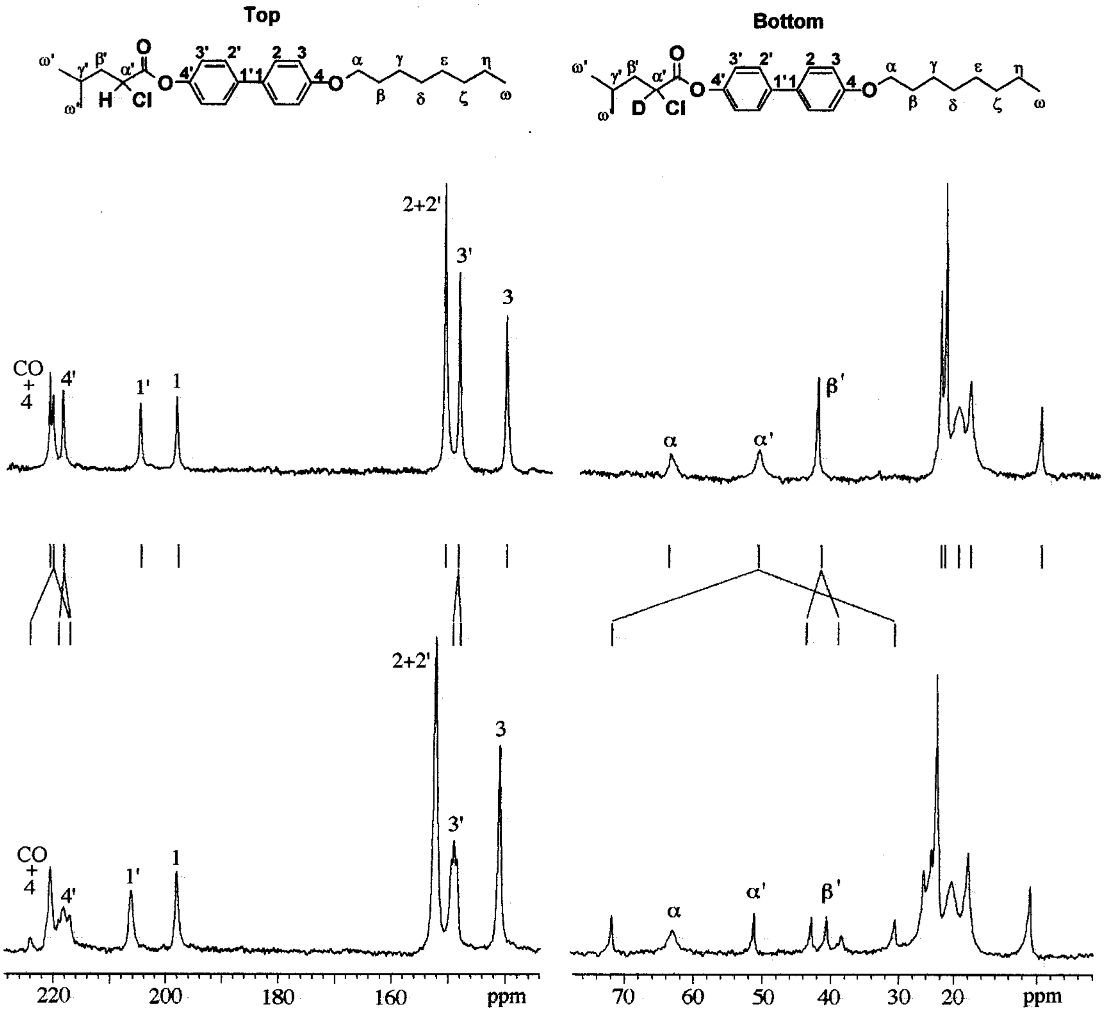


Figure 1. ^{13}C NMR spectra of 4M2CPOOB (top) and its monodeuterated analogue 4M2C2DPOOB (bottom) at 100.58 MHz and 65°C. The spectra were obtained with cross polarization, using the SPINAL-64 broadband ^{1}H decoupling sequence with $\gamma B_2/2\pi = 18$ kHz. The first set of vertical bars shows the peak positions of the non-deuterated homologue; the second set of vertical bars shows the positions of the outer peaks for each resolvable triplet due to ^{1}H splitting.

