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A study of long range dipolar coupling constants in 4′-pentyloxy-4-biphenylcarbonitrile (5OCB)

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It was shown previously that long range ^{2}H–^{13}C dipolar coupling constants in liquid crystals could be obtained from the proton-decoupled ^{13}C NMR spectrum of monodeuterated compounds. This approach has now been applied to the study of 4′-(1-deuteropentyloxy)-4-biphenylcarbonitrile (5OCB-d1). The ^{13}C spectrum of this compound gives nine ^{2}H–^{13}C dipolar coupling constants for carbon ranging from one to six bonds away from the dueterium nucleus. The ^{2}H NMR and 5OCB-d1 gives the deuterium quadrupole coupling constant and the ^{1}H–^{2}H dipolar coupling constant for the α-CHD group. In addition, eleven 2-bond and two 3-bond ^{1}H–^{13}C dipolar coupling constants have been obtained for 4′-pentyloxy-4-biphenylcarbonitrile (non-deuterated 5OCB) by using the 2D ^{13}C method of proton-encoded local field spectroscopy.

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1. Introduction

Cyanobiphenyls, namely 4′-alkyl-4-biphenylcarbonitriles and 4′-alkyloxy-4-biphenylcarbonitriles, are benchmark liquid crystals that have been widely studied in basic research and used in display devices. The application of nuclear magnetic resonance (NMR) spectroscopy to investigate the orientational ordering and phase transition of cyanobiphenyls has been reported in many publications. In general, measurements of quadrupole coupling constants by using ^{2}H NMR, and dipolar coupling constants by using ^{1}H and ^{13}C NMR, are very fruitful for the determination of order parameters of molecular segments in cyanobiphenyls and other liquid crystals.

For the measurement of 1-bond and some 2-bond ^{1}H–^{13}C dipolar coupling constants in 4′-pentyl-4-biphenylcarbonitrile (5CB), the 2D NMR method of separated local field (SLF) spectroscopy [1] and the improved version called PDLF (proton detected local field) spectroscopy [2] are very useful. For the determination of long range dipolar coupling constants, other methods have been employed. Using partially deuterated 5CB with deuterium decoupling, long range ^{1}H–^{1}H dipolar coupling constants have been determined [3, 4]. Some three- and four-bond ^{1}H–^{13}C dipolar coupling constants in 5CB have been studied by the use of 3D PDLF [5], and some long range coupling constants have been determined using 2D ^{2}H–^{13}C correlation [6]. Many pairs of ^{13}C–^{13}C coupling constants in the phenyl rings of 5CB have been measured using double-quantum 2D NMR [7]. Recently we have demonstrated that long range ^{2}H–^{13}C dipolar coupling constants in liquid crystals can be obtained from the 1D ^{13}C spectra of monodeuterated compounds [8, 9]. This approach is the revival of a strategy introduced by Ernst and co-workers [10], and has been used quite successfully to study the nematic liquid crystal 4′-cyanobiphenyl 2-deuterohexanoate and its 6-deutero analogue [8] and several monodueterated ferroelectric liquid crystals [9].

To the best to our knowledge, long range dipolar coupling constants have not been reported for 4′-pentyloxy-4-biphenylcarbonitrile (5OCB), which is another benchmark liquid crystal. Therefore, we have synthesized 5OCB monodueterated in the 1-position of the pentyl chain and studied its ^{13}C NMR to obtain long range ^{2}H–^{13}C dipolar coupling constants. In addition, 2D PDLF (which is alternatively called PELF, proton-encoded local field spectroscopy [11]) experiments on non-deuterated 5CB have been carried out to provide ^{1}H–^{13}C dipolar coupling constants for other ^{13}C nuclei in the molecule.

2. Experimental

4′-Pentyloxy-4-biphenylcarbonitrile (5OCB) was obtained from EM Chemicals; its nematic range is from 48 to 68°C. 4′-(1-Deuteropentyloxy)-4-biphenylcarbonitrile (5OCB-d1) was synthesized in the following way.

