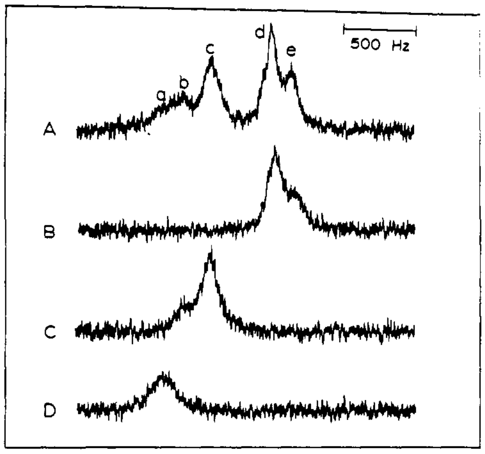

Figure 1. Cobalt-59 nmr spectra of aqueous (A) 0.41 *m* $[\mathrm{Co}((\pm)\text{-}\mathrm{pn})_3]\mathrm{Cl}_3$, (B) 0.15 *m* $[\mathrm{Co(pn)_3}]\mathrm{Cl}_3$ from fraction 1 described in the text, (C) 0.15 *m* $[\mathrm{Co(pn)_3}]\mathrm{Cl}_3$ from fraction 2, and (D) 0.08 *m* $[\mathrm{Co(pn)_3}]\mathrm{Cl}_3$ from fraction 3.

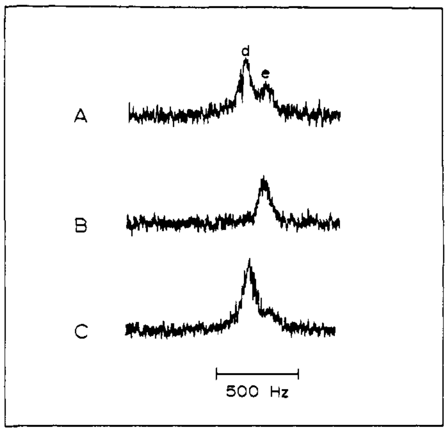

Figure 2. Cobalt-59 nmr spectra of aqueous (A) Δ-$[\mathrm{Co}((-)\mathrm{pn})_3]\mathrm{Br}_3$ and Λ-$[\mathrm{Co}((+)\mathrm{pn})_3]\mathrm{Br}_3$, [Co(III)] = 0.07 *m*, (B) 0.03 *m* *cis*-Δ-$[\mathrm{Co}((-)\mathrm{pn})_3]\mathrm{Br}_3$, and (C) supernatant liquid from crystallization of *cis*-Δ-$[\mathrm{Co}((-)\mathrm{pn})_3]\mathrm{Br}_3$, containing primarily *trans*-Δ-$[\mathrm{Co}((-)\mathrm{pn})_3]\mathrm{Br}_3$ and a small amount of the cis isomer.

calculated to be 1:(3.9 ± 0.3):(4.9 ± 0.2). These ratios are 1:(2.5 ± 0.3):(2.1 ± 0.1) for $[\mathrm{Co}((\pm)\mathrm{pn})_3]\mathrm{Cl}_3$ prepared in the presence of charcoal. The latter ratios compare favorably with the 1:2.1:2.1 values determined previously by Dwyer, *et al.*[1] The different relative isomer abundances obtained for different preparations of $\mathrm{Co}((\pm)\mathrm{pn})_3{}^{3+}$ show that the presence of the charcoal catalyst establishes a different equilibrium distribution of diastereomers, producing a greater abundance of energetically less favored but statistically more probable species.