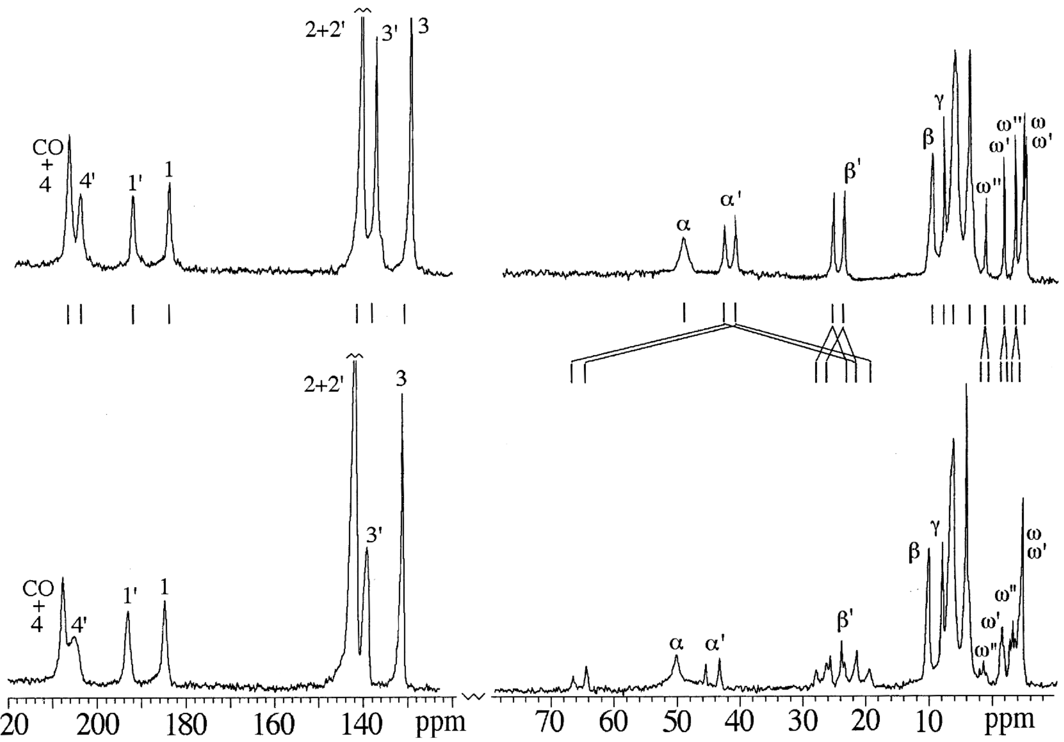


Figure 2. ^{13}C NMR spectra of 3M2CPOOB (top) and its monodeuterated analogue 3M2C2DPOOB (bottom) at 100.58 MHz and 37°C. Two sets of diastereo isomers, a [(2*S*, 3*S*) and (2*R*, 3*R*)] pair and a [(2*S*, 3*R*) and (2*R*, 3*S*)] pair, were present in each compound. The spectra were obtained with cross polarization, using the SPINAL-64 broadband ^{1}H decoupling sequence with $\gamma B_2/2\pi = 18$ kHz. The first set of vertical bars shows the peak positions of the non-deuterated homologue; the second set of vertical bars shows the positions of the outer peaks for each resolvable triplet due to ^{2}H splitting.

On the aromatic side, the 3′ carbon is separated from the deuterium atom by five bonds. In the aliphatic region, many peaks overlap with each other because of the large number of aliphatic carbons in the molecule. Therefore, although the spectrum of the monodeuterated compound shows a new peak at 26 ppm, unambiguous ^{2}H-^{1}C dopolar couplings could be obtained only for the α′ and β′ carbons, which are one and two bonds away from the deuterium, respectively.

For 3M2CPOOB, the ^{13}C peaks for the two sets of diastereo isomers are distinguishable (figure 2). Seven sets of ^{2}H-^{13}C splittings are observed for 3M2C2DPOOB due to couplings of the two sets of isomers with the α′, β′, ω′, and ω″ carbons. Further discussion on this point will be made later. In the aromatic region, the peaks are broad and the ^{2}H-^{13}C couplings could not be resolved.

