Cross Polarization and Magic Angle Sample Spinning NMR Spectra of Model Organic Compounds. 2. Molecules of Low or Remote Protonation

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Abstract: Cross polarization/magic angle sample spinning (CP/MAS) ^{13}C NMR spectra were obtained at various contact times on five solid organic compounds containing carbon atoms far from intramolecular protons or containing very few hydrogen atoms. Carbon atoms four or more bonds from the nearest intramolecular proton cannot be fully polarized before $T_{1\rho}(H)$ effects begin to dominate the proton magnetization. Rapid molecular motion aggravates the problem because of motional attenuation of the dipolar interaction. Computer-fitted T_{CH} and $T_{1\rho}(H)$ parameters are consistent with these experimental results. The simple theories of cross polarization account for incomplete polarization in these cases. In 1,2:4,5-benzenetetracarboxylic dianhydride, $C_{10}H_2O_6$, the relative aromatic and carbonyl signal intensities are only 5% from the ideal values on the basis of atomic ratios, but absolute intensities can be seriously reduced. In general, CP/MAS NMR provides a convenient and useful quantitative method for studying diamagnetic, organic solids of low molecular weight that is competitive to other physical methods even for molecules of low or remote protonation.

Introduction

The results in the preceding paper[1] show that highly protonated, organic diamagnetic solids can give relative signal intensities that agree with atomic ratios. However, certain highly protonated compounds contain carbon atoms in environments that have not yet been studied by CP/MAS NMR. The cross-polarization dynamics of a tetrahedrally buried carbon atom (at least three bonds from the nearest intramolecular proton) provide information on the effective magnitude of the ^{13}C–^{1}H dipolar interaction experienced by a carbon nucleus for which intermolecular cross polarization[2-7] should be particularly unfavorable. An investigation of the cross-polarization dynamics of any carbon atom removed by several angstroms from the nearest proton is equally desirable as a way to study the structural limitations for the normally dominant intramolecular cross-polarization process. This is because the equation for T_{CH}, the time constant for cross polarization, contains an $r_{CH}{}^6$ term.[8] Thus, it is really the distance between a carbon atom and the nearest proton, and not the number of bonds between them, that affects the dipolar interaction.

Compounds containing very few hydrogen atoms provide a probe of the structural limitations not only of the important intramolecular cross polarization but also of the effect of spin dilution upon intermolecular spin–spin interactions. The spectra of five compounds of either remote or low protonation show that accurate relative signal intensities cannot always be obtained. The theory of cross polarization offers a rationale for these observations.[8,9]

Theoretical Considerations

In the previous paper,[1] it was demonstrated that carbon atoms should polarize according to the following relative rates, based on the theoretical model of Demco et al.:[8] CH_3(static) > CH_2 > CH ≃ CH_3(rotating) > C(nonprotonated). Except for the failure to observe a static methyl, data in that paper verified this theoretical model. Thus, it was shown that when a carbon has one or more directly bonded protons, the dominant feature in the CP becomes the r^{-6} distance dependence and the number of directly bonded protons. In these cases, all other remote protons become negligible in their effect on the carbon spin.

In contrast, if the carbon is nonprotonated, this model begins to break down as the average distance increases to the nearest protons (intramolecular or intermolecular). Such conditions will unavoidably obtain for some carbons in systems where the proton concentration becomes very dilute. In these instances, the ^{13}C–^{1}H dipolar interaction is definitely reduced, and T_{CH} may become so long that these carbons cannot polarize to the same extent as carbons having proximate protons. Quantitative measures of the various structural moieties may no longer be reliable in such molecules. Furthermore, the proton spin diffusion processes also become considerably less efficient in proton-dilute samples, and this mechanism of replenishing the spin magnetization of protons closest to the observed carbon-13 nuclei also becomes limited. The lack of proper proton–proton spin diffusion decreases the effectiveness and the linearity of the cross polarization in successive proton–carbon Hartman–Hahn[10] spin matches. This would require longer delay periods for the spin system to approach either thermodynamic equilibrium or acceptable steady-state conditions that will provide carbon-13 signals that respond linearly with the atomic ratios.

Further complications are encountered for nonprotonated carbons. First, the sum over remote protons discussed in the previous paper[1] does not enjoy the sharp cutoff feature possessed by directly bonded protons because now the distances of various interacting protons to the carbon-13 of interest become comparable, and therefore the $r_{CH}{}^{-6}$ function does not discriminate between such remote protons. Furthermore, intermolecular interactions may now be comparable or even larger than remote intramolecular interactions. Nonetheless, it is unlikely that intermolecular interactions will ever exceed the interactions encountered for a carbon separated from an intramolecular hydrogen by one or two bonds unless rapid internal motion makes these intramolecular interactions totally ineffective. The theory in this proton-dilute limit rapidly becomes very difficult to apply, and

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[1] Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.*, preceding paper in this issue.

[2] Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–590.

[3] Alla, M.; Lippmaa, E. *Chem. Phys. Lett.* **1976**, *37*, 260–264.

[4] Schaefer, J.; Sefcik, M. D.; Stejskal, E. O.; McKay, R. A. *Macromolecules* **1981**, *14*, 188–192.

[5] Blann, W. G.; Fyfe, C. A.; Lyerla, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 4030–4033.

[6] Ripmeester, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 289–290.

[7] While two reports[2,3] do indicate that the carbon atoms in adamantane[2] and norbornadiene[3] experience only intermolecular cross polarization, these are very special cases. Norbornadiene is nearly spherical, adamantane is spherical, and both rapidly tumble, which averages the intramolecular dipolar coupling to zero. Consequently, only much slower intermolecular cross polarization can occur.

