

Figure 5. Bond lengths and principal torsion angles for the 4-*O*-β-D-galactopyranosyl-β-D-fructofuranose isomer. The standard deviations for the galactosyl residue are 0.007 Å and 0.6°. For the fructose residue, they are 0.009 Å and 0.7°.

(3)-C(4) is 97.4 vs. 105.6°. This is the region of overlap with the electron density of the two minority isomers, and these anomalies are therefore not considered significant.

The hydrogen-bond distances and selected angles are given in Table IV. The hydroxyl hydrogen positions for the fructofuranose residue are poorly defined due to overlap with the carbon and

oxygen atoms of the minor components, which are of comparable electron density. The hydrogen atom positions for the minor components were not determined.

The galactosyl hydroxyls form three two-center and one three-center hydrogen bonds of the type commonly observed in carbohydrate crystal structures.³⁰ In the region of the fructose residue, there are a large number of O...O distances in directions appropriate for hydrogen bonding, both between like isomers and between unlike isomers. It is the flexibility of choice in hydrogen-bond formation that permits the coexistence of the three molecules in the same crystal structure.

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Supplementary Material Available: Tables of valence angles, secondary torsion angles, anisotropic thermal parameters, and structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Cross Polarization and Magic Angle Sample Spinning NMR Spectra of Model Organic Compounds. 1. Highly Protonated Molecules

Lawrence B. Alemany, David M. Grant,* Ronald J. Pugmire, Terry D. Alger, and Kurt W. Zilm

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. Received December 21, 1981

Abstract: CP/MAS ¹³C NMR spectra were obtained at various contact times on ten solid organic compounds containing a variety of simple functional groups. The spectra show that signal intensities that agree with atomic ratios can be obtained with a contact time of 2.25 ms and often with a contact time as short as about 1 ms. Computer analysis of signal intensities obtained at a minimum of ten different contact times provides *T*_{CH} data that are consistent with these experimental results. The experimental results are also consistent with the previously reported lack of significant variation in the spectra of complex organic solids obtained with contact times of about 1-3 ms. In general, nonprotonated carbon atoms polarize more slowly than protonated carbon atoms. The compounds exhibit a wide range of proton spin lattice relaxation times. Some compounds exhibit more resonances than are found in the ¹³C{¹H} spectra of the compounds in solution because the crystalline environment removes the nominal spatial equivalence found for carbon atoms related to each other by unimolecular symmetry elements.

Introduction

The last several years have seen a tremendous growth in the use of ¹³C NMR spectroscopy of solids in many areas of chemistry.¹⁻³ The combination of dipolar decoupling (to remove C-H dipolar broadening), magic angle spinning (to remove chemical shift anisotropy), and cross polarization (to reduce the time needed to acquire a spectrum) has proven extremely useful. However, investigators have expressed concerns about the possible limitations

in obtaining signal intensities that agree with atomic ratios and thus of the significance of cross polarization ¹³C NMR spectra of diamagnetic solids.⁴⁻⁶ Nevertheless, only limited investigations of this central aspect have occurred.⁷⁻¹⁷ Accurate relative signal

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intensities at unspecified contact times⁷⁻⁹ and at contact times ranging from 0.5 to 5 ms^{10-14,16,17} have been reported. These reports clearly indicate that it would be desirable to investigate in more detail the dynamics of cross polarization in a wide variety of organic compounds to determine if accurate relative signal intensities could consistently be obtained under a given set of conditions. For this initial study, several relatively small, proton-rich organic compounds were chosen in which it was felt that molecular motions (except methyl rotation) were minimal and of small amplitude. By use of a proper Hartmann-Hahn¹⁸ match, these criteria were used to focus on cases in which the magic angle spinning, the dipolar decoupling, the molecular motion, and a small proton-proton second moment are not causing complications.^{1,2,10,16,19,20} The results of this investigation agree with previously advanced theories²¹ and indicate that for relatively small, proton-rich organic compounds, accurate relative signal intensities can be obtained with a contact time of about 2.25 ms and often with contact times as short as about 1 ms.

Theoretical Considerations

Adequate models involving thermodynamic descriptions of spin-locked cross polarization have been developed.^{18,21-24} These include the theories of Demco et al.²¹ for molecules in the rigid lattice approximation and of Cheung and Yaris²⁴ for solids that undergo internal motion. Briefly, the essence of these useful theoretical approaches is outlined, and the resulting concepts are stressed. The cross-polarization rate, $1/T_{SI}$, for a given rare spin S results from a summation over all $S-I$ spin interactions. The expression is given as follows:^{21,25a}

$$1/T_{SI} \approx (1/2) \sin^2 \theta_I \sin^2 \theta_S M_{2,SI} J_x(\Delta\omega_{\text{eff}}) \quad (1)$$

where θ_I and θ_S are the angles between the B_0 field and the effective magnetic fields in the I and S rotating frames, respectively. The expression for the power density J is

$$J_x(\Delta\omega_{\text{eff}}) = \int_0^\infty d\tau \exp(i\Delta\omega_{\text{eff}}\tau) C_x(\tau) / \text{Tr}\{(\sum_i b_{Si} I_{ix})^2\} \quad (2)$$

and for the Van Vleck second moment $M_{2,SI}$ is^{25b}

$$M_{2,SI} = \frac{1}{2} \gamma_I \gamma_S^2 \hbar^2 I(I+1) \sum_i b_{Si}^2 \quad (3)$$

where²¹

$$C_x(\tau) = \sum_i \{b_{Si} I_{xi} \exp[-iP_2(\cos \theta_I) \tilde{H}_{II}^\circ \tau] b_{Si} I_{xi}\} + \sum_{k \neq l} \{b_{Sk} I_{xk} \exp[-iP_2(\cos \theta_I) \tilde{H}_{II}^\circ \tau] b_{Sl} I_{xl}\} \quad (4)$$

and

$$b_{Si} = -2P_2(\cos \theta_S) / r_{Si}^3 \quad (5)$$

The trace over $(\sum_i b_{Si} I_{ix})^2$ in the denominator of J is a normalizing

term that to a first approximation cancels a similar summation over b_{Si}^2 appearing in the expression for M_2 . This leaves $C_x(\tau)$ as the significant spatially dependent term in the relaxation expression. We have restructured the expression for C_x from that found elsewhere in the literature into an autocorrelation term (the summation of the i th set of I spins) and into a cross-correlation term (the double summation over the pair of $k \neq l$ set of I spins) in order to emphasize important differences in these two types of terms. One assumes that the S th spin is dilute, and in this approximation, no $S-S$ spin interactions are considered to be important.

As the r_{Si} distance will commute with the exponential operators in C_x , it is easy to see that the autocorrelation term will depend on r_{Si}^{-6} , and thus there will be a significant contribution only for those terms in the summation for which the r_{Si} distance is minimal. Thus, directly bonded protons (I spins) should completely dominate the cross polarization of carbon-13 nuclei (S spins) provided that internal motion does not reduce the angular portion of b_{Si} to a negligible value. Furthermore, the now linear summation for the autocorrelation term will make the cross-polarization rate for a specific ^{13}C spin directly proportional to the number of directly bonded protons. Thus, cross polarization in CH_2 should be twice as effective as in CH , all other factors being equal. The cross correlation term appearing in C_x can be large for CH_2 and CH_3 groups and will modify the autocorrelation term depending upon the spatial arrangement of the CH_n group in the solid. As these cross terms may assume both positive and negative signs depending upon the relative orientations of the $S-I_k$ and $S-I_l$ bonds, a distribution of rates then becomes possible for the cross term, making it more difficult to deal with theoretically. When one constructs an ensemble of S spins and uses an average $1/T_{SI}$ rate, the negative and positive components will cancel in part, thereby reducing the significance of the cross-correlation term in the effective cross-polarization process. Thus, neglecting the cross terms, one would predict for rigid, directly bonded $^{13}\text{C}-^1\text{H}$ moieties in molecular, microcrystalline powders that the rate of cross polarization to a first-order approximation will be proportional to the number of directly bonded protons. Rapid internal motion such as that encountered in methyl and *tert*-butyl groups, however, modifies this conclusion dramatically, as all of the dipolar interactions are reduced in effectiveness through an averaging of the angular portion $P_2(\cos \theta_{Si})$ of b_{Si} . Such internal motion is usually adequate to reduce the effectiveness of the cross-polarization process for a CH_3 group below that encountered for a rigid CH moiety.