For the liquid crystal HBO1M1DHOB, the coupling of the ^{2}H nucleus with five types of carbons (the 12- and 11- and 9-carbons of the nearby phenyl ring, and the carbons α and β of the aliphatic chain) was observed (figure 3). Splittings for the 10-carbon, α-CH_3, and some other carbon atoms in the aliphatic region are clearly visible, but we could not determinate the corresponding values of the dipolar coupling constants because of overlapping peaks. The 9-carbon is separated from the deuterium atom by six bonds; although the splitting is not obvious in the spectrum, its value could be determined by spectral deconvolution.

The ^{2}H-^{13}C dipolar coupling constant (*D*) is related to the observed splitting $\Delta\nu$ by

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

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 non-zero. For some of the peaks, spectral deconvolution was needed to obtain the value of $\Delta\nu$. A complete analysis of the results for the three monodeuterated compounds has been made over their entire liquid crystalline ranges. For comparison with previous data, the ^{2}H-^{13}C dipolar coupling constants are converted to ^{1}H-^{13}C dipolar coupling constants

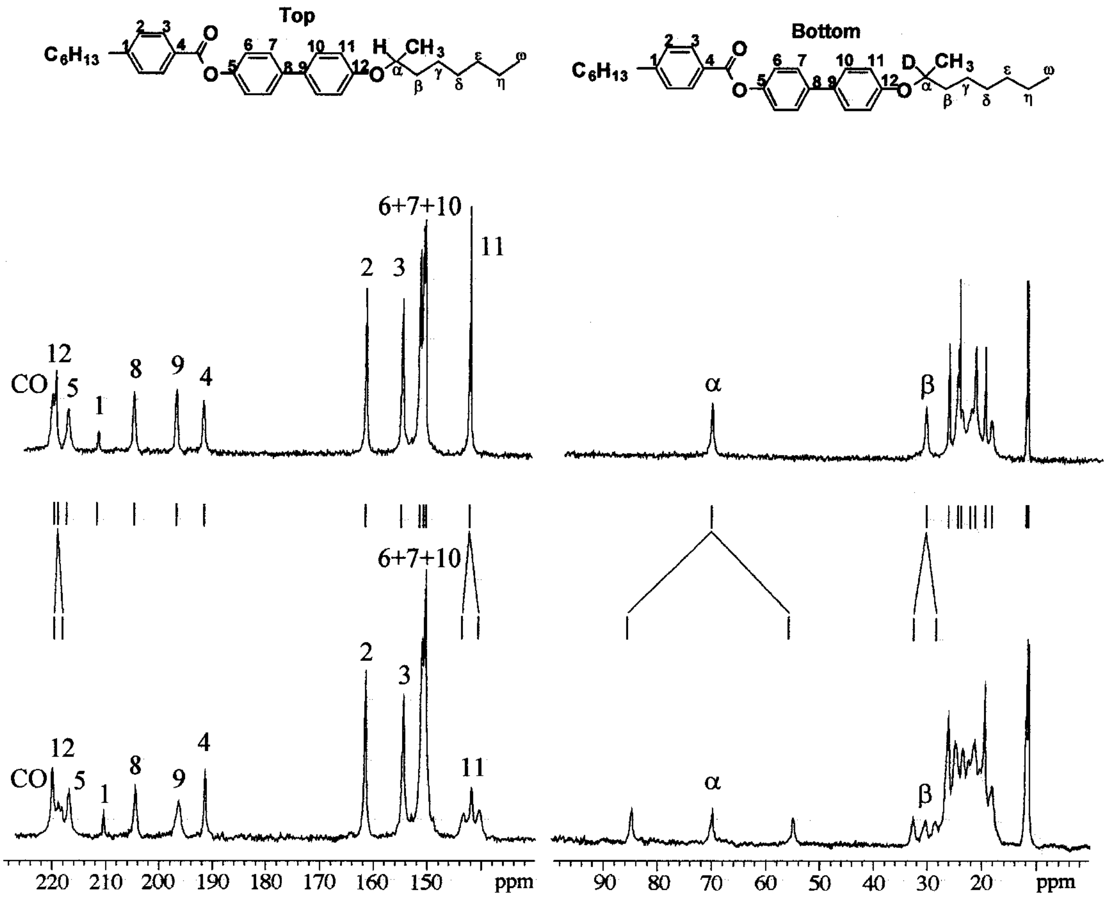


Figure 3. ^{13}C NMR spectra of HBO1MHOB (top) and its monodeuterated analogue HBO1M1DHOB (bottom) at 100.58 MHz and 48°C. The spectra were obtained with cross polarization, using the SPINAL-64 broadband ^{1}H decoupling sequence with $\gamma B_2/2\pi = 18\,\text{kHz}$. The first set of vertical bars shows the peak positions of the non-deuterated homologue; the second set of vertical bars shows the positions of the outer peaks for each resolvable triplet due to ^{2}H splitting.

using the equation:

$$D_{\mathrm{CH}} = (\gamma_{\mathrm{H}}/\gamma_{\mathrm{D}})D_{\mathrm{CD}} = 6.5142D_{\mathrm{CD}} \qquad (2)$$

where γ_{H} and γ_{D} are the magnetogyric ratios of proton and deuteron, respectively. The data for the compounds 4M2CPOOB, 3M2CPOOB and HBO1MHOB are presented in tables 1, 2, and 3, respectively.