[8] Demco, D. E.; Tegenfeldt, J.; Waugh, J. S. *Phys. Rev. B* **1975**, *11*, 4133–4151.

[9] Cheung, T. T. P.; Yaris, R. *J. Chem. Phys.* **1980**, *72*, 3604–3616.

[10] Hartmann, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042–2053.

[11] Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra: A Collection of Assigned, Coded, and Indexed Spectra"; Wiley-Interscience: New York, 1972.

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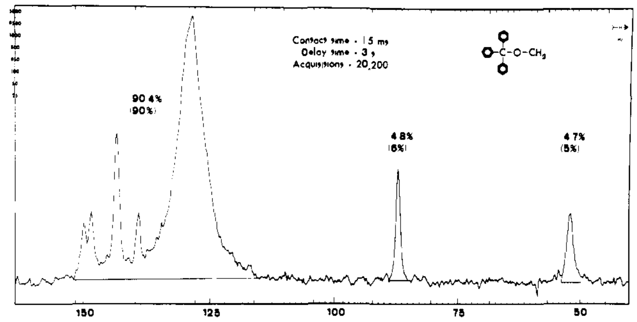

Figure 1. Expanded region from a 25.15-MHz, 2K, CP/MAS ^{13}C NMR spectrum of **1**, methyl trityl ether, obtained with a spectral width of 10000 Hz (398 ppm) and a frequency resolution of 4.9 Hz: acquisition time = 0.2000 s; line broadening = 5 Hz. The four resonances furthest downfield (probably resulting from C-1) clearly indicate crystalline nonequivalence of different molecules. 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 of the first paper[1]).

Table I. Relative Signal Intensities in Methyl Trityl Ether as a Function of Contact Time

contact time, ms	rel intensities: aromatic	trityl	methoxy	std error,[a] %	std rel error,[a] %
	Theoretical				
	90	5	5		
	Experimental				
3.000	90.4	4.4	5.2	0.4	7.3
2.250	90.2	5.5	4.3	0.5	9.9
1.500	90.4	4.8	4.7	0.3	4.2
1.000	91.9	3.8	4.3	1.4	16.1

[a] As defined in Table I of the preceding paper.[1]

about all that one can conclude with any certainty is that for nonbonded carbons three or more bonds from an intramolecular proton, the cross-polarization rate will be slow and probably not exceed greatly, if at all, relatively inefficient intermolecular cross-polarization rates.

Finally, in the absence of proximate protons, not only is the relaxation process controlled by remote protons that contribute to the autocorrelation relaxation term but now, because of relatively smaller subtended angles between two protons and the perturbed carbon, the cross correlation terms in eq 4 of the previous paper[1] become larger, approaching in magnitude the corresponding autocorrelation term. This complication can be expected to distort the linear response of the cross-polarization rate with the number of effective hydrogens. Thus, for nonbonded carbons, there are probably as many cases as there are unique crystal structures, and no simple rules exist for estimating the magnitude of T_{CH}. However, when the nonbonded carbon is both separated intramolecularly by several normal bond distances and is in a relatively dilute-proton environment, significant deviations from behavior that is quantitative in the number of carbons can generally be anticipated.

Results

Spectra of five compounds were obtained as previously described. One compound, methyl trityl ether (**1**), contains a tetrahedrally buried carbon atom three bonds from the nearest proton. Three compounds contain a carbon atom at least four bonds from the nearest intramolecular proton: di-*tert*-butyl oxalate (**2**), diphenylcyclopropenone (**3**), and tetraphenylphthalic anhydride (**4**). One compound contains very few hydrogen atoms, 1,2:4,5-benzenetetracarboxylic dianhydride (**5**), even though all carbons are within three bonds of at least one proton.

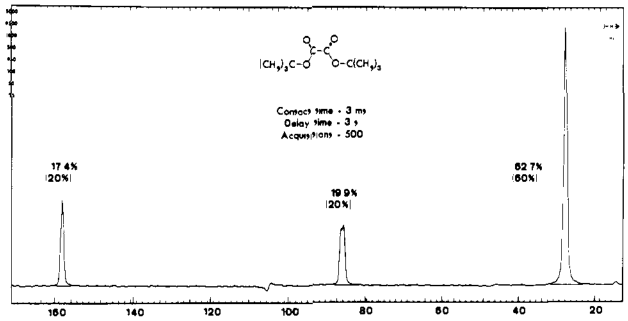

Figure 2. Expanded region from a 25.15-MHz, CP/MAS ^{13}C NMR spectrum of **2**, di-*tert*-butyl oxalate, obtained with a spectral width of 10000 Hz (398 ppm): acquisition time = 0.1000 s; line broadening of 5 Hz applied before spectrum was zero-filled to 2 K for a frequency resolution of 4.9 Hz. A slight splitting is evident for the quaternary aliphatic carbon atom. The I_{exptl} and I_{theor} values (in parentheses) are given.

