Figure 10. Experimental photoabsorption spectrum of $(SiMePr)_n$.
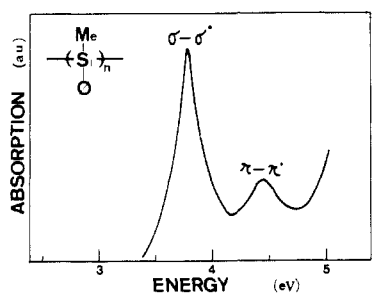
Figure 11. Experimental photoabsorption spectrum of $(SiMePh)_n$.

also to appear in a similar energy region (3.7 eV) slightly less than that of $-(SiMePr-)_n$. The next possible transition is a $\pi-\pi^*$ transition, which occurs in the individual Ph side chains and corresponds to the benzene $\pi-\pi^*$ transition.

Two characteristic absorption peaks are observed for (Si-MePh-)$_n$ (Figure 11). The sharp of the peak at 3.7 eV is similar to that in $-(SiMePr-)_n$. The other peak is observed at about 4.5 eV, which is inherent in $-(SiMePh)_n$. The experimental photoabsorption spectra can thus be assigned as follows. The peak at 3.7 eV is thought to originate from the $\sigma-\sigma^*$ interband transition

on the skeleton axis. The peak at 4.5 eV corresponds to the $\pi-\pi^*$ transition in the Ph side chains.

Summary

Poly(organosilane) exhibits a directly allowed type band structure. The existence of the isolated skeleton π- and π^*-like bands causes the skeleton σ- and σ^*-band-edge states to be displaced upwards. This feature is significantly different from the corresponding electronic structure of polyethylene. The poly(organosilane) band-edge states are formed mainly of skeleton Si AOs, which produces the skeleton band gap. This skeleton band gap tends to be compressed when larger alkyl groups are substituted in side chains. The amount of reduction is not significant, however, because of the weak electronic contribution from the side chains.

In poly(arylsilane), the $\sigma-\pi$ band mixing due to skeleton-side-chain interaction changes the poly(alkylsilane) single VB structure to a multiple structure. Two of them are delocalized along the skeleton axis, and the other is localized in the individual Ph side chains. On the contrary, no $\sigma^*-\pi^*$ band mixing occurs in the CB states, and no change is seen in the CB structure. The unoccupied π^*-states localized in the individual Ph side chains also intrude in the skeleton band gap.

The well-delocalized band-edge states seen in polysilane suggest that simple band conduction occurs along the skeleton Si axis for both electrons and holes. When Ph groups are used as the side chains (poly(arylsilane)), electrons and/or holes are localized in Ph side chains as well as delocalized along the skeleton axis. For these materials, carries in localized π- and/or π^*-states tend to exhibit hopping conduction between Ph side chains, in addition to the band conduction by carriers in the delocalized skeleton band-edge states.

13C Differential Line Broadening and the Experimental Measurement of the Absolute Signs of the One-Bond Carbon–Hydrogen Spin-Coupling Constants in Phenylacetylene[†]

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Abstract: The widths of the carbon-13 resonance lines in phenylacetylene have been measured as a function of temperature and magnetic field strength. The line widths of the various carbon-13 doublets are differentially broadened due to interference effects caused by the presence of two relaxation mechanisms, dipolar and chemical shift anisotropy, which have common correlation times. Since the signs of the chemical shift anisotropies for the acetylenic and aromatic carbons are known from independent solid-state measurements, the absolute sign of the carbon–hydrogen spin-coupling constant can be determined from the differential line broadening. For the acetylenic carbon $J_{C-H} = +252.1$ Hz at -30 °C. For the ring carbon para to the acetylene, which lies on the symmetry axis, $J_{C-H} = +162.1$ Hz.