1-Deutero-1-pentanol was prepared by the reduction of pentanal (valeraldehyde; obtained from Aldrich) with

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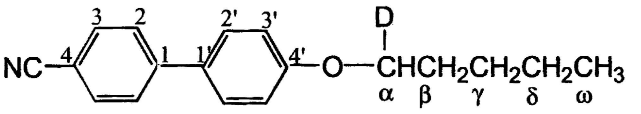
$NaBD_4$ in ethanol. The alcohol was reacted with distilled thionyl chloride to give 1-deutero-1-chloropentane. Finally, the alkylation of 4′-hydroxy-4-biphenylcarbonitrile with 1-deutero-1-chloropentane in the presence of $KHCO_3$ in tetraethylene glycol/dioxane (1/1) at 80°C yielded 4′-(1-deuteropentyloxy)-4-biphenylcarbonitrile (5OCB-d1):



The final product was purified by column chromatography using CH_2Cl_2 as eluent, followed by recrystallization from hexane.

The ^{13}C and ^{2}H NMR experiments were performed using a Varian 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 nematic to isotropic transition. The SPINAL-64 sequence [12] was used for broadband decoupling for both 1D and 2D experiments, and the BLEW-48 sequence [13] was used for dipolar decoupling for the 2D PELF experiments. The ^{1}H decoupler power was $\gamma B_2/2\pi = 44.6$ kHz for homonuclear dipolar decoupling and 27.8 kHz for broadband decoupling. Even with these moderate decoupler powers, radiofrequency (rf) heating is appreciable; therefore, a cycling time of 30 s was used to minimize the effect of rf heating.

3. Results and discussion

3.1. *1D ^{13}C NMR study of monodeuterated 5OCB*

The proton-decoupled 1D ^{13}C spectra of 5OCB and its monodeuterated analogue 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, but the signal enhancement based on the Nuclear Overhauser effect is less.

The inset in figure 1 (*a*) shows the effect of rf heating: when the cycling time is reduced from 30 to 5 s, the linewidth of the quaternary carbons increases by a factor of about 2. The spectrum in figure 1 (*b*) shows that ^{2}H–^{13}C splittings are observed for all five carbons in the pentyloxy chain and all four types of carbon in the phenyl ring to which the chain is attached. In other words, except for the phenylcarbonitrile moiety, each ^{13}C peak is split by the deuterium nucleus into a triplet. It should be noted that the 1′-carbon and the ω-carbon are both six bonds away from the deuterium in the α-position of the pentyloxy chain, but triplets are clearly observed for both ^{13}C peaks. The very good resolution is the result of using an efficient broadband decoupling sequence (SPINAL-64 [12]) with moderate decoupler power. The linewidths of the three components in each triplet are slightly different due to a differential relaxation effect. The peaks that overlap slightly were analysed with spectral deconvolution to obtain the ^{2}H–^{13}C splitting, $\Delta\nu$, which is related to the dipolar coupling constant D and the