Table II. Relative Signal Intensities in Di-*tert*-butyl Oxalate as a Function of Contact Time

contact time, ms	rel intensities: carbonyl	quaternary	methyl	std error,[a] %	std rel error,[a] %
	Theoretical				
	20	20	60		
	Experimental				
6.000	15.8	18.0	66.2	4.5	14.7
5.250	16.4	18.7	64.9	3.6	12.0
4.500	17.1	19.5	63.3	2.6	9.1
3.750	16.9	19.3	63.8	2.9	9.9
3.000	17.4	19.9	62.7	2.2	7.9
2.250	16.8	19.4	63.8	2.9	10.1
1.500	15.3	19.6	65.1	4.0	14.5
1.000	14.6	19.7	65.7	4.5	16.5
0.700	12.6	18.2	69.2	6.9	23.7
0.500	11.2	15.4	73.4	9.6	31.4
0.400	9.1	12.8	78.1	12.9	41.5
0.300	8.0	11.3	80.7	14.7	47.2
0.225	7.1	10.7	82.2	15.8	50.6
0.150	7.3	11.3	81.4	15.2	49.0

[a] As defined in Table I of the preceding paper.[1]

Table III. Computer-Fitted T_{CH}, R_{CH}, and $T_{1\rho}(\text{H})$ Values in Di-*tert*-butyl Oxalate

carbon atom	T_{CH}, ms	R_{CH}, ms^{-1}	$T_{1\rho}(\text{H})$, ms
carbonyl	2.938 ± 0.198	0.340 ± 0.023	2.941 ± 0.180
quaternary	1.483 ± 0.241	0.674 ± 0.110	5.119 ± 1.120
methyl	0.430 ± 0.052	2.326 ± 0.281	26.82 ± 11.74

Table IV. Absolute Intensity of the Signals for Diphenylcyclopropenone as a Function of Contact Time

contact time, ms	absolute intensity: carbonyl	alkenes	aromatics	all signals	rel intensity of all signals
4.500	1.14	2.41	12.85	16.40	42.9
3.750	1.30	3.29	17.47	22.06	57.7
3.000	1.58	4.07	23.01	28.66	74.9
2.250	1.60	3.80	24.63	30.03	78.5
1.500	1.61	3.78	28.30	33.69	88.1
1.000	1.28	3.37	33.59	38.24	100
0.700	1.00	2.31	28.64	31.95	83.6

A representative spectrum for **1** is given in Figure 1, and the relative line intensities as a function of contact time, t_{cp}, appear in Table I. The relative signal intensities in the spectra for **2** (Figure 2 is representative) as a function of t_{cp} appear in Table II. The absolute intensity data (Table VIII, supplementary material) were analyzed with a computer[1] to estimate values of T_{CH} and $T_{1\rho}(\text{H})$ for each type of carbon atom, and these fitting parameters are given in Table III. The success of the computer fits is graphically illustrated in Figure 3.

The results obtained on **3** are presented in Tables IV and V. The signal intensities clearly are very sensitive to the contact time. At $t_{\text{cp}} \simeq 1.50$ ms, the carbonyl carbon atom achieves maximum

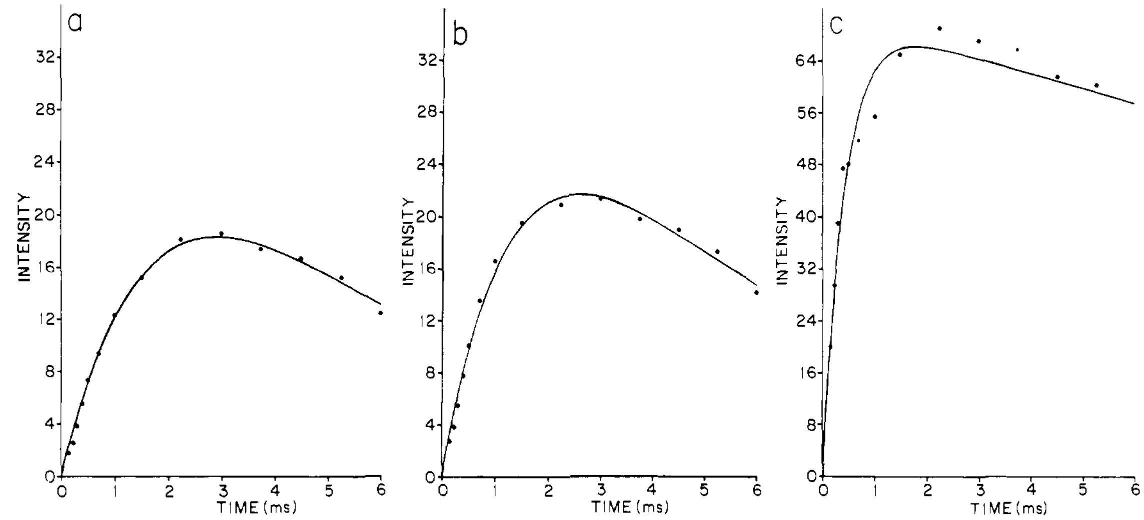

Figure 3. Computer-generated plot of the rate of cross polarization of the (a) carbonyl, (b) quaternary aliphatic, and (c) methyl carbon atoms in di-*tert*-butyl oxalate (the vertical scale in c differs by a factor of 2).