Most of the dipolar coupling constants listed in the tables decrease with the increase of temperature, reflecting the decreased ordering of the LC molecules. However, a few of them (e.g. α′-β′, α′-ω′, and α′-ω″ in table 2) do not follow this trend because these values depend on the average of many conformations. Although it is difficult to use the long range dipolar coupling constants to extract order parameters, they serve as a useful database for the study of conformational properties of LCs and as stringent criteria for judging the success of molecular dynamics simulations.

Table 1. ^{1}H-^{13}C dipolar coupling constants for 4M2CPOOB at different temperatures.

T/°C	α′-CO	α′-3	α′-4	α′-α′	α′-β′
53	—	—	—	7574	795
54	—	—	—	7446	772
55	—	—	—	6954	762
56	1362	—	—	6944	759
57	1316	—	—	6931	756
58	1287	—	—	6908	755
59	1257	—	—	6876	747
60	1251	—	—	6840	745
61	1228	—	—	6804	743
62	1189	180	—	6775	743
63	1124	175	—	6746	739
64	1124	171	168	6711	730
65	1120	170	160	6697	728
66	1117	169	152	6671	726
67	1114	168	140	6638	726
68	1107	165	132	6602	723

Table 2. ^{1}H-^{13}C dipolar coupling constants for 3M2CPOOB at different temperatures. The values listed correspond to two sets of diastereo isomers, a [(2*S*, 3*S*) and (2*R*, 3*R*)] pair and a [(2*S*, 3*R*) and (2*R*, 3*S*)] pair present in each compound. One set of α′-ω′ coupling could not be determined because of peak overlapping.

T/°C	α′-α′	α′-α′	α′-β′	α′-β′	α′-ω″	α′-ω″	α′-ω′
35	7635	7713	933	827	202	189	117
37	7517	7654	886	827	195	182	111
39	7433	7537	899	814	195	163	104
41	7289	7413	860	788	182	156	117
43	7159	7237	847	749	195	163	111
45	6781	6853	808	736	195	163	104
47	6026	6123	775	743	195	150	111
49	6000	6104	801	749	189	150	111
51	6000	6058	795	749	182	143	104
53	6006	6052	808	749	176	143	104
55	5987	5993	808	749	176	143	104
57	5921	5960	801	736	163	143	104
59	5876	5889	801	736	156	143	104
61	5804	5843	795	730	143	130	91
63	5765	5785	762	717	130	124	85

Table 3. ^{1}H-^{13}C dipolar coupling constants for HBO1MHOB at different temperatures.