The theoretical problems encountered for nonprotonated carbons are considerably more difficult to deal with. First, subtended angles between the ^{13}C spin and the k and l protons can make cross-correlation terms under certain conditions more nearly comparable to the autocorrelation terms. This could introduce considerable nonlinearity in the number of interacting protons even assuming a constant distance. The other major problem arises from the larger nonbonded $^{13}\text{C}-^1\text{H}$ distances. The sharp cutoff at the directly bonded $^{13}\text{C}-^1\text{H}$ distance is replaced by a more diffuse dependence upon the nonbonded proton-carbon distance. In this instance, one may encounter many more protons that could effectively contribute to both the auto- and cross-correlation terms. However, the effective sixth-order falloff in the $S-I$ distance will significantly limit the $1/T_{SI}$ rate for nonprotonated carbons. Furthermore, as the proton or I spin is diluted in molecules with low protonation, one may well expect the contribution from the sum over protons to decrease also and a lengthening in T_{CH} to result. The experimental results that follow will be interpreted in terms of these theoretically derived concepts.

Thus, based upon straightforward theoretical arguments, one may expect that carbon atoms polarize at the following relative rates: $\text{CH}_3(\text{static}) > \text{CH}_2 > \text{CH} \geq \text{CH}_3(\text{rotating}) > \text{C}(\text{non-protonated})$.

Experimental Section

$^{13}\text{C}\{^1\text{H}\}$ spectra (75 MHz, Varian SC-300) of compounds 1-10 in CDCl_3 solution (40° pulses spaced at least 6 s apart) indicated that they were pure enough for quantitative CP/MAS NMR investigations. Where necessary, gated decoupling was used to secure assignments.

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Table I. Relative Signal Intensities in 1,2-Bis(4-tolyl)ethane as a Function of Contact Time

contact time, ms	rel intensities					std error, ^a %	std rel error, ^b %
	C-1	C-4	C-2,6;3,5	CH ₂	CH ₃		
	Theoretical						
	12.5	12.5	50.0	12.5	12.5		
	Experimental						
3.000	12.5	12.8	48.9	11.1	14.7	1.3	9.4
2.250	12.8	12.9	49.3	11.1	13.9	1.0	7.3
1.500	11.0	13.2	50.9	10.8	14.1	1.3	10.3
1.000	12.4	12.1	51.8	10.9	12.9	1.1	6.3
0.700	12.6	12.8	48.7	11.4	14.6	1.2	8.6
0.500	12.4	12.4	49.8	11.3	14.2	0.9	7.5
0.400	10.0	11.1	52.2	12.7	14.0	1.8	11.8
0.300	9.7	10.2	52.8	13.4	13.9	2.2	14.5
0.225	8.7	9.8	56.0	12.2	13.3	3.4	17.8
0.150	6.1	6.9	59.1	17.3	10.5	6.0	36.6

^a Standard error in percent units defined as $[(1/n)\sum d_i^2]^{0.5}$,

where n = the number of different signals and $d_i = I_i^{\text{exptl}} - I_i^{\text{theor}}$.

^b Standard relative error in percent units defined as $[(1/n)\sum (d_i/I_i^{\text{theor}})^2]^{0.5} \times 100\%$.

CP/MAS ¹³C NMR spectra were obtained on an extensively modified^{26,27} Varian XL-100 and on a Bruker CXP-100. Both spectrometers employ single-coil, doubly tuned probes. The data were obtained with proton spin temperature inversion.²⁸

As the Hartmann-Hahn match¹⁸ is modulated by the sample rotation rate ω_r (i.e., the nonequivalent T_{CH} minima for a given carbon atom are each separated by variations of ω_r in the ¹³C rf field²⁹), the spectra obtained depend critically on this match. This is especially true for relatively short contact times where optimization of the match becomes more critical. Both spectrometers were tuned with hexamethylbenzene until the signal intensities obtained with $t_{\text{cp}} = 1.00$ ms nearly equaled the signal intensities obtained with $t_{\text{cp}} = 3.00$ ms. Prior to optimization of the match, the angle of the sample spinning axis relative to B_0 was adjusted to minimize the line width of the aromatic carbon atoms, whose large chemical shift anisotropy makes them much more sensitive to deviations from the magic angle than are the aliphatic carbons. The sharpness of the aromatic and carbonyl resonances in the compounds subsequently examined indicates that the angle of the spinning axis remains unchanged when the rotor with hexamethylbenzene is replaced. The ultimate resolution is then limited by the intrinsic line widths of the resonances.

Data tables of 8K were acquired on the 25.16-MHz Varian XL-100 spectrometer with an external D₂O lock. A spectral width of 12 kHz, a computer-controlled filter band width, 12-bit digitizer resolution, an rf field of 50 kHz for ¹H spin locking, and 150 W of decoupling power were used. The waiting period with decoupling between the end of the cross-polarization step and the start of data acquisition was 50 μ s. The maximum possible acquisition time of 200 ms and a delay time of 3 s for 6 and 7 and 4.8 s for 1 and 2 were used. The samples were spun with nitrogen at about 3.1 kHz in a 120- μ L rotor made of Kel-F.

Data tables of 4K (usually zero-filled 1K or 2K data tables) were acquired in quadrature on the 25.15-MHz Bruker CXP-100 spectrometer equipped with a Z32 PE/MAS probe without an external lock. A spectral width of 10 kHz, a computer-controlled filter band width, 12-bit digitizer resolution, and an rf field of 50 kHz for ¹H spin locking and decoupling produced with 200 W of power were used. A waiting period of 50 μ s (one dwell time) with decoupling between the end of the cross-polarization step and the start of data acquisition was used. The receiver was blanked until the start of data acquisition, and an acquisition time no more than 200 ms and no more than 10% as long as the delay time was employed. The samples were spun with nitrogen at about 3.5 kHz in a 200- μ L rotor made of boron nitride with the stator made of Kel-F.

Signal intensities were determined by cutting the peaks from the spectrum and weighing the pieces. The intensities of the very weak

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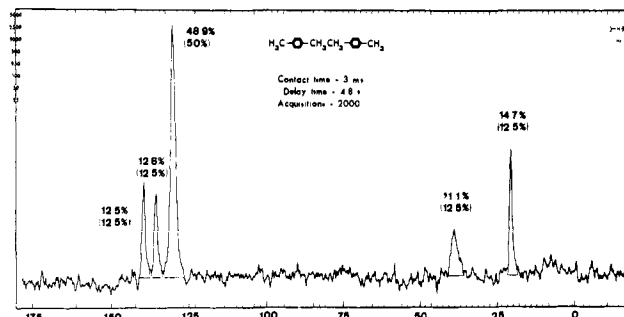


Figure 1. Expanded region from a 25.16-MHz, 4K, CP/MAS ¹³C NMR spectrum of 1,2-bis(4-tolyl)ethane obtained with a spectral width of 12 341 Hz (490 ppm) and a frequency resolution of 3.0 Hz: acquisition time = 0.200 s; sensitivity enhancement factor = 0.04. For each type of carbon atom, the I_{exptl} value and I_{theor} value (in parentheses) are given (I_{exptl} and I_{theor} are defined in Table I).