Table V. Relative Signal Intensities in Diphenylcyclopropenone as a Function of Contact Time

contact time, ms	rel intensities carbonyl	alkenes	aromatics	std error,[a] %	std rel error,[a] %
	Theoretical				
	6.67	13.33	80.00		
	Experimental				
4.500	7.0	14.7	78.3	1.3	6.7
3.750	5.9	14.9	79.2	1.1	9.5
3.000	5.5	14.2	80.3	0.9	10.8
2.250	5.3	12.7	82.0	1.4	12.3
1.500	4.8	11.2	84.0	2.8	18.9
1.000	3.3	8.8	87.9	5.6	35.6
0.700	3.1	7.2	89.6	6.9	41.3

[a] As defined in Table I of the preceding paper.[1]

Table VI. Computer-Fitted T_{CH}, R_{CH}, and $T_{1\rho}(H)$ Values in Diphenylcyclopropenone

functional group	T_{CH}, ms	R_{CH}, ms^{-1}	$T_{1\rho}(H)$, ms
carbonyl	2.139 ± 0.001[a]	0.468 ± 0.000[a]	2.139 ± 0.001[a]
alkene	2.093 ± 1.031	0.478 ± 0.235	2.090 ± 0.945
aromatic[b]	0.436 ± 0.131	2.294 ± 0.689	3.697 ± 0.765

[a] The very small errors are meaningless. As T_{CH} and $T_{1\rho}(H)$ approach the same value, the numerator and denominator in the equation for carbon magnetization (eq 6 in the previous paper[1]) both approach zero. In this case, while the supplied T_{CH} and $T_{1\rho}(H)$ values clearly allow the computer to complete the calculation, supplying slightly different values can result in very different, equally meaningless, errors in the calculated T_{CH} and $T_{1\rho}(H)$ values [e.g., T_{CH} = 2.15 ± 22.98 ms and $T_{1\rho}(H)$ = 2.13 ± 22.76 ms] because the computer has found a local minimum but not the absolute minimum in the surface. However, only the calculated errors are sensitive to the supplied values. [b] The signals for the four types of carbon atoms are not resolved.

signal intensity, which does not change significantly for $1.50 \le t_{cp} \le 3.00$ ms (Table IV); the alkene carbon atoms achieve maximum signal intensity at $t_{cp} \simeq 3.00$ ms but at $t_{cp} = 1.50$ ms have already achieved about 93% of maximum intensity (Table IV); the aromatic carbon atoms achieve maximum signal intensity at $t_{cp} \simeq 1.00$ ms, but by $t_{cp} = 3.00$ ms only 69% of the maximum intensity remains (Table IV). The data in Table IV were also computer analyzed to estimate values of T_{CH} and $T_{1\rho}(H)$ for each type of carbon atom. The computer-derived parameters appear in Table VI. Representative spectra of **3** appear in Figure 4. The results obtained with **4** (representative spectrum in Figure 5) are presented in Table VII.

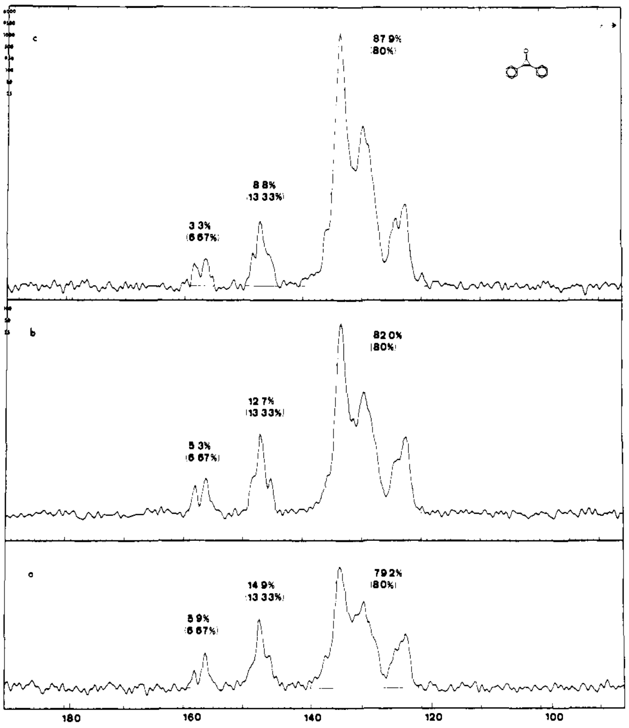

Figure 4. Expanded regions from 25.15-MHz, scaled CP/MAS ^{13}C NMR spectra of **3**, diphenylcyclopropenone, obtained with a spectral width of 10 000 Hz (398 ppm); contact time = 3.750 ms (a), 2.250 ms (b), and 1.000 ms (c); acquisition time = 0.0500 s; delay time = 3.00 s; number of acquisitions = 10 500; line broadening of 5 Hz applied before spectra were zero-filled to 2K for a frequency resolution of 4.9 Hz. A pair of resonances for the carbonyl carbon atom, at least three resonances for the alkene carbon atoms, and a multitude of resonances for the aromatic carbon atoms are clearly evident. The I_{exptl} and I_{theor} values (in parentheses) are given.

Not surprisingly, **5**, $C_{10}H_2O_6$, has a long $T_1(H)$, which greatly increases the amount of time needed to acquire a spectrum with adequate signal:noise (S/N). The only spectrum obtained of this compound appears in Figure 6. With signal shapes near the base line estimated as shown, the carbonyl and aromatic carbon atoms constitute 35% and 65% of the signal intensity, respectively.

Discussion

Even though methyl trityl ether (**1**) has a tetrahedrally buried carbon atom three chemical bonds from the nearest proton, all the carbon atoms in **1** are essentially fully polarized with a contact time as short as 1.50 ms, and, because $T_{1\rho}(H)$ is long enough, all

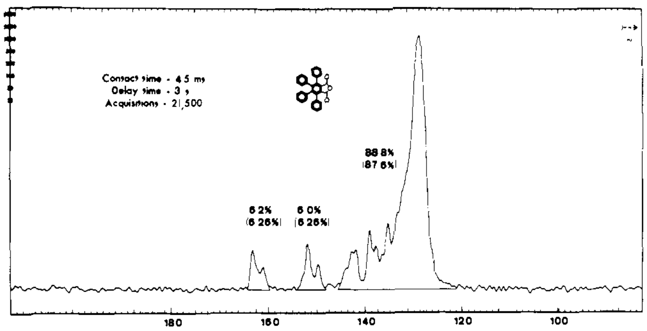

Figure 5. Expanded region from a 25.15-MHz, CP/MAS ^{13}C NMR spectrum of **4**, tetraphenylphthalic anhydride, obtained with a spectral width of 10 000 Hz (398 ppm); acquisition time = 0.0500 s; line broadening of 5 Hz applied before spectrum was zero-filled to 2K for a frequency resolution of 4.9 Hz. Pairs of resonances each separated by 2.1 ppm are clearly evident for the carbonyl and the ring junction carbon atoms. A multitude of resonances for the aromatic carbon atoms is clearly evident. The I_{exptl} and I_{theor} values (in parentheses) are given.