T/°C	α-α	α-β	α-12	α-11	α-9
44	4818	816	127	496	67
46	4785	765	130	491	66
48	4712	747	126	485	64
50	4639	683	115	479	65
52	4562	651	107	478	58
54	4496	619	101	480	56
56	4417	638	95	475	56
58	4337	640	90	464	50
60	4249	637	—	446	—
62	4176	614	—	430	—
64	4091	634	—	449	—
66	3990	607	—	421	—
68	3900	571	—	423	—
70	3795	540	—	407	—
72	3682	505	—	391	—
74	3553	528	—	365	—
76	3392	474	—	353	—
78	3223	459	—	323	—
80	3010	419	—	313	—
82	2737	348	—	—	—
84	2332	319	—	—	—

3.2. ^{2}*H quadrupole coupling*

For the monodeuterated compounds, the deuterium quadrupole coupling constants can be determined from the ^{2}H NMR spectra directly. Each of the deuterium NMR spectra of 3M2C2DPOOB, 4M2C2DPOOB, and HBO1M1DHOB shows a doublet. The doublet separation is due to deuterium quadrupole splitting, which is related to the components of the order parameter tensor 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 asymmetry parameter η is zero in equation (3), S_{aa} is simply the order parameter of the C–D bond, S_{CD}. By using the commonly accepted value of $e^2qQ/h = 168\,\text{kHz}$ for deuterium bonded to aliphatic carbons, the value of S_{CM} can be readily calculated from $\Delta\nu$, which is taken to be negative from geometric considerations.

The values of the order parameters S_{CD} for the three compounds studied are listed in tables 4, 5, and 6. For comparison, the corresponding S_{CH} values were calculated from ^{2}H-^{13}C dipolar coupling constants (tables 1, 2, and 3) by using equation (2) and the relation [6]

$$S_{CH} = -4.407 \times 10^{-5}\, D_{CH} \tag{4}$$

Table 4. Order parameters S_{CD} calculated from quadrupolar splittings and dipolar coupling constants for the α′ carbon in 4M2C2DPOOB at different temperatures.

T/°C	S_{CD} from quadrupolar splittings	S_{CD} from dipolar coupling constant
55	−0.319	−0.306
56	−0.319	−0.306
57	−0.318	−0.305
58	−0.317	−0.304
59	−0.316	−0.303
60	−0.315	−0.301
61	−0.313	−0.300
62	−0.312	−0.299
63	−0.311	−0.297
64	−0.309	−0.296
65	−0.307	−0.295
66	−0.306	−0.294
67	−0.304	−0.293

Table 5. Order parameters S_{CD} calculated from quadrupolar splittings and dipolar coupling constants for the α′ carbon in 3M2C2DPOOB at different temperatures.

T/°C	S_{CD} from quadrupolar splittings		S_{CD} from dipolar coupling constant
47	−0.266	−0.270	−0.296
49	−0.264	−0.269	−0.296
51	−0.264	−0.267	−0.294
53	−0.265	−0.267	−0.293
55	−0.264	−0.264	−0.291
57	−0.261	−0.263	−0.289
59	−0.259	−0.260	−0.286
61	−0.256	−0.258	−0.284
63	−0.254	−0.255	−0.280

Table 6. Order parameters S_{CD} calculated from quadrupolar splittings and dipolar coupling constants for the α′ carbon in HBO1M1DHOB at different temperatures.

T/°C	S_{CD} from quadrupolar splittings	S_{CD} from dipolar coupling constant
44	−0.209	−0.212
46	−0.206	−0.211
48	−0.203	−0.208
50	−0.200	−0.204
52	−0.197	−0.201
54	−0.194	−0.198
56	−0.191	−0.195
58	−0.187	−0.191
60	−0.184	−0.187
62	−0.180	−0.184
64	−0.176	−0.180
66	−0.172	−0.176
68	−0.167	−0.172
70	−0.163	−0.167
72	−0.157	−0.162
74	−0.151	−0.157
76	−0.144	−0.149
78	−0.136	−0.142
80	−0.125	−0.133
82	−0.113	−0.121
84	−0.088	−0.103

and the data are listed in the same tables. The small systematic differences are probably due to the assumptions involved in the calculations ($e^2qQ = 168$ kHz, $\eta = 0$, and $r_{CD} = 0.110$ nm).