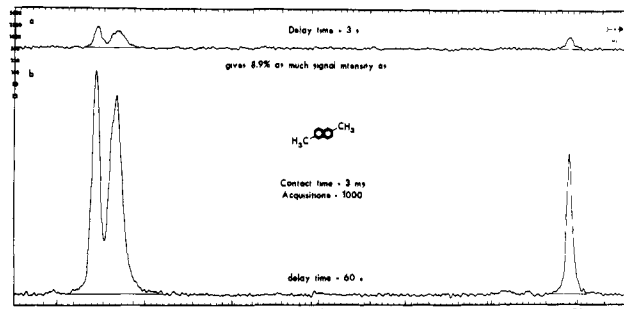


Figure 2. Expanded regions from 25.15-MHz, scaled CP/MAS ¹³C NMR spectra of 2,6-dimethylnaphthalene obtained with a spectral width of 10 000 Hz (398 ppm), acquisition time = 0.0500 s. Line-broadening factor of 5 Hz applied before spectra were zero-filled to 2K for a frequency resolution of 4.9 Hz.

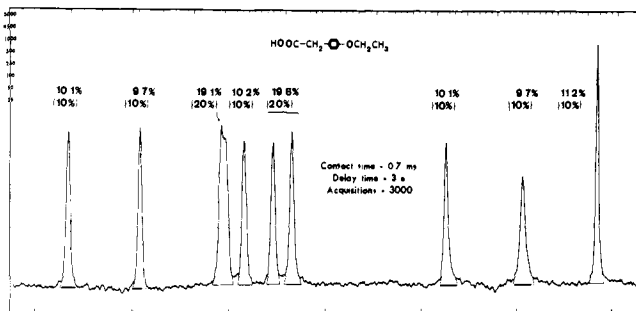


Figure 3. Expanded region from a 25.16-MHz, 4K, CP/MAS ¹³C NMR spectrum of (4-ethoxyphenyl)acetic acid obtained with a spectral width of 12 341 Hz (490 ppm) and a frequency resolution of 3.0 Hz: acquisition time = 0.200 s; sensitivity enhancement factor = 0.04. A pair of resonances separated by 6.0 ppm is clearly evident for C-3,5, while only a slight splitting is evident for C-2,6. For each type of carbon atom the I_{exptl} value and I_{theor} value (in parentheses) are given.

spinning sidebands (not shown in the figures) were not measured.³⁰ In some compounds, the spread in isotropic chemical shifts exceeds the rotation rate, and therefore, a weak sideband could be under another isotropic resonance. A method has recently been reported for minimizing sideband intensities.³¹

(30) To have measured meaningful sideband intensities would have required obtaining spectra with much higher signal:noise (S/N) ratios. However, we felt that data on many compounds would be more useful than more precise data on just a few compounds. Furthermore, in highly complex solids, it is not always possible to match by sight an isotropic resonance with its corresponding sidebands. Thus, our results provide an estimate of the accuracy of the relative signal intensities that can be obtained in such solids and a slightly low estimate of the accuracy that can be obtained in simple solids. However, our results are particularly relevant if sideband-suppressed spectra³¹ are obtained.

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Table II. Relative Signal Intensities in (4-Ethoxyphenyl)acetic Acid as a Function of Contact Time

contact time, ms	rel intensities								std error, ^a %	std rel error, ^a %
	C=O	C-4	C-2,6	C-1	C-3,5	OCH ₂	CH ₂ CO	CH ₃		
	Theoretical									
	10	10	20	10	20	10	10	10		
	Experimental									
3.000	10.8	9.8	16.9	10.2	20.0	9.4	10.4	12.5	1.5	11.1
2.250	10.4	10.2	18.5	10.1	20.2	8.7	10.3	11.6	0.9	8.0
1.500	10.8	10.9	18.3	10.8	19.1	9.2	9.8	11.0	1.0	7.7
1.000	10.8	10.1	18.6	9.8	20.1	10.0	9.2	11.5	0.8	7.1
0.700	10.1	9.7	19.1	10.2	19.8	10.1	9.7	11.2	0.6	4.9
0.500	9.6	8.4	20.0	9.0	20.2	10.4	10.0	12.3	1.1	10.7
0.400	8.5	7.9	20.2	9.4	20.6	10.4	10.7	12.4	1.3	13.0
0.300	8.2	6.9	20.3	8.6	21.0	11.1	10.8	13.2	1.9	18.4
0.225	6.8	5.6	21.4	6.8	23.0	11.9	10.9	13.7	2.9	27.5
0.150	5.1	4.4	22.6	6.7	24.1	12.2	12.7	12.2	3.7	33.4

^a As defined in Table I.

Table III. Relative Signal Intensities in 4-Butoxybenzoic Acid as a Function of Contact Time

contact time, ms	rel intensities								std error, ^a %	std rel error, ^a %	
	C=O	C-4	C-2,6	C-1 ^b	C-3,5 ^b	α-CH ₂	β-CH ₂	γ-CH ₂			CH ₃
	Theoretical										
	9.09	9.09	18.18	9.09	18.18	9.09	9.09	9.09	9.09		
	Experimental										
3.000	9.7	9.7	16.9	8.9	17.4	8.0	8.8	9.6	11.0	1.0	9.3
2.250	9.9	9.0	16.0	8.9	17.9	8.3	8.3	9.7	12.0	1.3	12.7
1.500	10.0	8.8	16.8	9.2	18.1	7.9	8.9	9.0	11.3	1.0	10.2
1.000	9.3	8.3	17.4	8.7	17.9	8.8	9.3	9.3	11.1	0.8	8.3
0.700	9.1	7.8	17.2	7.3	18.8	9.5	10.1	9.0	11.2	1.1	12.1
0.500	8.5	7.4	17.9	6.2	19.5	8.9	10.6	9.9	11.2	1.5	16.2
0.400	7.8	6.8	16.8	5.8	19.7	9.7	10.3	10.1	13.1	2.1	22.5
0.300	7.0	5.4	18.0	5.8	19.4	9.9	10.6	10.7	13.1	2.4	26.1
0.225	5.9	5.8	17.9	4.7	21.8	10.5	10.9	10.3	12.2	2.8	28.4
0.150	4.1	3.5	20.5	2.9	21.6	11.6	12.1	12.5	11.3	4.0	42.5

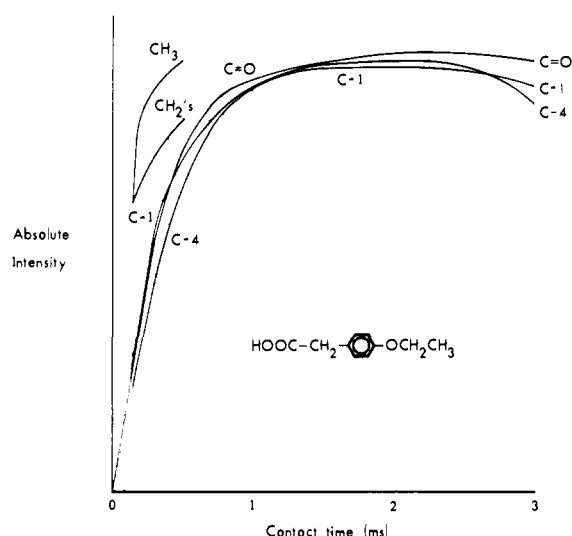
^a As defined in Table I. ^b C-1 and one of the resonances due to C-3,5 overlap (Figure 5). A perpendicular was dropped at the intersection of the overlapping resonances in order to estimate the intensity of each resonance.

Figure 4. Rate of cross polarization of each of the nonprotonated carbon atoms in (4-ethoxyphenyl)acetic acid (for comparison, the initial rate of cross polarization of the protonated aliphatic carbon atoms is also shown). At $t_{cp} \approx 2.25$ ms, each of the nonprotonated carbon atoms achieves maximum absolute intensity (Table VIII, supplementary material) and each is fully polarized (Table II).

Chemical shift scales in the figures are approximate; without an internal standard for referencing the chemical shifts of 1–10, one signal in the solid was assigned a chemical shift based upon the spectrum obtained in $CDCl_3$.