During the past year or so reports have been given of differential line broadening (DLB) in simple two-spin systems such as $^{31}P-H^1$ and $^{13}C-H$.[2] No clear explanation of the effect was given in the

reports. We have shown[3] that the observed differential transverse relaxation (which determines the observed NMR line widths) is

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C-H Spin-Coupling Constants in Phenylacetylene

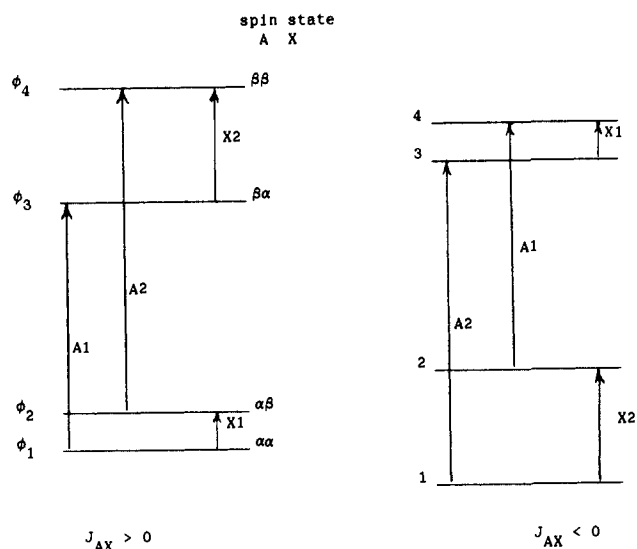*J. Am. Chem. Soc., Vol. 108, No. 26, 1986* 8191

Figure 1. Energy-level diagram for a two-spin A–X system, both spin $^1/_2$. If $J_{AX} > 0$, then the X1 transition (low frequency) is between levels 1 and 2. If $J_{AX} < 0$, then the X1 transition is between levels 3 and 4.

Figure 2. NMR spectra for the A and X nuclei. The doublet splitting in each case is J_{AX}. The low-frequency line in each spectrum is to the right and the high-frequency line to the left. For a normal spectrum with only dipolar relaxation, both lines in each spectrum have equal heights and widths.

in complete accord with the theoretical predictions of Shimizu.[4a] Other quite recent experimental work has also reported the presence of DLB effects.[5-8] Shimizu[4a] first called attention to the fact that such effects might be observed experimentally. Early experimental work by Mackor and MacLean[4b] showed that when both dipolar and CSA relaxation are present the longitudinal relaxation becomes rather complex. And they were able to show that the HF coupling constant in $CHFCl_2$ was positive. Only recently, however, has it been clear that rather special experimental conditions are required in order to see such relaxation behavior.[3] The experimental conditions required are the following:

(1) One relaxation mechanism in addition to dipolar relaxation is required, for example, chemical shift anisotropy (CSA) or quadrupole relaxation.[9,10]

(2) The relaxation mechanisms must have common correlation times. This usually, but not always, implies that the relaxation is primarily intramolecular.

(3) The correlation time should be relatively long, that is the product of the resonance frequency and the correlation time $\omega_0\tau_c$ should be greater than about 0.01.

(4) The spins, for example, A and X, must be scalar coupled and must have comparable relaxation times.

Carbon nuclei that are directly bonded to a single proton are excellent candidates for such differential relaxation. Such relaxation is normally not seen for a number of reasons: (a) in most ^{13}C NMR studies the protons are decoupled; (b) at magnetic field strengths of 4.7 T (200 MHz for proton NMR) or less, the carbon chemical shift anisotropy (CSA) interaction is small compared to the C–H dipolar interaction; (c) for nonviscous solutions at room temperature τ_c is quite short and $\omega_0\tau_c$ is about 10^{-4} or less. The earlier DLB effects observed in the literature[1,2] and that reported here are at high field (8 T or higher) and are for large biological or polymer molecules,[2] or for surface-bound molecules,[1] where the correlation times are relatively long.

As has been shown elsewhere,[3] the analysis of the differential broadening can provide useful and important information about molecular structure (bond distances), electronic structure (chemical shift anisotropies), and molecular dynamics (molecular correlation times and/or rotational diffusion tensors). The analysis can also allow one to obtain the absolute sign of J_{A-X}, the A–X spin coupling constant.

Theory

Consider a two-spin system, A and X, where both nuclei have a spin of $^1/_2$. The energy–level diagrams for such a system for the cases $J > 0$ and $J < 0$ are shown in Figure 1, and the typical spectra for such a spin system are shown in Figure 2. We designate the low-frequency lines in the A and X spectra by A1 and X1, respectively. Similarly, the high-frequency lines in the two spectra are labeled A2 and X2. Normally, there is no way to ascertain the absolute sign of the spin coupling constant, since one is not able to determine which lines in the spectra are associated with the transitions between the various energy levels. However, if we could show that the X1 (i.e., low frequency) line in the spectrum belongs to the transition between energy levels 1 and 2, then the sign of J_{AX} is positive. On the other hand, if the X1 line is shown to be associated with the transition between levels 3 and 4, then J_{AX} is negative.