Table VII. Relative Signal Intensities in Tetraphenylphthalic Anhydride as a Function of Contact Time

	rel intensities				
contact time, ms	carbonyl	most downfield aromatic[b]	other aromatics	std error,[a] %	std rel error,[a] %
	Theoretical				
	6.25	6.25	87.50		
	Experimental				
4.500	5.2	6.0	88.8	1.0	10.0
3.000	4.3	5.2	90.5	2.2	20.6

[a] As defined in Table I of the preceding paper.[1] [b] Most likely the ring junction carbon atoms. (Phthalic anhydride gives a ring junction C=C resonance at δ 131.1; maleic anhydride gives a C=C resonance at δ 136.6; methyl substitution gives a $H_3C-C{=}C$ resonance at δ 149.5.[11])

the carbon atoms remain fully polarized even with a contact time of 3.00 ms (Table I). Apparently, spin diffusion among the many protons is efficient enough to equilibrate them, and the nearest protons are still sufficiently close to produce adequate cross polarization of the trityl carbon atom. The trityl carbon atom gives a significantly narrower resonance than the methoxy carbon atom (Figure 1).

The excellent results obtained with $1.50 \le t_{\text{cp}} \le 3.00$ ms prompted us to study compounds containing a well-resolved carbon atom further removed from the nearest intramolecular proton to minimize the intramolecular dipolar interaction. Unfortunately, no such compounds with tetrahedrally buried carbon atoms were found. As alternatives, **2**–**4** were studied. In each of these compounds, nonprotonated carbons exist that are separated by at least four bonds from intramolecular protons. The three compounds have differing overall proton concentrations, which can be expected to provide a variety of intermolecular interactions.

The carbonyl carbon atoms in di-*tert*-butyl oxalate (**2**), four bonds from the nearest intramolecular proton, are not fully polarized. They apparently do not have an effective intramolecular polarization process, and the intermolecular process is likewise inefficient. At best, they contribute only 17.4% of the total signal intensity compared with the theoretical value of 20% based on atomic ratios (Table II). Furthermore, a relatively long contact time ($t_{\text{cp}} = 3.00$ ms) is required to effect even this extent of polarization. The exceptionally high S/N ratio (see Figure 2) was acquired with time averaging in 26 min, enabling us to study **2** at additional, longer contact times. As noted in the preceding paper,[1] T_{CH} and $T_{1\rho}$(H) data suggested that contact times less than about 3 ms are normally adequate for maximing the intensity of the ^{13}C signals. The data for **2** with $3 \le t_{\text{cp}} \le 6$ ms show the eventual decay in carbon magnetization before a fully developed signal height can be achieved. In this case $T_{1\rho}$(H) processes begin to limit the cross-polarization processes. Each of the three types of carbon nuclei achieves maximum absolute intensity at $2.25 < t_{\text{cp}} < 3.00$ ms (Table VIII, supplementary material, and Figure 3), in keeping with the parameters describing the spin dynamics of the system. Nevertheless, the carbon atom furthest from the intramolecular protons does not fully polarize for any t_{cp}, and this is ascribed to a proton-distance effect for both the intra- and intermolecular interactions. Rapid rotation of the *tert*-butyl group will attenuate the intermolecular cross polarization as well as the intramolecular processes, and this probably accounts for the intermolecular process not being more competitive.

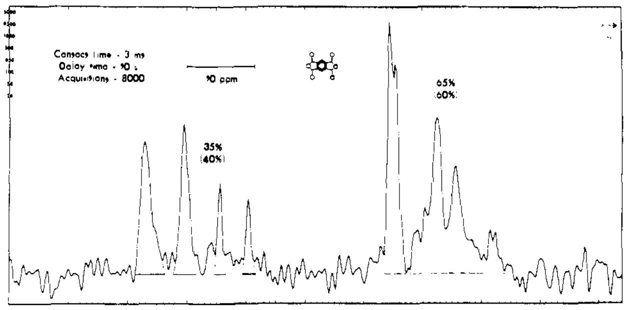

Figure 6. Expanded region from a 25.15-MHz, CP/MAS ^{13}C NMR spectrum of **5**, 1,2:4,5-benzenetetracarboxylic dianhydride, obtained with a spectral width of 10 000 Hz (398 ppm); acquisition time = 0.0500 s; line broadening of 5 Hz applied before spectrum was zero-filled to 2K for a frequency resolution of 4.9 Hz. Four resonances with a spread of 15.3 ppm are clearly evident for the carbonyl carbon atoms. A multitude of resonances for the aromatic carbon atoms is clearly evident. [A chemical shift scale does not appear because the extremely limited solubility of the compound in several solvents precluded obtaining solution chemical shift values (relative to Me_4Si) that would serve as approximate values in the solid. The spectrum is 91 ppm wide.] The I_{exptl} and I_{theor} values (in parentheses) are given.