Results

Five arenes, 4,4'-dimethylbiphenyl (**1**), 1,2-bis(4-tolyl)ethane (**2**), 1,8-dimethylnaphthalene (**3**), 2,6-dimethylnaphthalene (**4**),

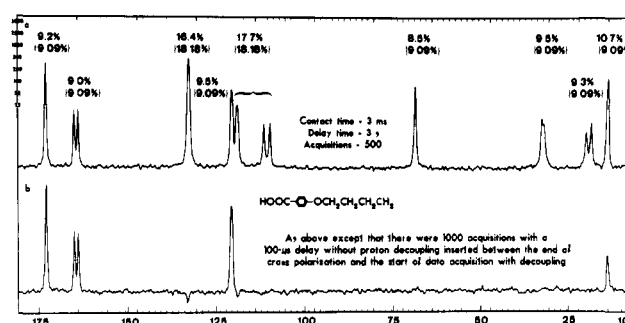


Figure 5. (a) Expanded region from a 25.15-MHz, 2K, CP/MAS ^{13}C NMR spectrum of 4-butoxybenzoic acid obtained with a spectral width of 10000 Hz (398 ppm) and a frequency resolution of 4.9 Hz: acquisition time = 0.200 s; line-broadening factor = 5 Hz. Pairs of resonances separated by 1.2 and 1.4 ppm are clearly evident for C-4 and γ -CH₂, respectively, while only a slight splitting is evident for β -CH₂. For each type of carbon atom, the I_{exptl} value and I_{theor} value (in parentheses) are given. The percentage intensity values differ slightly from those in Table III, $t_{cp} = 3.000$ ms, because this spectrum was acquired under slightly different conditions. (b) The 100- μ s delay (see figure) prevents protonated aromatic ring carbon resonances (and certain others) from appearing. Consequently, in a, the three most upfield aromatic carbon resonances, with a spread of 9.1 ppm, result from C-3,5.

and 9,10-dimethylantracene (**5**), were studied. While all five compounds give accurate relative signal intensities, only the first three have a proton spin lattice relaxation time, $T_1(H)$, that is short enough to conveniently permit obtaining spectra with usable S/N at a variety of contact times. Representative results for **2** appear in Table I. Spectra of **2** and **4** appear in Figures 1 and 2.

The several studies^{7,9,11–14,17} of carbonyl compounds under a wide variety of conditions prompted us to further investigate such

Table IV. Selected Absolute Intensity Data and Computer-Fitted T_{CH} Values in a Variety of Simple Organic Compounds

position	no. of atoms	abs intensity		computer-fitted T_{CH} and R_{CH} values ^a	
		$t_{cp} = 0.225$ ms ^b	$t_{cp} = 2.25$ ms	T_{CH} , ms	R_{CH} , ms ⁻¹
4,4'-Dimethylbiphenyl					
C-1,4	4	1.56	3.59	0.375 ± 0.105	2.667 ± 0.747
C-2,6;3,5	8	5.23	7.13	0.218 ± 0.036	4.587 ± 0.758
CH ₃	2	1.28	2.00	0.276 ± 0.076	3.623 ± 0.998
1,8-Dimethylnaphthalene					
aromatic	10	5.54	9.57	<i>c</i>	<i>c</i>
CH ₃	2	1.39	2.00	0.209 ± 0.036	4.785 ± 0.824
1,2-Bis(4-tolyl)ethane					
C-1	2	0.90	2.00	0.377 ± 0.087	2.653 ± 0.612
C-4	2	1.01	2.03	0.368 ± 0.058	2.717 ± 0.428
C-2,6;3,5	8	5.78	7.73	0.162 ± 0.033	6.173 ± 1.257
CH ₂	2	1.26	1.74	0.092 ± 0.033	10.870 ± 3.899
CH ₃	2	1.38	2.17	0.254 ± 0.056	3.937 ± 0.868
4-Butoxybenzoic acid					
C=O	1	0.47	1.10	0.410 ± 0.044	2.439 ± 0.262
C-4	1	0.45	1.00	0.478 ± 0.096	2.092 ± 0.420
C-2,6	2	1.42	1.78	0.137 ± 0.023	7.299 ± 1.225
C-1	1	0.37	1.00	0.546 ± 0.075	1.832 ± 0.252
C-3,5	2	1.72	1.99	0.119 ± 0.015	8.403 ± 1.059
α -CH ₂	1	0.83	0.92	0.087 ± 0.014	11.494 ± 1.850
β -CH ₂	1	0.86	0.93	0.100 ± 0.014	10.000 ± 1.400
γ -CH ₂	1	0.81	1.08	0.108 ± 0.027	9.259 ± 2.315
CH ₃	1	0.96	1.33	0.150 ± 0.026	6.667 ± 1.156
4-Butoxyphenol					
C-1 or C-4	1	0.32	1.00	0.453 ± 0.063	2.208 ± 0.307
C-4 or C-1	1	0.48	1.08	0.596 ± 0.068	1.678 ± 0.191
C-2,6;3,5	4	2.62	3.53	0.182 ± 0.026	5.495 ± 0.785
α -CH ₂	1	0.62	0.79	0.132 ± 0.036	7.576 ± 2.066
β -CH ₂	1	0.64	0.84	0.149 ± 0.033	6.711 ± 1.486
γ -CH ₂	1	0.71	0.83	0.132 ± 0.026	7.576 ± 1.492
CH ₃	1	0.76	1.21	0.265 ± 0.046	3.774 ± 0.655
(4-Ethoxyphenyl)acetic Acid					
C=O	1	0.45	1.02	0.387 ± 0.037	2.584 ± 0.247
C-4	1	0.37	1.00	0.440 ± 0.064	2.273 ± 0.331
C-2,6	2	1.41	1.80	0.133 ± 0.017	7.519 ± 0.961
C-1	1	0.45	0.99	0.334 ± 0.030	2.994 ± 0.269
C-3,5	2	1.52	1.97	0.144 ± 0.025	6.944 ± 1.206
OCH ₂	1	0.79	0.85	0.114 ± 0.013	8.772 ± 1.000
CH ₂ CO	1	0.72	1.00	0.136 ± 0.030	7.353 ± 1.622
CH ₃	1	0.90	1.14	0.153 ± 0.026	6.536 ± 1.111
Bis(3,5-di- <i>tert</i> -butyl-4-hydroxybenzyl) Ether ^d					
C-4	2	0.72	2.00	0.437 ± 0.091	2.288 ± 0.477
C-3,5	4	1.44	4.01	0.506 ± 0.063	1.976 ± 0.246
C(CH ₃) ₃	4	1.23	4.82	0.769 ± 0.126	1.300 ± 0.213
CH ₃	12	4.57	13.44	0.515 ± 0.141	1.942 ± 0.532
3,5-Diisopropylphenol					
C-1,3,5 ^e	3	1.40	2.73	0.310 ± 0.039	3.226 ± 0.406
C-2,6,4 ^f	3	1.97	2.73	0.179 ± 0.038	5.587 ± 1.186
CH ^g	2	1.41	2.00	0.201 ± 0.046	4.975 ± 1.139
CH ₃ ^g	4	2.96	4.30	0.213 ± 0.030	4.695 ± 0.661

^a For a description of the computer program, see: Mayne, C. L.; Alderman, D. W.; Grant, D. M. *J. Chem. Phys.* 1975, 63, 2514-2523. $R_{CH} = 1/T_{CH}$; $T_{1\rho}(H) \cong 50$ ms. ^b For 4,4'-dimethylbiphenyl, $t_{cp} = 0.200$ ms. ^c The six types of aromatic carbon atoms give overlapping signals. ^d C-1 and C-2,6 overlap. ^e The nonprotonated aromatic carbon atoms give four overlapping resonances, spread = 4.1 ppm. ^f The protonated aromatic carbon atoms give five (sometimes six) overlapping resonances, spread = 6.4 ppm. ^g The methine and methyl carbon atom resonances are not fully resolved, which limits the accuracy with which their relative intensities can be measured.

compounds. Two carboxylic acids, (4-ethoxyphenyl)acetic acid (6) and 4-butoxybenzoic acid (7), were studied. The results and representative spectra appear in Table II and Figures 3 and 4 for 6 and in Table III and Figures 5 and 6 for 7.