The differential broadening experiment allows one to determine which lines in the spectra are associated with the various energy levels. By methods shown elsewhere,[4a] the transverse relaxation rates are calculated to be[3]

$$R_{1313} = -0.2[4(\delta_A - p)^2 J(0) + 3(\delta_A - p)^2 J(\omega_A) + 3(\delta_X^2 + p^2)J(\omega_X) + 6p^2 J(\omega_+) + p^2 J(\omega_-)] \quad (1a)$$

$$R_{2424} = -0.2[4(\delta_A + p)^2 J(0) + 3(\delta_A + p)^2 J(\omega_A) + 3(\delta_X^2 + p^2)J(\omega_X) + 6p^2 J(\omega_+) + p^2 J(\omega_-)] \quad (1b)$$

$$R_{1212} = -0.2[4(\delta_X - p)^2 J(0) + 3(\delta_X - p)^2 J(\omega_X) + 3(\delta_A^2 + p^2)J(\omega_A) + 6p^2 J(\omega_+) + p^2 J(\omega_-)] \quad (1c)$$

$$R_{3434} = -0.2[4(\delta_X + p)^2 J(0) + 3(\delta_X + p)^2 J(\omega_X) + 3(\delta_A^2 + p^2)J(\omega_A) + 6p^2 J(\omega_+) + p^2 J(\omega_-)] \quad (1d)$$

the line widths are given by

$$\Delta_{1/2}(i \rightarrow j) = -\pi^{-1} R_{ijij} \quad (2)$$

and the parameters used in the above equations are defined by

$$\delta_A = (1/3)(\sigma_\parallel - \sigma_\perp)_A \gamma_X B_0 (3 \cos^2 \Theta_{0A} - 1) \quad (3a)$$

$$\delta_X = (1/3)(\sigma_\parallel - \sigma_\perp)_X \gamma_X B_0 (3 \cos^2 \Theta_{0X} - 1) \quad (3b)$$

$$p = \gamma_A \gamma_X \hbar / 2r^3 \quad (4)$$

$$J(\omega) = \tau_c/(1 + \omega^2 \tau_c^2) \qquad \omega_\pm = \omega_A \pm \omega_X \quad (5)$$

where for simplicity we have assumed isotropic reorientation. The angle Θ_0 is the angle between the principal axis of the chemical shift tensor and the dipolar tensor. This angle is not to be confused with θ which is generally used to designate the angle between the A–X internuclear vector and the B_0 magnetic field.

As can be seen from the above R_{ijij} formulae, R_{1212} contains terms $(\delta_X - p)$ which depend upon the *difference* between the CSA

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(9) (a) Vold, R. L.; Vold, R. R. *Prog. NMR Spectrosc.* **1978**, *12*, 79. (b) Blicharsky, J. S. *Z. Naturforsch. A* **1972**, *A27*, 1355.
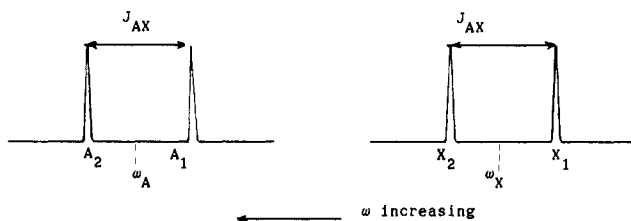
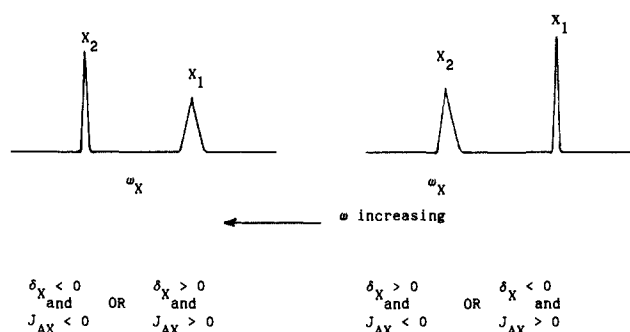(10) Anderson, J. M. *Mol. Phys.* **1964**, *8*, 505.