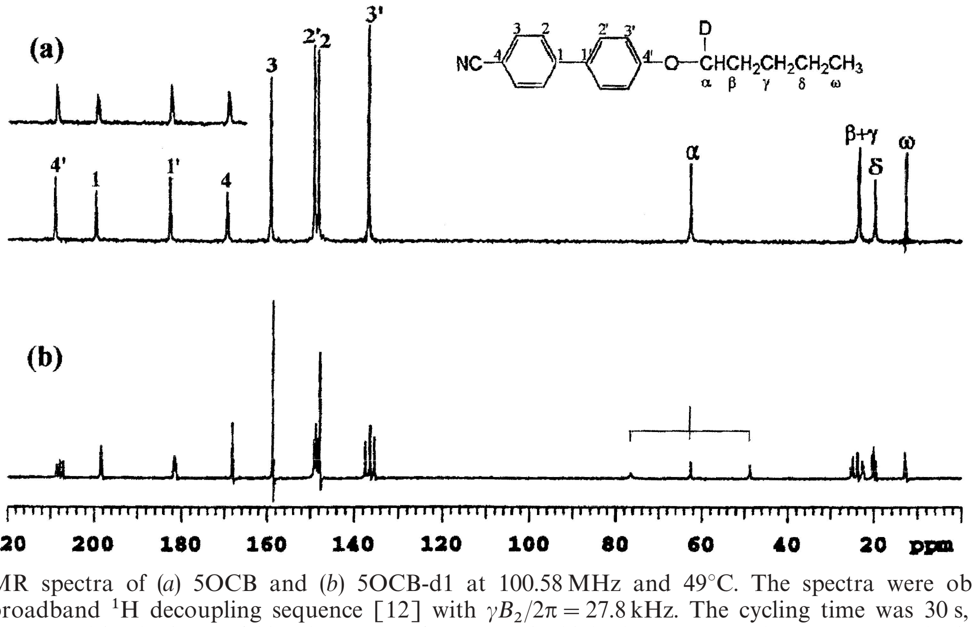


Figure 1. ^{13}C NMR spectra of (*a*) 5OCB and (*b*) 5OCB-d1 at 100.58 MHz and 49°C. The spectra were obtained using the SPINAL-64 broadband ^{1}H decoupling sequence [12] with $\gamma B_2/2\pi = 27.8$ kHz. The cycling time was 30 s, but only 5 s for the spectrum presented in the inset of (*a*). The spectra for 5OCB in (*a*) had 40 scans and were processed without exponential multiplication; the spectrum for 5OCB-d1 in (*b*) had 400 scans and was processed with a line broadening factor of −25 and Gaussian factor of 0.03 for resolution enhancement.

scalar coupling constant J by

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

The signs of $\Delta\nu$ cannot be determined experimentally, but that for the directly bonded ^{2}H–^{13}C pair can be assigned as positive based on geometric considerations. The J value for this pair was determined from the spectrum in the isotropic phase to be 33.5 Hz; the J values for other ^{2}H–^{13}C pairs are essentially zero. For comparison with other data, the ^{2}H–^{13}C dipolar coupling constants D_{CD} calculated from equation (1) are converted to ^{1}H–^{13}C dipolar coupling constants D_{CH} using the equation

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

where γ_{H} and γ_{D} are the magnetogyric ratios of proton and deuterium, respectively. The results are listed in table 1. The data show that the coupling constant between the α-hydrogen and each carbon nucleus in the pentyloxy chain decreases with the increase of the number of bonds separating the two, but the coupling constant for the 3′-carbon in the phenyl ring is larger than that for the 4′-carbon. These results are very important for the consideration of conformational constraints in the liquid crystal.

The ^{1}H–^{13}C dipolar coupling constant for directly bonded C–H pairs in an alkyl chain can be used to calculate the order parameter of the corresponding C–H bond from the equation [1]

$$S_{\mathrm{CH}} = -\frac{4\pi^2 r^3 D_{\mathrm{CH}}}{\gamma_{\mathrm{C}}\gamma_{\mathrm{H}} h} = -4.407 \times 10^{-5} D_{\mathrm{CH}}/\mathrm{Hz} \quad (3)$$

where the C–H distance is taken to be $r = 0.110$ nm. The value is $S_{\mathrm{CH}} = -0.196$ for the α-carbon at 49°C. However, the long range ^{1}H–^{13}C dipolar coupling constants cannot be used directly to calculate order parameters because they involve molecular segments that are flexible. Nevertheless, they serve as a useful database for the study of conformational properties of liquid crystals and stringent criteria for judging the success of computer simulations.

3.2. ^{2}H NMR spectrum

The ^{2}H spectrum of a polydeuterated analogue of 5OCB shows one doublet for each type of deuterium in the chain as a result of deuterium quadrupole coupling [14]. For monodeuterated liquid crystals, there is only one doublet, which is quite broad due to coupling with many protons. With broadband ^{1}H decoupling, the linewidth is greatly reduced (to ~100 Hz). With ^{1}H–^{1}H dipolar decoupling using the BLEW-48 sequence, dipolar splitting caused by the adjacent proton can be observed in the ^{2}H NMR spectrum [8]. This is also the case for the monodeuterated compound 4′-(1-deuteropentyloxy)-4-biphenylcarbonitrile (5OCB-d1) studied in this work.