For 3M2C2DPOOB and 4M2C2DPOOB, the order parameters of the C–D bonds, S_{CD}, become slightly more negative with the decrease of temperature, indicating an increase in the ordering of the smectic phases. Compared with HBO1M1DHOB, the values of S_{CD} for 3M2C2DPOOB and 4M2C2DPOOB are substantially larger in absolute value. It is possible that the large chlorine atom bonded to the α′-carbon causes a considerable change in the C–C–H bond angle, so that the average conformation of the aliphatic chain is quite different from a normal alkyl chain. During the transition from the SmC to SmA phase, there is a discontinuity in the order parameters.

3.3. *Comparison with 2D ^{13}C NMR results*

The orientational ordering of the protonated compound 2M2CPOOB was previously studied using the 2D SLF/OMAS method, and all one-bond and some two-bond dipolar coupling constants were determined [9]. Thus, the C–H dipolar coupling constants for the α′-carbon determined from the 2D method can be compared with that obtained from the 1D spectra of the monodeuterated compound. The data obtained from the two types of experiment at two temperatures are shown in table 7, and they agree with each other very well. Actually, the ^{2}H-^{13}C dipolar coupling constants obtained from the 1D spectra are more accurate, because the ^{1}H-^{13}C dipolar coupling constants obtained from the SLF/OMAS method depend on the accuracy of the scaling factor of the dipolar decoupling sequence and the angle between the spinning axis and the magnetic field.

Table 7. Comparison of one-bond ^{1}H-^{13}C dipolar couplings (Hz) for the α′-carbon in 3M2CPOOB obtained from two kinds of experiments. Two sets of diastereo isomers, a [(2*S*, 3*S*) and (2*R*, 3*R*)] pair and a [(2*S*, 3*R*) and (2*R*, 3*S*)] pair, were present in the compound.

T/°C	From ^{2}H-^{13}C	From SLF/OMAS
45 (smectic C phase)	6781; 6853	6780
58 (smectic A phase)	5921; 5960	5880

When optically pure L-isoleucine [(2*S*, 3*S*)-(+)-2-amino-3-methylpentanoic acid] is used as the starting material to synthesize 3M2CPOOB (scheme 1), the product contains only one optical isomer. When racemic DL-isoleucine is used as the starting material, because the molecule has two chiral centres, the final product is composed of two sets of diastereo isomers, a [(2*S*, 3*S*) and (2*R*, 3*R*)] pair and a [(2*S*, 3*R*) and (2*R*, 3*S*)] pair. In the synthesis of the monodeuterated compound (scheme 2), the optical isomers produced in the deuteration step were not isolated, and the final product 3M2C2DPOOB has two sets of diastereo isomers. It is interesting to observe that the two pairs of diastereo isomers show different ^{13}C peaks for the α′, β′, ω′, and ω″ carbons in the chiral chain of the protonated compound (figure 2, top); separate peaks for the γ′ carbon are not observed because of overlapping. Furthermore, the ^{2}H-^{13}C dipolar splittings for the two sets of diastereo isomers are also dissimilar (figure 2, bottom and table 2). The different ^{13}C chemical shifts and ^{2}H-^{13}C dipolar splittings imply that the orientational ordering (conformational averaging) of the C–H bonds in the chiral chain of these two sets of diastereo isomers is quite different, but we cannot assign the data to the individual pairs. In contrast, these kinds of difference were too small to be clearly distinguished in the SLF/OMAS experiments [9] for 3M2CPOOB, but were observed for the racemates of 4′-(3-methyl-2-bromopentanoyloxy)-4-hexyloxybiphenyls [13].

^{13}C chemical shift data, when combined with results obtained from 2D SLF/OMAS experiments, can be used to study the temperature dependence of the order parameters over a wide temperature range [6]. The S_{CH} values thus calculated for the α′-carbon in 3M2CPOOB at 15 temperatures are compared with those obtained in this work, and the results are presented in table 8. The data are very similar except that we can determinate the order parameters of the two diastereoisomers with the

Table 8. Comparison of local order parameters S_{CH} of the α′-carbon in 3M2CPOOB obtained from two kinds of experiments. Two sets of diastereo isomers, a [(2*S*, 3*S*) and (2*R*, 3*R*)] pair and a [(2*S*, 3*R*) and (2*R*, 3*S*)] pair, were present in the compound.