Figure 3. A–X spectra showing differential line broadening. The relative signs of the chemical shift anisotropy for each nucleus and the indirect J coupling determine whether the high-frequency or the low-frequency line in the spectrum is broadened.

interaction and the dipolar interaction. R_{3434} contains terms which depend on the *sum* of δ_X and p. In particular since

$$R_{1212} - R_{3434} = 4p\delta_X[4J(0) + 3J(\omega_X)] \qquad (6)$$

the differential line broadening will increase as the magnetic field, B_0, increases and as the molecular correlation time, τ_c, increases (see eq 5), as long as $\omega_0\tau_c < 1$. If the sign of the CSA, δ_X, is positive, then the magnitude of $\Delta_{1/2}(1\rightarrow2)$ is less than the magnitude of $\Delta_{1/2}(3\rightarrow4)$, that is, the line associated with the transition $(1\rightarrow2)$ will be narrower than the line for the $(3\rightarrow4)$ transition. Conversely, if δ_X is negative the $(3\rightarrow4)$ transition will be the narrower line.

To be more specific, we consider the phenylacetylene molecule, numbered as shown below

I
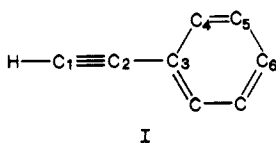
The physical origin of such DLB effects is clear if we consider the local fields at the C_1 acetylene carbon nucleus in a single crystal sample. It is well-known that the local field at the X nucleus (carbon) arising from the dipolar interaction with the A nucleus (proton) is given by

$$B_{local}(\text{dipolar}) = \frac{\pm\gamma_A\hbar}{r^3}(3\cos^2\theta - 1) \qquad (7)$$

In eq 7 θ is the angle between the A–X internuclear vector and the B_0 magnetic field. Approximately one-half of the X nuclei (carbon) are directly bonded to A nuclei (protons) with spin α (that is, these protons are aligned parallel to the B_0 magnetic field) and the other half are bonded to protons with spin β (protons aligned antiparallel to the magnetic field). The positive sign in eq 7 is due to the spin-α protons and the negative sign is due to the spin-β protons. In a similar way there is an angle-dependent local field which arises from the fact that the chemical shift is orientation dependent. For the C_1 carbon we have

$$B_{local}(\text{CSA}) = (1/3)(\sigma_\parallel - \sigma_\perp)_X\gamma_XB_0(3\cos^2\zeta - 1) \qquad (8)$$

In eq 8 ζ is the angle between the major principal axis of the X chemical shift tensor and the B_0 magnetic field. For the present simple case θ and ζ are equal. That is, the principal axes of the two tensors are coincident.

As the orientation of the crystal is changed, the local field at the carbon (X) nucleus changes. If the sign of the chemical shift anisotropy (CSA), $(\sigma_\parallel - \sigma_\perp)_X$, is positive, then the local fields arising from the chemical shift interaction and the A-nucleus spin-α dipolar interaction will add constructively. In contrast, the chemical shift local field and the spin-β proton local dipolar field will cancel or partially cancel. The extent of the cancellation is dependent upon the value of B_0.