Figure 2A shows the cobalt-59 nmr spectrum of the enantiomers from fraction 1 after conversion to the bromide salts. Figure 2B shows the cobalt-59 spectrum of the cis geometrical isomer isolated from Δ-$[\mathrm{Co}((-)\mathrm{pn})_3]\mathrm{Br}_3$, and Figure 2C is the spectrum of the supernatant liquid separated from the cis crystals. The different intensities are due to different cobalt(III) concentrations. Figure 2 clearly permits an unambiguous assignment of peaks e and d in Figure 1 to the cis and trans geometrical isomers of Δ-$\mathrm{Co}((-)\mathrm{pn})_3{}^{2+}$ and Λ-$\mathrm{Co}((+)\mathrm{pn})_3{}^{3+}$, respectively. Similarly, peaks b and c can be assigned to the geometrical isomers present in fraction 2. Trans to cis ratios (3.4 ± 0.3):1 and (2.9 ± 0.3):1 are calculated from the relative integrated intensities of these peaks (the ratios of c:b and d:e). These correspond to the expected 3:1 statistical distribution. Actually, fraction 2 contains a mixture of eight distinguishable isomers. For example, in the Δ complex only one cis isomer may be formed but three distinguishable trans isomers may be formed. If all four of these diasteriomers exist, four separate cobalt-59 signals could exist. The resolution of only two peaks does not distinguish between the possibilities that only one trans isomer is formed or that all three trans isomers are formed but have very similar chemical shifts. The possibility that peak b could be assigned to one of the trans isomers rather than to the cis isomer must also be considered. However, the c:b intensity ratio of 3:1 strongly suggests that a statistical distribution of geometrical isomers also occurs in fraction 2.

This work demonstrates the advantages of using cobalt nmr rather than pmr for the detection of optical and geometrical isomerism in cobalt complexes. Proton shifts in diamagnetic complexes are relatively small, whereas cobalt shifts in the same complexes may be quite large, providing better resolution. The lack of resolved spin coupling with protons simplifies assignments in cobalt spectra and allows a straightforward estimation of relative abundances. Because of the excellent resolution, isomerism in complexes formed from unresolved ligands may be investigated directly. There is currently much interest in the stereoisomerism of tris-chelate metal complexes.[7,15] In view of the utility of cobalt-59 nmr for the detection of optical and geometrical isomers of cobalt complexes, cobalt-59 nmr should be a valuable tool for the investigation of stereoisomerism in tris-chelate cobalt complexes.

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Virtual Coupling in Carbon-13 Nuclear Magnetic Resonance Spectra with Off-Resonance Continuous Wave Proton Spin Decoupling

Sir:

Continuous wave proton spin decoupling (CWSD) has become a routine procedure for assignment of carbon-13 resonance absorptions.[1] An intense CW rf field several hundred hertz upfield from the proton resonances is used to irradiate the proton transitions. The resulting carbon-13 spectrum retains the nuclear

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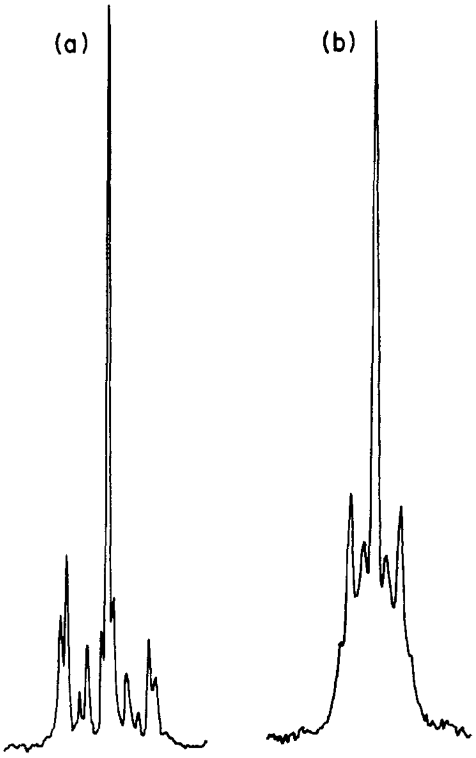

Figure 1. Carbon-13 nmr spectra with proton CWSD of (a) 1,2-dichloroethane and (b) poly(*cis*-butadiene). Spectra are from a Varian XL-100 nmr spectrometer operated in the Fourier transform mode. The proton decoupling frequency is 250 Hz upfield from Me_4Si.