The computer-fitted T_{CH} and $T_{1\rho}$(H) values for **2** (Table III) aid significantly in understanding the qualitative results. As expected, the methyl carbon atoms polarize the most rapidly. However, like the methyl carbon atoms in the other *tert*-butyl group studied,[1] the *tert*-butyl methyl carbon atoms in **2** have a considerably longer T_{CH} value than other methyl carbon atoms (compare with Table V in the previous paper[1]). The *tert*-butyl quaternary carbon atom in **2** has a T_{CH} value nearly 3.5 times longer than the T_{CH} value for the methyl carbon atoms. Clearly, this *tert*-butyl quaternary carbon atom has a T_{CH} value much longer than nonprotonated aromatic carbon atoms.[1] With $T_{1\rho}$(H) (5.12 ms) less than 3.5 times as long as T_{CH} (1.48 ms), the quaternary carbon atom barely polarizes (Table II, $t_{\text{cp}} = 3.00$ ms). Finally, the carbonyl carbon atoms in **2**, furthest from the intramolecular protons, have equal T_{CH} and $T_{1\rho}$(H) values (2.94 ms) that are not distinguishable from one another. With T_{CH} more than 7 times longer than either of the T_{CH} values for the carbonyl carbon atoms in (4-ethoxyphenyl)acetic acid and 4-butoxybenzoic acid,[1] the carbonyl carbon atoms in **2** apparently never fully polarized (Table II).

The calculated difference between the $T_{1\rho}$(H) value for the carbonyl carbon atoms (2.94 ms) and the $T_{1\rho}$(H) value for the quaternary aliphatic carbon atoms (5.12 ms) in **2** is not statistically significant. However, the calculated value for the $T_{1\rho}$(H) (26.82 ms) corresponding to the methyl carbons is mathematically significant, and this indicates a breakdown in our simple model as only one kind of proton exists in this molecule. However, the rigid lattice approximation describing the dynamics of ^{13}C–^{1}H magnetization transfer does not strictly apply to *tert*-butyl groups because of rapid rotation about the C_3 axis of each methyl group and also about the C_3 axis of the *tert*-butyl group itself. Rapid motion can seriously reduce the ^{13}C–^{1}H and ^{1}H–^{1}H dipolar interactions. Further discussion of this feature appears in a later paper.[12] Because of the rapid motion, $T_{1\rho}$(C) effects may not

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(12) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. submitted for publication in *J. Am. Chem. Soc.*

be negligible, and therefore, more detailed calculations taking into account this parameter might give a different value for $T_{1\rho}$(H) and a better fit of the data than that shown in Figure 3c. For the carbonyl carbon, the combination of rapid motion and only distant intramolecular protons clearly prevents complete polarization.

The carbonyl carbon atom in diphenylcyclopropenone (**3**), which also is four bonds from the intramolecular protons, polarizes more rapidly (Tables IV and VI) than in **2**, suggesting that intermolecular effects may now be more important and that motional attenuation of the ^{13}C–^{1}H and ^{1}H–^{1}H dipolar interactions is much less important. This point is supported by the results on the alkene carbon atoms, which are only three bonds from the nearest intramolecular protons but apparently polarize at the same rate (Table VI) as the carbonyl carbons. The two nonprotonated aromatic carbon atoms, only two bonds from the nearest intramolecular protons, and the ten protonated aromatic carbons polarize considerably more rapidly (Tables IV and VI), indicating that intramolecular protons no further than two bonds away generally dominate the cross polarization processes. At $t_{cp} = 1.00$ ms (a time when the aromatic carbon atoms are near to achieving maximum absolute intensity), the carbonyl and alkene carbon atoms give resonances whose percentage contributions are about $^1/_2$ and $^2/_3$, respectively, of their ideal values on the basis of atomic ratios (Table V). At $t_{cp} = 3.00$ ms (a time when the alkene and carbonyl carbon atoms are close to their maximum absolute intensity), the carbonyl carbon atom gives a resonance whose percentage contribution is still only about $^5/_6$ of its ideal value on the basis of atomic ratios (Table V). This makes the relative contributions of both the alkene and aromatic carbon atoms slightly higher than atomic ratios, as would be expected. Apparently, $T_{1\rho}$(H) effects influence the intensities after about 3 ms since the carbonyl carbon atom has not been fully polarized by this time. Nevertheless, **3** still gives reasonably accurate relative percentage contributions at the maximum point in the carbonyl curve, where $t_{cp} \simeq 3.00$ ms (Table V). The absolute error in the percentage contribution of the carbonyl carbon atom is $\simeq 1.5\%$, making the relative error $\simeq 20\%$. Such a large relative error clearly indicates the value of studying the cross-polarization dynamics of an uncharacterized diamagnetic solid with at least two contact times (perhaps 1.00 and 2.25 ms) to avoid being misled by a sample containing carbon atoms with a wide range of cross-polarization efficiencies or carbon atoms experiencing significantly different $T_{1\rho}$(H) effects (Figure 4). Cooling **3** to reduce molecular motion and thereby shortening[13] T_{CH} and lengthening[14–18] $T_{1\rho}$(H) would clearly be beneficial.