As the molecules move about in solution these local fields fluctuate in time and serve as a mechanism for coupling the
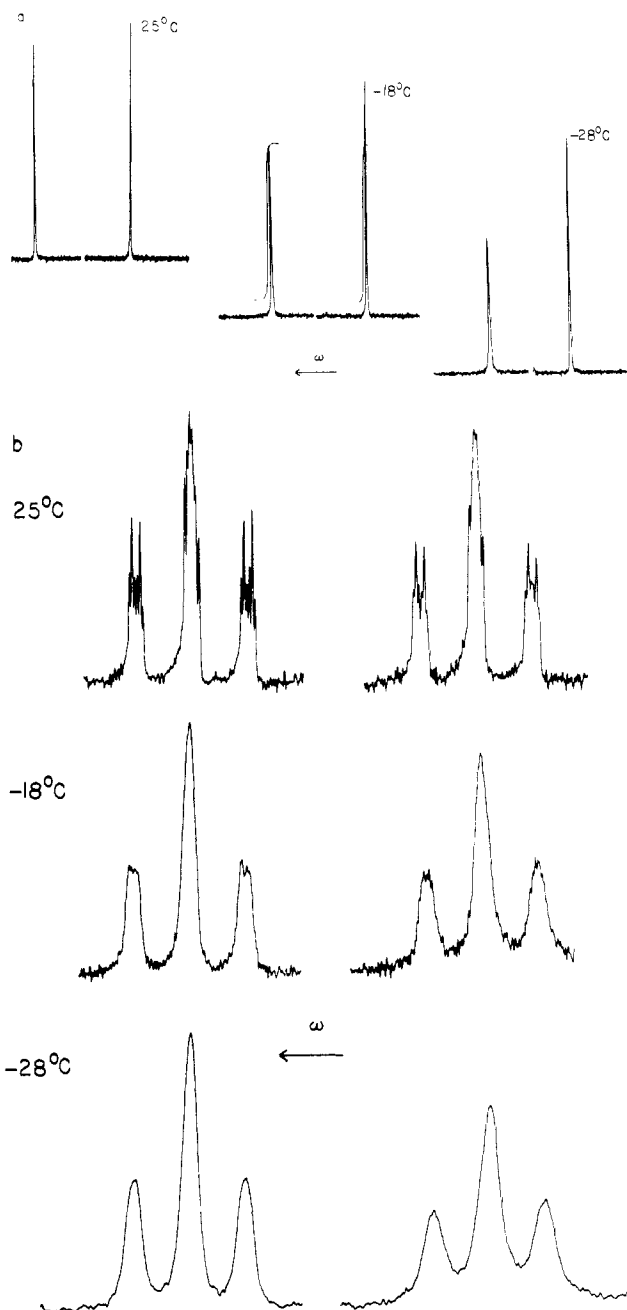

Figure 4. Carbon-13 NMR spectra of the acetylenic carbon (C1) and the para ring carbon (C6) at +25, –18, and –28 °C (from top to bottom, respectively). For the C1 carbon (a), the high-frequency line is broader, while for the C6 carbon (b), the low-frequency line is broader. The differential broadening increases as the temperature decreases. The differential broadening is much more pronounced for the C1 carbon than for the C6 carbon. The spectra were all obtained with a Bruker AM-360 NMR spectrometer. The magnetic field strength was about 8.5 T, and the carbon-13 resonance frequency was 90 MHz.

precessional motion of the nuclei to the rotational motion of the molecules, causing spin relaxation. For one of the carbon lines the magnitude of the fluctuating magnetic fields is the sum of the dipolar and CSA terms, the relaxation time is relatively short, and the line width, $\Delta_{1/2}$, is relatively large $(\Delta_{1/2} = 1/\pi T_2)$. For the other line the magnitude of the fluctuating local magnetic fields is relatively small due to the interference of the dipolar and the CSA term. For this line the relaxation time is relatively long and the line width, $\Delta_{1/2}$, is quite narrow.

Experimental Section

atom % D, purchased from MSD Isotopes). The final solution composition was 1:2:2 by volume.

Spectra were taken on Bruker AM-360 and AM-500 spectrometers, operating at field strengths of 8.5 and 11.7 T, respectively. Additional spectra were taken at 4.7 T, using a JEOL FX-200 spectrometer. Temperatures of 22, -18, and -28 °C were used for all spectra taken on the AM-360, while spectra on the AM-500 were taken at temperatures of 22, -15, and -20 °C for the ring carbons and -30 °C for the acetylenic carbons. Fully coupled carbon spectra were taken using (i) no signal enhancement, (ii) gated irradiation to generate an NOE, and (iii) the INEPT or coupled ERNST (INEPT+)[11] polarization transfer methods.

The polarization transfer spectra were taken by using a preliminary saturation pulse train applied to the carbon spins, so that the peak heights could be used as an indication of differential line widths. In all cases the total integrated intensities of the carbon "doublets" were equal. The differential broadening observed was independent of the method used to generate the carbon signal. This is in accord with theoretical predictions. Because long-range couplings were easily observable between the ortho ring protons and the acetylenic carbons, and between the aceylenic proton and the ortho ring carbons, spectra were also taken with selective decoupling of these proton resonances. In the cases where the acetylenic carbons were observed, selective decoupling of the ortho ring protons produced a sharp doublet (J = 50 Hz, line width of 0.4 Hz) for carbon C_2 (see I, above, for the labeling of the various carbon nuclei). Since the C2 carbon is not expected to show appreciable differential broadening, and does not, it serves as a convenient internal check of our results.