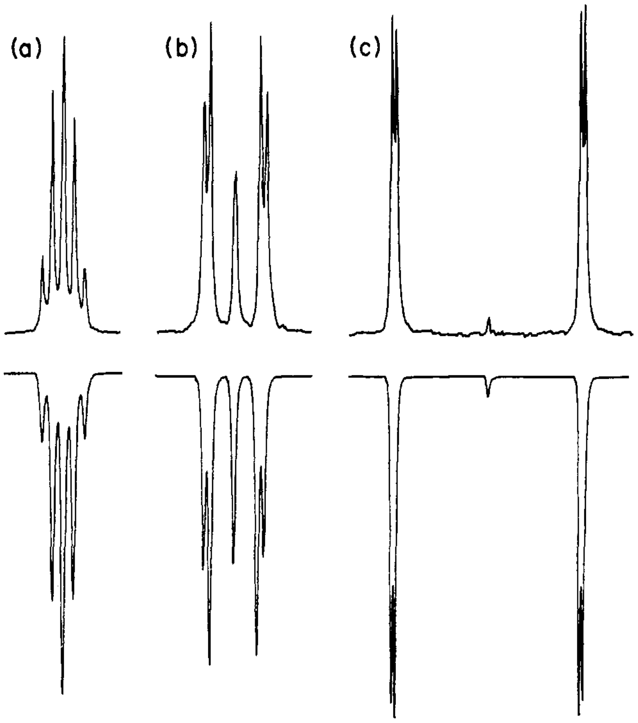

Figure 2. Carbon-13 nmr spectra of fumaric acid: (a) proton CWSD, offset 300 Hz from resonance; (b) offset 700 Hz; (c) no decoupling. Inverted spectra are calculated using the LAOCOON program and reduced coupling constants: (a) $J_{CH} = 19$, $J_{CCH} = -0.3$, $J_{HH} = 15.8$ Hz; (b) $J_{CH} = 42$, $J_{CCH} = -0.6$, $J_{HH} = 15.8$ Hz; (c) $J_{CH} = 167$, $J_{CCH} = -3$, $J_{HH} = 16$ *Hz*.

Overhauser enhancements found in noise decoupling, but shows splittings from the large one-bond coupling constants which are used to assign a carbon resonance to a methyl, methylene, methine, or quaternary carbon. These splittings, termed reduced coupling constants, are smaller than the actual coupling constants and greatly reduce the problem of overlapping peaks. The reduced coupling constant is given approximately by $(\Delta f/\gamma H_2)J_{CH}$ where Δf is the offset frequency and γH_2 the intensity of the decoupling field.[2] A systematic method to assign overlapping peaks in CWSD experiments has been given.[3]

It appears to be generally assumed that a methylene always gives a triplet in a CWSD experiment. We have observed interesting exceptions to this rule in the case of vicinal magnetically equivalent groups. For example, in 1,2-dichloroethane, the proton-undecoupled spectrum gives the expected triplet ($J_{CH} = 152$ Hz) of triplets ($J_{CCH} = 4$ Hz). However, with proton CWSD, a complex multiplet occurs instead of the expected simple triplet for the carbon (Figure 1a). The center peak of the triplet remains very sharp whereas the maximum intensity of the outside peaks becomes less than 20% of the middle peak. We first noticed this effect in the proton CWSD carbon-13 spectrum of poly(*cis*-butadiene) where the methylene appears as a weak doublet overlapping a triplet (Figure 1b). This spectrum could be incorrectly interpreted as a weak methine doublet impurity overlapping the methylene triplet of the polymer chain. The spectra of fumaric acid are even more dramatic. For typical CWSD offset frequencies, instead of the expected doublet, a five-line multiplet is observed in which the center line can be as tall as the outside lines (Figure 2a and 2b). Furthermore, the carbon-13 spectrum of undecoupled fumaric acid (Figure 2c) shows a weak peak at the center frequency as well as the expected doublet ($J_{CH} = 167$ Hz) of doublets ($J_{CCH} = 3$ Hz).