The data obtained for 4-butoxyphenol (8) and bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) ether (9) at the usual ten contact times

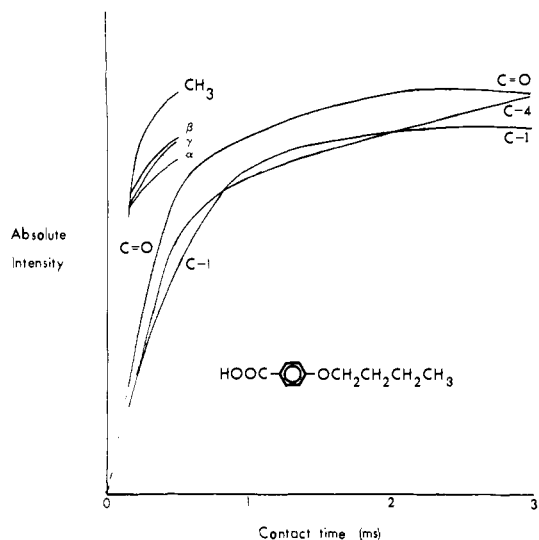


Figure 6. Rate of cross polarization of each of the nonprotonated carbon atoms in 4-butoxybenzoic acid. (For comparison, the initial rate of cross polarization of the protonated aliphatic carbon atoms is also shown.) While C=O and C-1 apparently achieve maximum absolute intensity at $t_{cp} \approx 2.25$ ms, C-4 apparently does not achieve maximum absolute intensity even after $t_{cp} = 3.000$ ms (Table IX, supplementary material). Nevertheless, relatively accurate signal intensities are obtained for C=O, C-1, and C-4 at contact times as short as about 1.00 ms (Table III).

(see Table I) are similar to those obtained with carboxylic acids 6 and 7 except for one feature of 9 that will be discussed briefly here and in more detail elsewhere. The data for 3,5-diisopropylphenol (10) were obtained at the usual ten contact times and also at contact times of 3.75, 4.50, 5.25, and 6.00 ms.

The data obtained on the eight compounds studied at ten or more contact times (1-3 and 6-10) were subjected to computer analysis to estimate values for T_{CH} , the time constant for cross polarization, for each type of carbon atom. The signal intensity (I) is a function of T_{CH} , of $T_{1\rho}(H)$, the proton spin lattice relaxation time in the rotating frame; of $T_{1\rho}(C)$, the carbon spin lattice relaxation time in the rotating frame; and of t_{cp} , the contact time.^{23,32} While an expression relating I , T_{CH} , $T_{1\rho}(H)$, $T_{1\rho}(C)$, and t_{cp} is available, the following simple expression^{33,34} neglects $T_{1\rho}(C)$ and is valid when $T_{1\rho}(C) > T_{1\rho}(H) \gg T_{CH}$:

$$I = C[\exp[-t_{cp}/T_{1\rho}(H)] - \exp[-t_{cp}/T_{CH}]]/[1 - T_{CH}/T_{1\rho}(H)] \quad (6)$$

where C is a constant of proportionality.

This expression appears adequate for estimating values of T_{CH} , especially if such values are used principally to compare parametrically relative rates of cross polarization for different types of functional groups.³⁵ With $T_{1\rho}(H)$ constrained to 50 ms, computer calculations for each type of carbon atom in 1-3 and 6-10 pro-

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(34) Methyl carbons are an example in which $T_{1\rho}(C)$ effects may not be negligible and therefore where more detailed calculations with the full expression³³ may be desirable.

(35) The observation, primarily in single crystals,³⁶ of a nonexponential, so-called "step" cross polarization of protonated carbons is at variance with the biexponential form of eq 6. These apparent "step" polarizations arise from a combination of coherent dipolar modulation terms that follow sinusoidal behavior and incoherent random spin relaxation terms best described with exponential laws. In our powders, we found that the exponential behavior dominates the response. Only a hint of coherent dipolar modulation has ever been observed superimposed on the exponential rate of cross polarization (e.g., see Figure 7). As such corrections barely exceed the experimental error, we content ourselves with eq 6 to characterize the dominant cross-polarization process.

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Table V. Summary of Computer-Fitted T_{CH} Values in Eight Compounds^a

functional group	T_{CH} in μ s (no. of calculations) when $T_{1\rho}(H)$ is			
	50 ms	unconstrained	20 ms	8 ms
methylene	87-149 (9)	97-107 (2)	100-172 (9)	136-235 (9)
Ar CH	119-218 (7)	127-216 (2)	134-236 (7)	177-292 (7)
isopropyl CH	201		228	308
methyl	150-276 (7)	308	167-295 (7)	214-381 (7)
	515 (<i>t</i> -Bu)		568 (<i>t</i> -Bu)	716 (<i>t</i> -Bu)
<i>t</i> -Bu quaternary	769	856	836	1022
nonprotonated aromatic	334-596 (11)	338-666 (6)	365-648 (11)	452-793 (11)
nonprotonated carbonyl	387-410 (2)	413	421-448 (2)	516-554 (2)

^a 4,4'-Dimethylbiphenyl, 1,2-bis(4-tolyl)ethane, 1,8-dimethylnaphthalene, (4-ethoxyphenyl)acetic acid, 4-butoxybenzoic acid, 4-butoxyphenol, bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) ether, and 3,5-diisopropylphenol.

Table VI. Effect of the Inclusion of I , t_{cp} Data at Longer Contact Times on the Computer-Fitted T_{CH} Values in 3,5-Diisopropylphenol

position	computer-fitted T_{CH} values, ms ^a	
	$0.15 \leq t_{cp} \leq 3.00$ ms	$0.15 \leq t_{cp} \leq 6.00$ ms
C-1;3,5 ^b	0.310 ± 0.039	0.345 ± 0.036
C-2,6;4 ^c	0.179 ± 0.038	0.210 ± 0.034
CH	0.201 ± 0.046	0.231 ± 0.039
CH ₃	0.213 ± 0.030	0.243 ± 0.030

^a $T_{1\rho}(H) \equiv 50$ ms. ^b The nonprotonated aromatic carbon atoms give four overlapping resonances. ^c The protonated aromatic carbon atoms give five (sometimes six) overlapping resonances.

duced the T_{CH} value that gave the best fit of the data through the ten (I , t_{cp}) data points. An example of such a fit appears in Figure 7. A summary of all the T_{CH} data so calculated appears in Table IV. Similar calculations were performed with $T_{1\rho}(H)$ constrained to 20 ms and to 8 ms. In addition, with both T_{CH} and $T_{1\rho}(H)$ unconstrained, computer calculations were attempted to generate for each type of carbon atom in 1-3 and 6-10 the pair of T_{CH} and $T_{1\rho}(H)$ values that gave the best fit of the data. A summary of the calculated T_{CH} values according to each functional group and as a function of $T_{1\rho}(H)$ (50, 20, 8 ms, or unconstrained) appears in Table V. With I vs. t_{cp} data available for 10 at four t_{cp} values >3 ms, we were able to obtain T_{CH} values from just the usual ten (I , t_{cp}) data points ($0.15 \leq t_{cp} \leq 3.00$ ms) and from all fourteen (I , t_{cp}) data points ($0.15 \leq t_{cp} \leq 6.00$ ms). Inclusion of data at longer contact times gave the same T_{CH} values within experimental error, although the larger data set appears to give slightly larger values. Table VI summarizes the results.