The ring-junction and carbonyl carbon atoms in tetraphenylphthalic anhydride (**4**) are four and five bonds, respectively, from the nearest intramolecular protons and apparently cannot be fully polarized by these or by intermolecular protons on adjacent molecules (Table VII). The carbonyl carbon atom clearly polarizes the most slowly. Preliminary investigations (6000 acquisitions) with $1.00 \leq t_{cp} \leq 4.50$ ms also showed that shorter contact times resulted in the carbonyl atom contributing an even smaller percentage of the total signal intensity. As in diphenylcyclopropenone (**3**), the multitude of resonances for the phenyl groups (Figure 5) indicates that the crystalline environment is removing the nominal spatial equivalence found for chemically equivalent carbon atoms related to each other by unimolecular symmetry elements.

These results on **2**–**4** show that carbon atoms far from a proton may not fully polarize due to a decay of the proton magnetization before the transfer in magnetization is complete. Rapid motion aggravates the problem by reducing the effective dipolar interactions. The measured relative intensities are affected even with contact times longer than the generally optimal contact time of 1–2 ms.[1] In this connection, it is interesting to note that CP/MAS ^{29}Si NMR studies of silica gel indicate that T_{SiH} for a Si atom at least four bonds from the nearest hydroxyl proton is more than 4 times the T_{SiH} for a Si atom only two bonds from the nearest hydroxyl proton.[19] Apparently, intermolecular processes are also not contributing significantly to the cross-polarization rate.

Unless the elemental analysis of an unknown solid indicates that it contains very little hydrogen, the likelihood of there being many carbon atoms far from the nearest proton is low. Thus, CP/MAS NMR generally appears to be very useful for quantitatively studying solids that cannot be adequately characterized by other means. Even in 1,2:4,5-benzenetetracarboxylic dianhydride (**5**), which contains ten carbons, six oxygens, but only two hydrogens, one may obtain with less than optimized contact and delay times absolute intensities for the carbonyl and aromatic signals that are within 5% of the ideal values based on atomic ratios. Even though T_1(H) is undoubtedly long and spin diffusion among the protons in **5** may be slow, a reasonable spectrum still results (Figure 6). While **5** is a highly symmetrical, planar molecule, the multiplicity of resonances arises from destruction of this symmetry in the crystal packing. The four carbonyl carbon signals, spread over 15.3 ppm, are unusual. Apparently, only a few times before has a single type of carbon atom given four or more resonances.[20–24] To reduce the delay time necessitated by the long T_1(H),[1] flipping the proton magnetization back along B_0 at the conclusion of data acquisition in **5** is advantageous.[25] Alternatively, the sample could be doped with a paramagnetic species.[18,26–28]

Conclusions

These and previous[1] results indicate that carbon atoms with intramolecular protons within two or three bonds will usually have signal intensities that agree with atomic ratios. Carbon atoms four or more bonds from the nearest intramolecular proton have very long T_{CH} values, indicating that intramolecular dipolar processes are inefficient for cross polarization. In the molecules studied, the intermolecular dipolar interactions also failed to provide adequate cross-polarization rates. Whether crystal geometries in the compounds studied are particularly unfavorable or whether lattice motions are seriously attenuating intermolecular interactions is not resolved, but that intermolecular dipolar interactions are inefficient becomes a major conclusion of this work. Reduced spin diffusion among the protons can limit the overall magnetization transfer from protons to carbons. For some polymers, $T_{1\rho}$(H) values can be as short as 0.1 ms,[29] and when this condition holds, considerable spectral distortion can result. On the basis of existing data, however, such effects do not appear

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(13) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384–405.

(14) VanderHart, D. L. In "Preprints of the 1976 Coal Chemistry Workshop"; Peters, H. M., Ross, D. S., Eds.; Stanford Research Institute: Menlo Park, CA, 1976; pp 202–218.

(15) Wemmer, D. E.; Pines, A.; Whitehurst, D. D. *Phil. Trans. R. Soc. London, Ser. A* **1981**, *300*, 15–41.

(16) VanderHart, D. L.; Earl, W. L.; Garroway, A. N. *J. Magn. Reson.* **1981**, *44*, 361–401.

(17) Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208–216.

(18) Sullivan, M. J.; Maciel, G. E. *Anal. Chem.* **1982**, *54*, 1615–1623.

(19) Maciel, G. E.; Sindorf, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 7606–7607.

(20) Balimann, G. E.; Groombridge, C. J.; Harris, R. K.; Packer, K. J.; Say, B. J.; Tanner, S. F. *Philos. Trans. R. Soc. London Ser. A* **1981**, *299*, 643–663.

(21) Hays, G. R.; Huis, R.; Coleman, B.; Clague, D.; Verhoeven, J. W.; Rob, F. *J. Am. Chem. Soc.* **1981**, *103*, 5140–5146.

(22) Iverson, D. J.; Hunter, G.; Blount, J. F.; Damewood, J. R., Jr.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6073–6083.

(23) Garroway, A. N.; Ritchey, W. M.; Moniz, W. B. *Macromolecules* **1982**, *15*, 1051–1063.

(24) Dicarbonyl(hexaethylbenzene)(triphenylphosphine)chromium(0) has yielded perhaps the most noteworthy multiplicity of resonances: a pair of carbonyl carbon resonances at δ 242.3 and 247.6, six aromatic carbon resonances between δ 129.4 and 146.8 for the triphenylphosphine moiety, and six aromatic carbon resonances between δ 104.5 and 114.6 for the hexaethylbenzene moiety.[22]

(25) Tegenfeldt, J.; Haeberlen, U. *J. Magn. Reson.* **1979**, *36*, 453–457.

(26) Brown, C. E.; Jones, M. B.; Kovacic, P. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 653–658.

(27) Ganapathy, S.; Naito, A.; McDowell, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 6011–6015.

(28) Brown, C. E. *J. Am. Chem. Soc.* **1982**, *104*, 5608–5610.