T/°C	From ^{2}H-^{13}C	From SLF/OMAS combined with ^{13}C chemical shift
35	−0.336; −0.340	−0.315
37	−0.331; −0.337	−0.312
39	−0.328; −0.332	−0.300
41	−0.321; −0.327	−0.308
43	−0.315; −0.319	−0.292
45	−0.299; −0.302	−0.285
47	−0.266; −0.270	−0.269
49	−0.264; −0.269	−0.265
51	−0.264; −0.267	−0.265
53	−0.265; −0.267	−0.265
55	−0.264; −0.264	−0.262
57	−0.261; −0.263	−0.260
59	−0.259; −0.260	−0.262
61	−0.256; −0.258	−0.262
63	−0.254; −0.255	−0.256

1D experiment. In both sets of data, there is a discontinuity in the order parameters during the transition from the SmC phase to SmA phase (46°C). This discontinuity was observed previously [11] and was attributed to the first order nature of the SmC–SmA transition for this liquid crystal.

3.4. *Temperature dependence*

The temperature dependence of the order parameters over a wide temperature range was studied for the liquid crystal 3M2CPOOB with the combination of PELF/OMAS results and ^{13}C chemical shift data, which were obtained from one-dimensional NMR experiments. The data for the aromatic rings and for the aliphatics carbons are presented in figures 4 and 5, respectively. They are fitted to the Haller equation:

$$S(T) = S_o(1 - T/T^*)^F \tag{5}$$

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

The values of S_o and F obtained by fitting the order parameters calculated from chemical shifts to equation (5) are listed in table 9. T^* was initially treated as a variable parameter for fitting each curve; then, the average value of 336.8 K was used as a fixed parameter for all final fittings. As expected, the values of S_o for the phenyl rings in 3M2CPOOB are close to unity (table 9). For a perfectly aligned all-*trans*-conformation of the aliphatic chain, S_o for each C–H bond should be close to −0.333 [i.e. $(3\cos^2 109°28' - 1)/2$]. Only two of the values listed

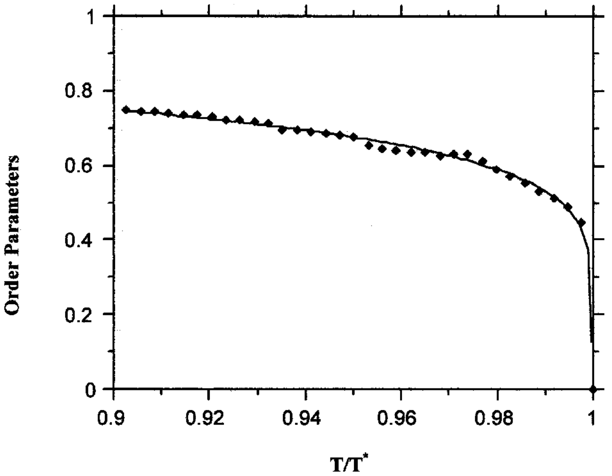


Figure 4. Plot of order parameters of the aromatic rings of 3M2CPOOB against T/T^*, with $T^* = 336.8$ K. The solid line was calculated from equation (5).

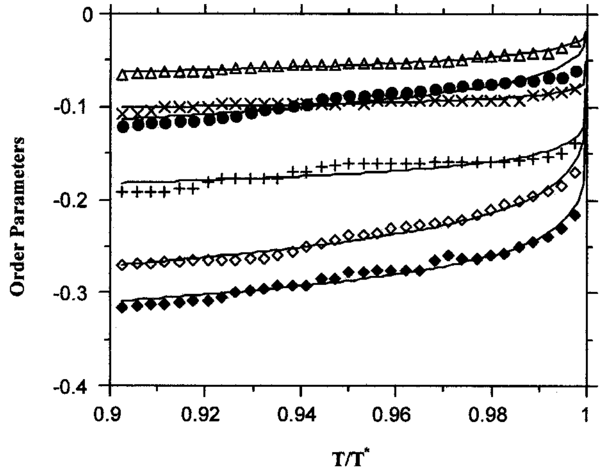


Figure 5. Plot of C–H order parameters of the aliphatic carbons of 3M2CPOOB against T/T^*, with $T^* = 336.8$ K. The symbols are: ◆ =α′, ● =β′, ◇ =α, + =ξ, × =η, and Δ = ω. The solid lines were calculated from equation (5).