Table 1. The absolute values of ^{1}H–^{13}C dipolar coupling constants (Hz) for 4′-pentyloxy-4-biphenylcarbonitrile (5OCB).

α-α	α-β	α-γ	α-δ	α-ω	α-1′	α-2′	α-3′	α-4′
4453	504	342	151	76	100	136	331	254

The ^{2}H quadrupole splitting of 5OCB-d1 is $\Delta\nu_{\mathrm{Q}} =$ 50.42 kHz at 49°C (spectrum not shown). This splitting is related to the tensor components of the order parameter of the C–D bond by

$$\Delta\nu_{\mathrm{Q}} = (3e^2qQ/2h)[S_{aa} + \eta(S_{bb} - S_{cc})]. \quad (4)$$

By assuming the deuterium quadrupole coupling constant $e^2qQ/h = 168$ kHz and the asymmetry parameter $\eta = 0$, the order parameter of the C–D bond, $S_{\mathrm{CD}} = S_{aa}$, is found to be -0.200 at 49°C (the negative sign is based on geometric considerations). This value is in good agreement with the result of a previous ^{2}H study (-0.201) [14] and that obtained from ^{13}C NMR (-0.196; presented in the previous section).

When a ^{1}H–^{1}H dipolar decoupling sequence is used to resolve the ^{1}H–^{2}H dipolar coupling in the ^{2}H NMR spectrum of a monodeuterated compound, equation (1) is modified by a scaling factor f determined by this sequence:

$$\Delta\nu = f[2D + J]. \quad (5)$$

The theoretical value of f is 0.424 for BLEW-48 [13], and the experimental value is 0.414 [11]. The geminal ^{1}H–^{2}H splitting observed for 5OCB-d1 is 530 Hz at 49°C; long range couplings are not resolved.

The order parameter of the H–D vector is related to the corresponding dipolar coupling constant D_{HD} by [8]:

$$S_{\mathrm{HD}} = -\frac{4\pi^2 r^3 D_{\mathrm{HD}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{D}} h} = -3.163 \times 10^{-4} D_{\mathrm{HD}}/\mathrm{Hz} \quad (6)$$

where $r = 0.180$ nm is obtained by assuming that the H–C–D bond angle is 109°28′. Since the scalar coupling constant J for the geminal ^{1}H–^{2}H pair is 1.7 Hz, the value of S_{HD} for the α-CHD group is 0.166 for 5OCB-d1 at 49°C; its sign is likely to be positive.

In a study of alkyl chains in a nematic field, it was shown that $|\Delta\nu_{\mathrm{DD}}/\Delta\nu_{\mathrm{Q}}|$, where $\Delta\nu_{\mathrm{DD}}$ is the geminal ^{2}H–^{2}H dipolar splitting, is about 2.2×10^{-3} for perdeuterated decane [15]. For the 1-methylene group in the pentyloxy chain of 5OCB-d1, the corresponding ratio (where $\Delta\nu_{\mathrm{DD}}$ is obtained by multiplying the ^{2}H–^{1}H splitting by $\gamma_{\mathrm{D}}/\gamma_{\mathrm{H}}$) is about 1.6×10^{-3}. For a monodeuterated liquid crystal with an ester chain, the ratio is about 1.0×10^{-3} for the 2-methylene group and 1.5×10^{-3} for the methyl group [8]. These comparisons show that the functional group attached

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to an alkyl chain has a small but significant effect on the conformational constraints of the chain, which is not unexpected.

3.3. *2D ^{13}C NMR study of the non-deuterated 5OCB*

Previously, the 2D SLF method had been applied to determine one-bond and some two-bond ^{1}H–^{13}C dipolar coupling constants of all the carbon atoms (except the cyano group) in 5OCB [16]. Because the 2D PELF method [2, 11] has a better resolution, we have used it to re-study non-deuterated 5OCB without off-magic-angle-spinning (OMAS). The ^{13}C spectra at 49°C are shown in figure 2, in which slices in the ω1 dimension exhibit ^{1}H–^{13}C splittings. Because a homonuclear dipolar decoupling sequence is used in the evolution period in the PELF sequence, the relation between the splitting and the dipolar coupling constant obeys equation (5). Using the J values determined in the isotropic phase [17], the dipolar coupling constants can be readily calculated. The results are listed in table 2. It should be noted that the higher resolution of the PELF method has enabled us to determine the ^{1}H–^{13}C dipolar coupling constants not only for the 13 directly bonded C–H pairs, but also for eleven 2-bond C–H pairs and two 3-bond C–H pairs. The assignments of the 2-bond and 3-bond coupling constants for the aliphatic chain are tentative because details of the conformational constraints have not been studied.