Discussion

The usefulness of studying spin-locked ^{13}C - 1H cross-polarization dynamics in a solid by using several contact times is well-known. This approach has been extensively used in π - π molecular complex,³⁷ biochemical,³⁸⁻⁴¹ polymer,^{7,13,16,42-47} fossil fuel,^{4,16,17,48-64}

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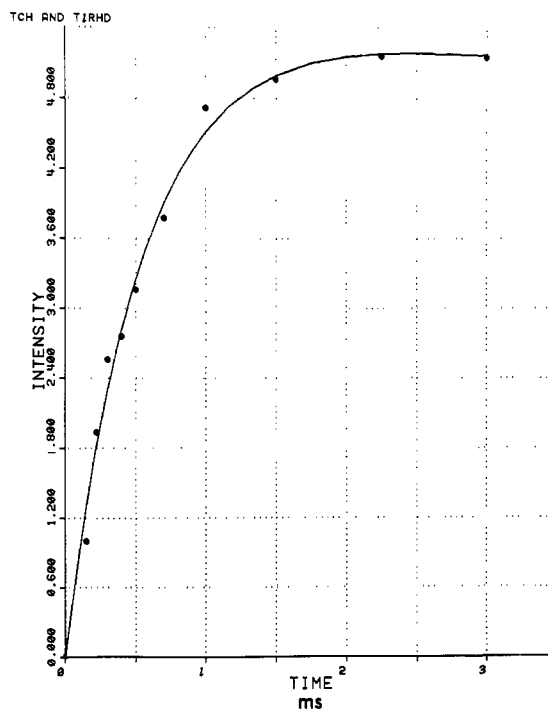


Figure 7. Computer-generated plot of the rate of cross polarization of ring C-1 in 4-butoxybenzoic acid, $T_{1\rho}(H)$ constrained to 50 ms.

zeolite,⁶⁵ and single-crystal³⁷ investigations. However, this approach apparently has been used to study ^{13}C - 1H cross-polarization dynamics in only one organometallic compound [tetracarbonyl-

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bis(cyclooctatetraene)triruthenium(0), $t_{cp} = 5$ and ≤ 2 ms¹² and three simple organic compounds [norbornadiene, numerous t_{cp} values;¹⁰ 4-(1-pyrenyl)butanoic acid, $t_{cp} = 0.5, 1.0, 2.0,$ and 3.0 ms;¹⁷ and 5-oxo-D-fructose (as a tricyclic, spiran dimer), $t_{cp} = 0.075$ and 1.8 ms⁶⁶]. This study probes the general applicability of the cross-polarization technique to a collection of small organic molecules.

If signal intensities are to be proportional to carbon atomic ratios, the ideal solid should have a uniform $T_{1\rho}(H)$ throughout, and $T_{1\rho}(C_i)$ and $T_{1\rho}(H)$ should be much longer than T_{CH} , the time constant for cross polarization of the i th carbon atom. Hence, all carbon atoms would polarize fully before relaxing at similar rates.^{4,5} A limited amount of data on $T_{1\rho}(H)$ at ambient temperature is available (mostly on polymers). For a series of 4,4'-disubstituted azobenzenes, $T_{1\rho}(H)$ generally is at least 30 ms,⁶⁷ while for polymers, $T_{1\rho}(H)$ usually ranges from 3 to 8 ms^{7,16,68-72,74} but occasionally is substantially longer^{7,71} or shorter.⁷⁵ Moreover, $T_{1\rho}(H)$ is sensitive to molecular motion and the efficiency of spin diffusion among the protons.^{4,5,7,16,70,71,76,77} As two simple organic compounds give accurate relative signal intensities with $t_{cp} \leq 3$ ms,¹⁷ several contact times ≤ 3 ms were selected to determine the rate at which the intensity of the ¹³C signals generated by cross polarization typically reaches a maximum.⁷⁸ The previously reported T_{CH} values, even for nonprotonated carbon atoms, appeared to be short enough to indicate that substantial cross polarization usually occurs for many compounds before $T_{1\rho}(H)$ processes begin to compete. The T_{CH} data (available only on polymers) indicated that T_{CH} for methine and methylene carbon atoms usually ranges from ≈ 15 to $50 \mu\text{s}$ ^{7,24,68,69} and that T_{CH} for protonated aromatic carbon atoms ranges from ≈ 45 to $100 \mu\text{s}$.^{7,68,79} Furthermore, these T_{CH} values are essentially independent of the rate of sample rotation.^{7,29,68,80} In contrast, the very limited amount of methyl T_{CH} data available indicated that T_{CH} ranges from ≈ 80 to $160 \mu\text{s}$ and increases slightly at faster rotation rates (≈ 3 kHz).^{68,81} The very limited amount of quaternary aliphatic, nonprotonated aromatic, or nonprotonated carbonyl T_{CH} data available indicates that $T_{CH} \approx 300 \mu\text{s}$ and that these values increase by about 50% at faster (≈ 3 kHz) rotation rates.^{68,80,81} Motion within the molecule also strongly affects T_{CH} values. More mobile carbon atoms generally take longer to cross polarize because molecular motion attenuates the ¹³C-H and the ¹H-H dipolar interactions^{13,38,39,41,44,57,76,81,82} (cf. T_{CH} for a spinning methyl group with T_{CH} for methine or methylene). This is reinforced by the observation that carbon atoms exhibiting too much mobility may not give a cross polarized signal.^{33,65,70,83}

Even though the five arenes studied exhibit substantial differences in their cross polarization and relaxation properties, all give accurate signal intensities. The results suggest that a contact time of about 2.25 ms is optimal for arenes.

Of the three arenes studied at a variety of contact times, only 4,4'-dimethylbiphenyl (**1**) exhibits resonances that all achieve maximum intensity at $t_{cp} \approx 0.7$ ms and that remain essentially constant over the range $0.7 \leq t_{cp} \leq 3.0$ ms. At $t_{cp} = 2.25$ ms, the nonprotonated aromatic carbon atoms give 28.2% of the total signal intensity;⁸⁶ the protonated aromatic carbon atoms, 56.1%;⁸⁶ and the methyl carbon atoms, 15.7%, as compared with the ideal values based on atomic ratios of 28.57%, 57.14%, and 14.29%, respectively. In contrast, neither 1,2-bis(4-tolyl)ethane (**2**) nor 1,8-dimethylnaphthalene (**3**) exhibits resonances that achieve maximum intensity by $t_{cp} = 3.00$ ms (Table VII, supplementary materials). Increasing t_{cp} from 2.25 to 3.00 ms in **2** results in the methyl signal increasing by 12% and the absolute intensity of each of the other signals by about 4% (Table VII). Increasing t_{cp} from 1.00 to 3.00 ms in **3** results in a 5% increase in the absolute methyl signal intensity and a 16% increase in the absolute aromatic signal intensity. The latter, relatively large increase in percentage may result from four of the ten aromatic carbon atoms being nonprotonated. Moreover, one of these four carbons also is three bonds from the nearest intramolecular proton and with relatively low intermolecular cross polarization rates is found to have a relatively long T_{CH} value. Nevertheless, accurate relative signal intensities are still obtained at $t_{cp} = 2.25$ ms (Tables I and IV)⁸⁷ even though the total polarization transfer was not complete in each compound. Regardless of the contact time, **1-3** all consistently give methyl signals that are relatively higher than the corresponding atomic ratios; the methylene signal percentages in **2** are correspondingly lower (Table I). Methyl and methylene groups typically give such results, as will be shown.