Table 9. Values of S_o and F for 3M2CPOOB obtained by fitting the calculated order parameters to equation (5); R is the correlation coefficient.

C	Ring	α′	β′	α	ξ	η	ω
S_o	1.04	−0.411	−0.300	−0.376	−0.222	−0.116	−0.099
F	0.15	0.14	0.15	0.14	0.09	0.07	0.09
R	0.995	0.991	0.965	0.991	0.975	0.988	0.993

in table 9 (the α and β′ atoms) are close to this estimation. The value for the α′ carbon is more negative because it is connected to a carboxy segment, and the increased mobility towards the end of the aliphatic chain reduces the limiting order parameter S_o for the three outer carbons atom (ξ, η and ω).

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, equation (6). Therefore, we tried to fit the data listed in table 2 to the following equation:

$$D(T) = D_o(1 - T/T^*)^F \tag{6}$$

where D_o and F are empirical constants, and T^* is a temperature at which the dipolar coupling constants become zero and should be the same as that in equation (5). The results are presented in figure 6, and the values of D_o and F are listed in table 10. The values of F are relatively constant, but the physical significance is not clear.

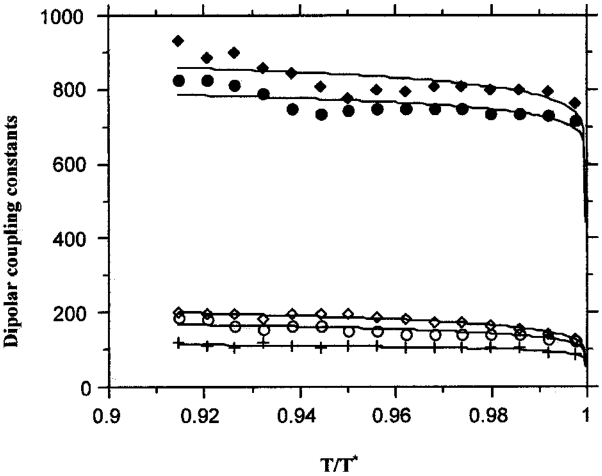


Figure 6. Plot of long range dipolar coupling constants of the carbons of 3M2CPOOB against T/T^*, with $T^* = 336.8$ K. The symbols are: ◆ and ● $= \alpha' - \beta'$, ◇ and ○ $= \alpha' - \omega''$, and + $= \alpha' - \omega'$. The solid lines were calculated from equation (6).

Table 10. Values of D_o and F for 3M2CPOOB obtained by fitting the ^{1}H-^{13}C dipolar coupling constants to equation (6): R is the correlation coefficient.

C	α′-β′	α′-β′	α′-ω″	α′-ω″	α′-ω′
D_o	956	856	275	221	137
F	0.143	0.135	0.128	0.110	0.077
R	0.987	0.992	0.994	0.977	0.990

4. Conclusion

Long range dipolar coupling constants are important in the investigation of detailed chain motions and rapid rotations or jumps of the rings. The selective deuteration of liquid crystals provides a simple and powerful method for the determination of long range dipolar coupling constants. Ferroelectric liquid crystals have been widely studied because of their interest in display applications. In this report, we have presented an example of using one-dimensional ^{13}C NMR to obtain long range H–C dipolar couplings in three FLCs. These data can be used to study molecular motions and conformational properties of FLCs over the whole mesomorphic temperature range. The results have been compared with those obtained from the 2D SLF/OMAS method. Additional data for the monodeuterated liquid crystals were obtained from 1D ^{2}H NMR.

This work was supported by the U.S. National Science Foundation under grant numbers DMR-9809555 (Ferroelectric Liquid Crystal Materials Research Center) and DMR-0090218.

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