Table 2. ^{1}H–^{13}C dipolar coupling constants (Hz) for 4′-pentyloxy-4-biphenylcarbonitrile (5OCB) from 2D PELF.

Bond	Experimental values	Calculated values
C1–H2	778	778
C1–H3	−176	−190
C2–H2	1543	1543
C2–H3	−1249	−1289
C3–H3	1250	1249
C3–H2	−1333	−1293
C4–H3	793	792
C4–H2	−192	−188
C1′–H2′	772	778
C1′–H3′	−179	−187
C2′–H2′	1616	1616
C2′–H3′	−1272	−1275
C3′–H3′	1374	1374
C3′–H2′	−1282	−1279
C4′–H3′	796	790
C4′–H2′	−172	−185
Cα-Hα	4415	—
Cβ-Hα[a]	334	—
Cβ-Hβ	4311	—
Cβ-Hγ[a]	141	—
Cγ-Hγ	2940	—
Cγ-Hβ[a]	386	—
Cγ-Hδ[a]	193	—
Cδ-Hδ	3013	—
Cω-Hδ[a]	123	—
Cω-Hω	309	—

[a] Tentative assignment; signs undetermined.

The method for calculating the order parameters of the phenyl rings is the same as that for SLF [1, 16]; therefore it is not repeated here. For the phenyl ring containing the pentyloxy chain, the order parameters at 49°C are: $S_{zz} = 0.590 \pm 0.002$ and $S_{xx} - S_{yy} = 0.050 \pm 0.003$; the bond angles are: $H_{2'}$–$C_{2'}$–$C_{3'} = 118.89 \pm 0.08°$, and $C_{2'}$–$C_{3'}$–$H_{3'} = 119.70 \pm 0.08°$. For the phenyl ring bearing the cyano group, the corresponding values are: $S_{zz} = 0.597 \pm 0.012$, $S_{xx} - S_{yy} = 0.057 \pm 0.016$, H_2–C_2–$C_3 = 119.0 \pm 0.4°$, and C_2–C_3–$H_3 = 120.0 \pm 0.4°$. The order parameters are about 20% larger than those obtained previously at a higher temperature (58°C) [16]. The bond angles obtained by the two methods are in very good agreement with each other.

For the aliphatic chain, the order parameter of directly bonded C–H pairs can be calculated by using equation (3). At 49°C, the $S_{\text{C-H}}$ values for the α, β, γ, δ, and ω-carbons in the pentyloxy chain are: −0.195, −0.190, −0.130, −0.133, and −0.014, respectively. These values are slightly more negative than those obtained previously at 58°C by using the SLF/OMAS technique [16], which is expected. It should be noted that the ^{1}H–^{13}C splitting for the α-carbon is very large (figure 2) and the peaks are quite broad due to the limitation in achieving complete homonuclear dipolar decoupling. Nevertheless, the S_{CH} value for the α-carbon obtained from the PELF study agrees well with those obtained from the ^{13}C and ^{2}H NMR spectra of the monodeuterated compound, as discussed in the two previous sections. The problem of incomplete homonuclear dipolar decoupling is less severe when OMAS is used [16], but then the smaller splittings due to long range couplings cannot be resolved.

The temperature dependence of the order parameters was studied previously [14, 18] and has not been repeated in this work.