Spectra of 2,6-dimethylnaphthalene (**4**) and 9,10-dimethylanthracene (**5**) obtained under conditions very similar to those used with **1-3** give much lower S/N ratios. Lengthening the delay between the end of data acquisition and the start of another pulse sequence indicates whether this S/N limitation results from a very

(83) In some circumstances, increasing the mobility of a carbon atom may actually increase the signal intensity. For example, the CP/MAS spectrum of the diglycidyl ether of bisphenol-A cured with piperidine exhibits at 151 K a broad methyl carbon signal, at 305 K exhibits a sharper and more intense signal, and at 352 K exhibits a much sharper and more intense signal. As the methyl reorientation slows down, $T_{1\rho}(C)$ for the methyl carbons decreases, and the decoupler cannot eliminate the rapidly fluctuating carbon-proton dipolar fields. Since methyl group rotation has an extremely low activation energy relative to other kinds of molecular motion, lowering the temperature from 305 to 151 K corresponds to a change from very fast motion to motional frequencies on the order of the irradiating rf (ω_{IH}). Therefore, at low temperature, the line width contribution from molecular motion is very large, and the methyl carbon signal may appear as a broad hump in the base line. At a temperature far enough below 151 K for the motional frequencies to be substantially less than ω_{IH} , the methyl carbon signal should reappear,¹⁹ as has been shown for the methyl carbon signal in poly(methyl methacrylate),¹⁹ polypropylene,² and the methylene and methine carbon signals in adamantane.²⁰ Additional examples of motional broadening at low temperatures^{20,84} and at a phase transition at ambient temperature⁸⁵ have appeared and indicate that when motional broadening does occur, the resonances for protonated carbons are broadened much more than the resonances for nonprotonated carbons.^{19,20,84} In addition to motional modulation of carbon-proton coupling, significant line broadening is also possible in the vicinity of $T_{1\rho}(H)$ minima. Since $T_{1\rho}(H)$ is determined by the spectral density of magnetic fluctuations at ω_{IH} , a change in the spin-locking field strength or a change in the temperature can alter $T_{1\rho}(H)$.^{2,5,16,19,77} Nevertheless, as our results and others indicate, significant line broadening resulting from motional modulation of carbon-proton coupling or from very short $T_{1\rho}(H)$ values usually does not present a serious problem with relatively simple compounds.

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short $T_{1\rho}(\text{H})$ or a very long $T_1(\text{H})$. Spectra of **4** and **5** obtained with a 60-s delay instead of the usual 3-s delay exhibit much higher S/N ratios (Figure 2), indicating that each of these compounds has a relatively long $T_1(\text{H})$. In spite of the $T_1(\text{H})$ limitation, full-scale plots of **4** obtained with only a 3-s delay give accurate relative signal intensities compared with atomic ratios. For example, at $t_{\text{cp}} = 2.25$ ms the relative signal intensities are 84.2% for the aromatic carbons and 15.8% for the methyl carbons (ideal values 83.33% and 16.67%).⁸⁸ Because the T_{CH} values are short enough for full polarization to occur and because the protons seem to have a common $T_1(\text{H})$, the carbon signal intensities are merely attenuated but not distorted significantly in relative intensity.^{16,33} The proton spin temperature in a domain of small radius around each ^{13}C atom becomes uniform after a few seconds of delay, even when the delay is much less than $T_1(\text{H})$. With a 60-s delay, only $t_{\text{cp}} = 3.00$ ms was used. The corresponding relative signal intensities were 83.1% and 16.9%. For 9,10-dimethylanthracene (**5**), the value of $T_1(\text{H})$ is long enough to prevent measuring accurate signal intensities with a 3-s delay. With $t_{\text{cp}} = 3.00$ ms and a 3-s delay, only 7.5% of the total signal intensity is present in the spectrum of **5** compared with a 60-s delay. With a 60-s delay, only $t_{\text{cp}} = 3.00$ ms was used. The relative intensities are 87.6% for the aromatic carbons and 12.4% for the methyl carbons (ideal values 87.5% and 12.5%).⁸⁸ Clearly, in spite of the unusually rapid rotation of the methyl groups resulting from the low 6-fold barrier to rotation,⁸⁹ significant distortions in the relative intensities are not encountered. It is interesting to note that while spectra of 9,10-dimethylanthracene (**5**) suffer from a relatively long $T_1(\text{H})$, spectra of anthracene also obtained at room temperature suffer from a very short $T_{1\rho}(\text{H})$;¹⁶ however, a spectrum is readily obtained at 140 K.¹⁶

Why $T_1(\text{H})$ for the 2,6-dimethyl isomer **4** is so much longer than $T_1(\text{H})$ for the 1,8-dimethyl isomer **3** has not yet been explained. Brown has very recently reported large variations in $T_1(\text{H})$ with only small variations in structure.⁹⁰ Perhaps, paramagnetic impurities are present in **3**, although the $^{13}\text{C}\{^1\text{H}\}$ spectrum of **3** in CDCl_3 (40° pulse every 6 s) exhibits much weaker resonances for the nonprotonated carbon atoms and does not exhibit any broadened resonances. Clearly, doping **4** and **5** with a paramagnetic species to shorten $T_1(\text{H})$ would be beneficial.^{16,90-92} Alternatively, flipping the proton magnetization back along B_0 at the conclusion of data acquisition could be done.⁹³

Carboxylic acids **6** and **7** exhibit similar cross-polarization behavior (Tables VIII and IX, supplementary material, and Figures 4 and 6). The results suggest that a contact time of ≈ 1.00 ms is optimal. However, for $0.7 \leq t_{\text{cp}} \leq 2.25$ ms, the changes in the percentage contribution of each signal are so slight that for either acid, the standard relative error from ideality per resonance is often $< 10\%$ for $t_{\text{cp}} \geq 0.7$ ms (Tables II and III).

Tables VIII and IX (supplementary material) clearly show, as expected, that rotating methyl carbons polarize more slowly than the methylene carbons. Figures 4 and 6 clearly show that the nonprotonated carbon atoms polarize much more slowly than the protonated carbon atoms. The three types of nonprotonated carbon atoms clearly polarize at similar rates (Figures 4 and 6), which is not surprising since in poly(*p*-oxybenzoyl) C=O and C-O polarize at similar rates.¹³ In each acid, the carbonyl carbon atom achieves maximum signal intensity at $t_{\text{cp}} \approx 2.25$ ms. This might be expected since T_{CH} for the carbonyl carbon atom in poly(methyl methacrylate) is $\approx 300 \mu\text{s}$,⁸¹ and the carbonyl carbon atom achieves maximum signal intensity at $1 < t_{\text{cp}} < 3$ ms.⁷ Although ring C-O in 4-butoxybenzoic acid (**7**) polarizes more slowly than ring C-O in (4-ethoxyphenyl)acetic acid (**6**), neither C-O reso-

nance achieves maximum signal intensity at $t_{\text{cp}} < 2$ ms. Again, this is not surprising in light of the slow rate at which C-O-C in poly(2,6-dimethylphenylene oxide) polarizes.⁷

Both **6** and **7** exhibit more resonances than are found in the $^{13}\text{C}\{^1\text{H}\}$ spectra of these compounds in solution. Over 60 such examples involving polymers,^{7,8,13,33,47,84,94-101} a wide variety of simple organic^{1,9,15,67,97,102-111} and organometallic^{109,112} compounds, and carbonium ions^{2,113} are known. The multiplicity of resonances indicates that the crystalline environment is removing the nominal spatial equivalence found for carbon atoms related to each other by unimolecular symmetry elements. Comparing the solution and solid chemical shift data for **6** shows that in the solid, a slight splitting is evident for C-2,6, while a pair of resonances separated by 6.0 ppm is present for C-3,5. Such a lifting of the degeneracy in para-substituted benzenes is well documented.^{1,7,13,33,67,69,84,97,103,105,108} However, merely comparing the solution and solid chemical shift data for **7** does not permit a secure assignment of the C-1, C-2,6, and C-3,5 resonances in the solid. The multiple contact time studies suggest that only the resonance at 118.9 ppm results from C-1 (a nonprotonated carbon atom) because the other four upfield aromatic resonances are much more intense at short contact times (Table IX, supplementary material). An experiment that discriminates against carbon atoms strongly coupled to protons^{114,115} verifies the assignment (Figure 5). Only a few cases of a single type of carbon atom giving three or more resolved signals in the solid spectrum apparently have been reported.^{15,84,97,104,107,109} Clearly, small line-broadening factors improve the resolution and the accuracy with which the intensity of overlapping resonances can be measured.