Simulations of the high-resolution NMR spectra for the ring carbons were done with a spin simulation program. (The program Spin Polarization Intensities of Numerous Nuclei Assigned by Key Eigenvector Rotations (SPINNAKER) was used for this calculation. The source code is available on request.) Carbon and hydrogen chemical shifts were taken from a two-dimensional shift correlation spectrum. Those coupling constants which could be easily observed were used, along with reasonable estimates for others (two and three bond couplings). In any event, the primary object was to check the origin of the notable asymmetry of the carbon doublets. The general features of the spectra were quite well reproduced by the simulations.

Results and Discussion

The proton-coupled carbon-13 (natural abundance) spectra for the acetylenic carbon and the para ring carbon are relatively simple and symmetric. The spectra of aromatic ring carbons which are not on the symmetry axis are complex and asymmetric due to the magnetic nonequivalence of the protons. That is, the asymmetric appearance of the room temperature spectra is due to magnetic nonequivalence and not to differential line broadening. At room temperature the observed spectra are in accord with what is predicted theoretically with the use of the standard quantum mechanical calculations cited above.

Independent measurements have shown that the CSA values for acetylene carbon nuclei and aromatic carbon nuclei are large and positive (about +200 ppm).[12-14] If δ_C is positive, $\Delta_{1/2}(1\rightarrow2)$

must be less than $\Delta_{1/2}(3\rightarrow4)$, since the dipolar parameter, p, is positive. We observe (see Figure 3) that the low-frequency line for the acetylenic carbon is narrower than the high-frequency line. Therefore, the low-frequency line arises from the transition $(1\rightarrow2)$. This tells us that the carbon–hydrogen spin-coupling constant, J_{C-H}, must be positive (see Figure 2). For *all* of the ring carbons, however, it is the high-frequency line in the doublet which is narrow, leading one at first glance to think that either the sign of J_{C-H} is negative for the ring carbons or that the CSA for the ring carbons is negative. In fact, both the CSA and J_{C-H} for all of the ring carbons are positive. The reason for the reversal of the sense of the DLB between the acetylene carbon and the ring carbons is clear from eq 3b.

The δ_C term (eq 3b) has associated with it a $(3\cos^2\Theta_0 - 1)$ term, where Θ_0 is the angle between the major principal axis of the chemical shift tensor and the principal axis of the dipolar tensor. (The actual situation is a bit more complex in the present case since the chemical shift tensor is not axially symmetric for the ring carbons. Consequently other, smaller, angular corrections are needed.) For the ring carbons Θ_0 is approximately 90°, since the most highly shielded component of the chemical shift tensor is perpendicular to the plane of the ring.[13,14] Consequently, $(3\cos^2\Theta_0 - 1) \simeq -1$. For the acetylenic carbon, the major principal axes of the two tensors are coincident, $\Theta_0 = 0$ and $(3\cos^2\Theta_0 - 1) = +2$. Thus, in addition to the reversal of the sense of the DLB, the magnitude of the DLB is also diminished for the ring carbons. This is due to the -1 factor, rather than $+2$, and to the addition of other terms which further diminish the magnitude of the interference effects. This is the reason for the fact that at -28 °C the ratio of the peak heights of the C_1 resonance lines is about 1 to 0.5 while for the para ring carbon the ratio of the peak heights is about 0.8 to 1.0 (see Figure 4). The fact that the dipolar and CSA interactions have only two common correlation times also diminishes the DLB for the para carbon.

The DLB for the C_2-acetylenic carbon is quite small since a major part of the dipolar relaxation for this carbon arises from ring protons whose motions are not fully correlated with that of the carbon (see points 2 and 4 in the introduction).

In summary, we have shown that the absolute signs for all of the single-bond carbon–hydrogen couplings are positive. For the C1 carbon the differential broadening is quite pronounced for long correlation times. For carbon nuclei which do not fully meet the criteria stated in the introduction and/or for carbon nuclei whose chemical shift and dipolar tensor axes are not coincident, the effects will be diminished and will probably have a reversed sense of differential broadening. Although the effects will be diminished they will still be observable for long correlation times, especially for those cases where an abundance of fine structure is present. The fine structure will be lost for the broad "doublet" peak, while it is still easily seen for the narrower peak (see, for example, Figure 4).[2]

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