4. Conclusion

The study of proton-decoupled 1D ^{13}C NMR of the monodeuterated compound 4′-(1-deuteropentyloxy)-4-biphenylcarbonitrile has yielded long range dipolar coupling constants in 5OCB for the first time. In addition, eleven 2-bond and two 3-bond ^{1}H–^{13}C dipolar coupling constants have been determined by using the 2d PELF technique to study non-deuterated 5OCB. These data are useful for the investigation of conformational equilibrium in this important liquid crystal. Although molecular dynamics simulations of 5OCB have been performed [19, 20], long range dipolar coupling constants have not been examined in these computer simulations. Because the long range dipolar couplings are determined by the average of many conformations of the pentyloxy chain in

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5OCB, to account for their values quantitatively requires a very good knowledge of the potentials governing various motions of the chain. Therefore, the experimental data presented in this work will serve as important and stringent criteria for judging the quality of future refined molecular dynamics simulations and other computation studies.

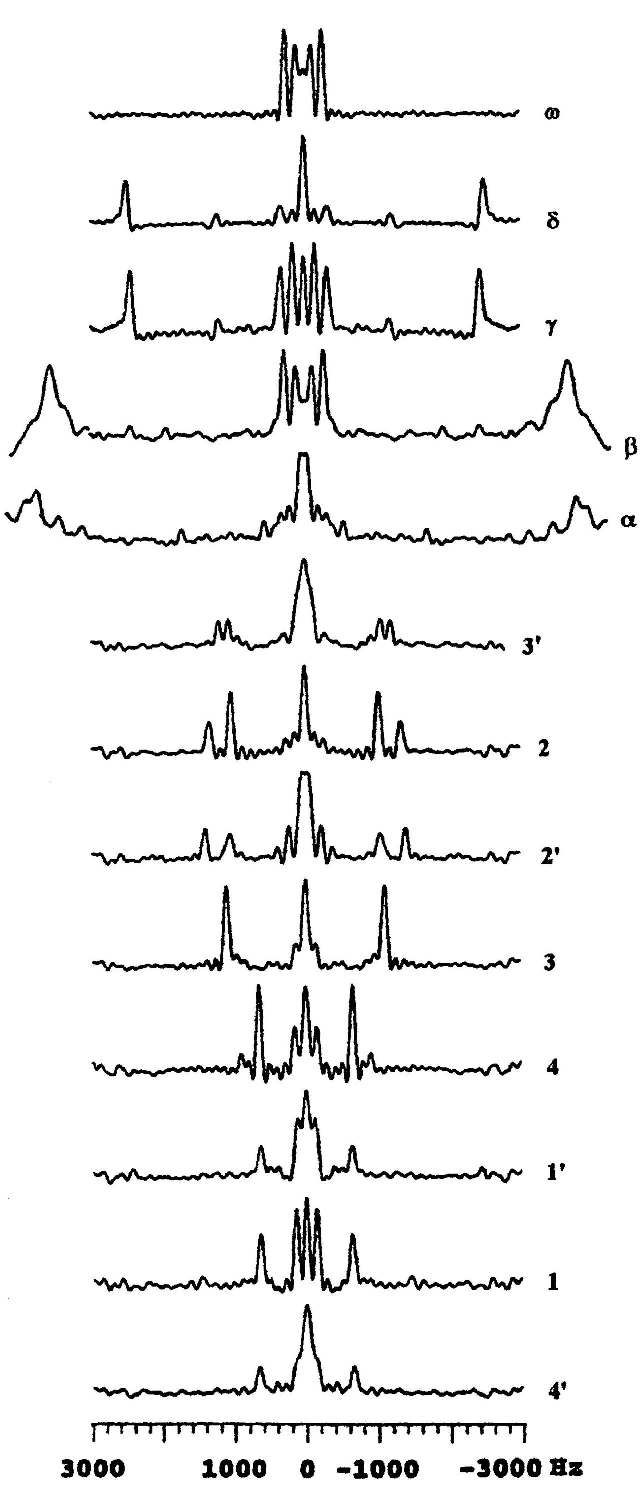

Figure 2. ^{13}C NMR spectra of 5OCB-d1 obtained by using the 2D proton-encoded local field (PELF) method. The spectra are slices in the ω2 dimension, showing ^{1}H–^{13}C splittings for individual carbons.

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