As in the carboxylic acids, 4-butoxyphenol (**8**) and bis(3,5-di-*tert*-butyl-4-hydroxybenzyl) ether (**9**) give the most accurate relative signal intensities at a contact time of ≈ 1.00 ms. The quaternary aliphatic carbon atoms in **9** give a pair of resonances separated by 1.7 ppm. The most striking aspect of any of the 14 spectra of 3,5-diisopropylphenol (**10**) ($0.15 \leq t_{\text{cp}} \leq 6.00$ ms) is the appearance of four overlapping resonances, spread by 1.9 ppm, for the methyl carbon atoms. While several examples are known of a methyl carbon atom giving two^{13,15,84,94,97,103,107,112} or three¹⁰⁹ resonances, **10** apparently is only the second example of a methyl

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carbon atom giving four resonances.¹⁰⁷ While the methine and methyl carbon atom resonances in **10** are not fully resolved, all the isopropyl signals for leucine overlap and give just one broad resonance.¹⁰⁵

The T_{CH} data given in Tables IV–VI and obtained from computer analysis provide a quantitative basis for the generalizations enumerated in this study. It has been noted that signal intensities that agree with atomic ratios can often be obtained with a contact time as short as about 1 ms. In this instance, $T_{1\rho}(H)$ is much longer than even the longest calculated T_{CH} value, as is evident from the relative insensitivity of T_{CH} when $T_{1\rho}(H)$ ranges from 8 to 50 ms.¹¹⁶ Thus, after a period of 3 times the longest T_{CH} value in a given compound, at least 95% of the maximum signal intensity has been achieved for each type of carbon. Accordingly, since the nonprotonated aromatic and carbonyl carbons often have T_{CH} values ≤ 0.4 ms (Table V), these carbons should exhibit 95% of their maximum signal intensity after ≤ 1.2 ms. Clearly, this is consistent with the observation of accurate relative signal intensities at $t_{cp} = 1$ ms even though the cross polarization may not be fully developed. On the other hand, some nonprotonated carbons were observed with a T_{CH} value of ≈ 0.6 ms (Table V) and would require ≈ 1.8 ms to achieve 95% of their maximum signal intensity. In this case, accurate relative signal intensities are obtained for a t_{cp} of 2.25 ms, a time that is still short compared to competing processes [i.e., $T_{1\rho}(H)$ and $T_1(H)$].

Thus, the data in Table VI strongly suggest that use of $t_{cp} \approx 1$ –2 ms will be entirely adequate in general for most moderate to small organic molecules. Accordingly, it is encouraging to note that the relative signal intensities in spectra of plasma-polymerized hydrocarbons are insensitive to the contact time used for $0.8 \leq t_{cp} \leq 3.0$ ms.⁴⁶ Similarly, marked changes are usually not observed in coal spectra obtained with $t_{cp} \geq 1$ ms.^{16,17,57,117}

The T_{CH} data for polymers^{7,24,68,69,79–81} and simple organic compounds are similar in that T_{CH} values decrease in the order nonprotonated carbon > methyl carbon > protonated aromatic carbon > methylene carbon. This was given a theoretical basis in the Theoretical Considerations. However, these data suggest that for the same functional group, T_{CH} is longer in a simple organic compound than in a polymer. The rate of cross polarization depends on a variety of factors: the nature of lattice motions, the spinning rate (especially for nonprotonated carbon atoms), and the exactness of the Hartmann–Hahn match.¹⁸ Furthermore, the signal intensities obtained with polymers are more sensitive to the magnitude of the rf fields employed because polymers have comparatively short $T_{1\rho}(H)$ values.^{19,75} In addition, different investigators have calculated T_{CH} values in somewhat different ways. Thus, conclusions regarding T_{CH} values must be made with some caution.

Finally, *tert*-butyl methyl carbons have a much longer T_{CH} value than other methyl carbon atoms (Table V), and similarly, the *tert*-butyl quaternary carbon has a considerably longer T_{CH} value than found for nonprotonated aromatic carbons (Table V). Rapid rotation about the C_3 axis of each methyl group and about the C_3 axis of the *tert*-butyl group strongly attenuates the ^{13}C – 1H and 1H – 1H dipolar interactions and thus reduces the rate at which the methyl and quaternary carbons polarize.

(116) Indeed, the data suggest that for simple organic compounds, $T_{1\rho}(H)$ often is between about 20 and 50 ms (Table V), which is consistent with the $T_{1\rho}(H)$ values generally found (≥ 30 ms) in a series of 4,4'-disubstituted azobenzenes.⁶⁷ Measurements at longer t_{cp} values are required to calculate $T_{1\rho}(H)$ more precisely. For example, the shape of the best curve through the ten (t_{cp}) data points for ring C-1 in 4-butoxybenzoic acid (**7**; Figure 7) does not change much whether $T_{1\rho}(H)$ is 50, 20, 8, or 31.34 ms [the latter calculated when $T_{1\rho}(H)$ is not constrained].

(117) Unpublished results, this laboratory.

Conclusions

CP/MAS ^{13}C NMR spectra obtained on a variety of organic compounds clearly show that accurate relative signal intensities can be obtained in general with contact times of 2.25–3.00 ms and often with contact times as short as about 1 ms. The T_{CH} values obtained from a computer fit of the data are consistent with these experimental results. Heteroatoms other than oxygen were not included in this study to preclude complications resulting from quadrupolar interactions. Since **1**–**10** contain a variety of simple organic functional groups (protonated and nonprotonated aromatic carbons and quaternary, methine, methylene, and methyl carbons), the results suggest that one may obtain quantitative CP/MAS ^{13}C NMR spectra of diamagnetic solids. However, no reports yet exist on cross-polarization dynamics in compounds for a carbon atom that is four or more bonds from the nearest intramolecular proton and that has no efficient intermolecular protons for cross polarization. Since the cross-polarization rates depend upon the magnitude of the ^{13}C – 1H dipolar interaction, such carbon atoms would polarize very slowly. The spectrum of acenaphthene, $t_{cp} = 1.5$ ms, displays signal intensities for the C-2a/C-8a pair and C-8b (three bonds from the nearest intramolecular proton) that are accurate to within 1%.¹⁷ 1,8-Dimethylnaphthalene (**3**), the only compound of the ten reported here containing a carbon atom three bonds from the nearest intramolecular proton, also gives accurate signal intensities.⁸⁷ Thus, either the intramolecular cross-polarization rate is adequate for these cases or intermolecular polarization transfer is providing an efficient mechanism. While these facts are highly encouraging, an investigation of the cross-polarization dynamics of a *tetrahedrally buried* carbon atom at least three bonds from the nearest intramolecular proton, so as to minimize any intermolecular cross polarization,^{10,23,37,70,118} is desirable. Similarly, investigation of the cross-polarization dynamics of other nonprotonated carbon atoms in proton-dilute samples could also be interesting. Because the equation for T_{CH} contains an r_{CH}^6 dependence,²¹ it is the distance between a carbon atom and the nearest proton, not necessarily the number of bonds between them, that really needs to be considered.¹¹⁹

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Registry No. **1**, 613-33-2; **2**, 538-39-6; **3**, 569-41-5; **4**, 581-42-0; **5**, 781-43-1; **6**, 4919-33-9; **7**, 1498-96-0; **8**, 122-94-1; **9**, 6922-60-7; **10**, 26886-05-5.

Supplementary Material Available: Absolute intensity of the signals for **2**, **6**, and **7** as a function of contact time (Tables VII–IX) (3 pages). Ordering information is given on any current masthead page.

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(119) **Note Added in Proof:** Several recent papers^{120–122} provide additional examples of accurate relative signal intensities with $t_{cp} = 1.0$ to 1.5 ms. Dipolar dephasing experiments¹¹⁷ on 4-butoxybenzoic acid (**7**) with $t_{cp} = 3.00$ ms show that the extra 0.5% of signal intensity assigned to C-1 (Figure 5) should be assigned to C-3,5. With respect to the large difference in $T_1(H)$ for 2,6-dimethylnaphthalene (**4**) and 1,8-dimethylnaphthalene (**3**), another paper¹²³ indicates that 1,5-dimethylnaphthalene and **3** have $T_1(H)$ values ≈ 6 and ≈ 3 s, respectively, and have unequal barriers to methyl rotation.

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