(29) Connor, T. M.; Hartland, A. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1005–1019.

J. Am. Chem. Soc. **1983**, *105*, 2147-2154

to be important in small organic molecules run as microcrystalline powders. In the atypical case of a simple compound exhibiting a very short $T_{1\rho}(H)$ value [e.g., anthracene[18] and 3,5-bis[(methylamino)carbonyl]-1-methyl-1,4-dihydropyridine[21]] and significantly different T_{CH} values, the signal intensities do not agree with atomic ratios. When polarization is incomplete, the equilibrium or steady-state condition in the thermodynamic model using a common spin temperature begins to break down, and quantitative results are not obtained.

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Supplementary Material Available: Absolute intensity of the signals for **2** as a function of contact time (Table VIII) (1 page). Ordering information is given on any current masthead page.

Metal–Nitroxyl Interactions. 30. Single-Crystal EPR Spectra of Two Spin-Labeled Copper Porphyrins

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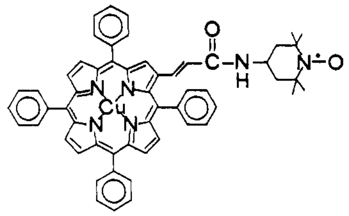
Abstract: Rotated single-crystal EPR spectra have been obtained for two spin-labeled copper porphyrins doped into zinc tetraphenylporphyrin. Four conformations of the spin-label linkage were observed in each of the crystals. Analysis of the rotation dependence of the spin–spin splittings gave the isotropic exchange and anisotropic dipolar contributions to the spin–spin interaction. Values of the exchange coupling constant, J, ranged from -30 to $+10 \times 10^{-4}$ cm^{-1}. The interspin distance, r, ranged from 9.2 to 15.5 Å. There was no correlation between the values of r and J.

Introduction

Nitroxyl spin labels that are used to study biological systems sometimes are observed to interact with paramagnetic metals or other radicals.[1,2] The second paramagnetic center may be intrinsic to the system or purposely added as a second probe. The interpretation of the frozen solution EPR spectra of such systems involves separately estimating the exchange and dipolar contributions to the spin–spin interaction. Many interpretations in the literature assume that the exchange contribution is negligible so that spectra can be interpreted in terms of purely dipolar interaction from which metrical information can be directly obtained. Recent results from these laboratories have demonstrated that exchange interactions are significant at longer distances than previously were believed possible.[3,4] In many cases the exchange interaction, J, results in high resolution "AB" patterns in the fluid solution EPR spectra due to electron spin–electron spin coupling. The same splitting presists, albeit with different effects on line shapes, in frozen solution EPR spectra. We have shown that when dipolar and exchange contributions to the spin–spin interaction are of similar magnitude, the magnitude of each and the sign of J can be obtained by analysis of frozen solution EPR spectra.[5] In some of the frozen solution spectra studied in this initial attempt the lack of spectral resolution due to overlapping lines made the derived parameters (J, distance) uncertain.[5] It is clear that development of a sense of which features in the frozen solution EPR spectra are the best measures of the exchange and dipolar contributions requires some calibration experiments with single-crystal spectra. The analysis of the single-crystal spectra also provides a more stringent test of the computational approach to the spin–spin interaction than the powder spectra do. In addition, the single-crystal spectra provide a definitive separation of the exchange and dipolar contributions to the spin–spin interaction.

We have therefore examined the single-crystal EPR spectra of two spin-labeled copper porphyrins, I and II, doped into zinc tetraphenylporphyrin. These complexes have previously been studied in fluid solution[3,6] and in frozen solution,[5] so the results of this study provide a comparison of the information which can be obtained in fluid solution, frozen solution, and single-crystal studies.



trans I

cis II

This study is the first complete analysis of the exchange and dipolar contributions to weak spin–spin interaction between nonequivalent unpaired electrons by single-crystal EPR spectroscopy.

Experimental Section

The compounds studied here were prepared by literature methods: I, II,[6] tetraphenylporphyrin,[7,8] zinc tetraphenylporphyrin (ZnTPP).[9] The visible spectrum of ZnTPP in benzene solution had bands at 589, 550, and 425 nm with log ϵ = 3.72, 4.45, and 5.85, respectively. The band positions agreed well with the literature values[10] and the extinction coefficients were greater than the literature values.[10] No EPR signal was

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* Address correspondence to this author at the University of Denver.

(1) Berliner, L. J., Ed. "Spin Labeling II"; Academic Press: New York, 1979.

(2) Eaton, S. S.; Eaton, G. R. *Coord. Chem. Rev.* **1978**, *26*, 207–262.

(3) More, K. M.; Eaton, G. R.; Eaton, S. S. *Can. J. Chem.* **1982**, *60*, 1392–1401, and references therein.

(4) More, J. K.; More, K. M.; Eaton, G. R.; Eaton, S. S. *Inorg. Chem.* **1982**, *21*, 2455–2460, and references therein.

(5) Eaton, S. S.; More, K. M.; Sawant, B. M.; Boymel, P. M.; Eaton, G. R. *J. Magn. Reson.*, in press.

(6) More, K. M.; Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1981**, *20*, 2641–2647.

(7) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(8) Rousseau, K.; Dolphin, D. *Tetrahedron Lett.* **1974**, 4251–4254.

(9) Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443–2444.

(10) Dorough, G. D.; Miller, J. R.; Huennekens, F. M. *J. Am. Chem. Soc.* **1951**, *73*, 4315–4320.

0002-7863/83/1505-2147$01.50/0