The physical explanation of this behavior is identical with that of virtual coupling in proton spectra.[4] The off-resonance decoupling reduces the effective J_{CH} coupling constant to the point where the coupling between the two equivalent protons becomes as large as the reduced J_{CH}. Then the carbon appears effectively coupled to both protons at the averaged coupling constant, $(J_{CH} + J_{CCH})/2$.[5] Thus, in fumaric acid, the center line grows more intense as the spectrum changes from a doublet to a triplet. But even in the normal (proton coupled) spectrum of fumaric acid a weak line is predicted at the center frequency and this is an example of a typical case of virtual coupling.[6] In dichloroethane or poly(*cis*-butadiene), $\text{-}\!\!\left(\mathrm{CH_2CH{=}CHCH_2}\right)\!\!\text{-}_n$, the additional peaks arise because the vicinal methylenes are magnetically equivalent and the large vicinal J_{HH} results in virtual coupling of the carbon-13 to the two vicinal methylene protons besides

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[2] A more accurate approximation is given by K. G. R. Pachler, *J. Magn. Resonance*, 7, 442 (1972).

[3] B. Birdsall, N. J. M. Birdsall, and J. Feeney, *J. Chem. Soc., Chem. Commun.*, 316 (1972).

[4] J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

[5] The reduced direct two-bond J_{CCH} is insignificant compared to the indirect virtual coupling in the examples shown in Figures 1 and 2.

[6] See Figure 4g in ref 4. The weak lines shown in Figure 4g are coalesced in Figure 2c of this paper because the difference between the proton and carbon chemical shifts is 75 MHz, not the 50 Hz used in the calculations in ref 4.

the direct coupling to the two protons in the $^{13}CH_2$ group.

The spectra, as shown in Figure 2, can be semiquantitatively reproduced using the LAOCOON computer program with reduced values for the carbon–proton coupling constants.[7] These calculations are approximate because they do not include the asymmetry introduced by the decoupling field or any relaxation effects.

We have performed additional experiments which show that it is not necessary for the protons to be equivalent to observe the additional splittings in a CWSD experiment, but the unusual effects shown in the figures are diminished as the difference between the chemical shifts of the vicinal protons increases or the vicinal proton–proton coupling constant decreases. For identical reduced J_{CH}, the "extra" middle peak in 1,1,2,2-tetrachloroethane is less than 20% that observed in fumaric acid because J_{HH} is 16 Hz in the latter but only 4 Hz in the former. A more detailed explanation of the conditions required for virtual coupling is given by Musher and Corey.[4] Our main point is to stress that caution must be exercised in interpreting CWSD experiments when there is strong coupling between two or more protons with similar chemical shifts on different carbon atoms in a molecule.

(7) Quantum Chemistry Program Exchange, Program No. 111, Indiana University, Bloomington, Ind.

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Pulsed Spin Decoupling in Nuclear Magnetic Resonance

Sir:

Time sharing versions of nmr, for example, time sharing pulsed double resonance,[1] are becoming increasingly popular these days. Concurrently, a number of myths concerning their theoretical interpretation have begun to pervade the literature. We should like to present a very brief preview of some of the problems which may be encountered in applying naively the concepts of coherent averaging theory[2] to time sharing or multiple-pulse experiments.

Examples of common misconceptions can be found in some recent communications on pulsed versions of spin decoupling and spin locking.[3] Basically, they take a common form; the rf field $H_1(t)$, at frequency ω, is applied in a series of pulses, of duration t_w and repetition period t_c, to permit facile simultaneous observation of the signal during the intense irradiation. For the case where $t_c \rightarrow 0$, the problem is then analyzed in terms of an "average perturbation" which is described as a continuous irradiation of intensity $\bar{H}_1$ at frequency ω, where $\bar{H}_1 = (t_w/t_c)H_1$. This corresponds to Fourier analyzing the rf pulse train and discarding the side bands (since, for $t_c \rightarrow 0$, they lie outside the spectral region) and retaining the resonant center band of intensity $\bar{H}_1$. This approach is successful on some occasions, but we would like to mention that in general it is simply wrong! Coherent averaging theory does *not* apply to the rf excitation; it is the complete interactions of rf and spins which must be transformed and averaged.

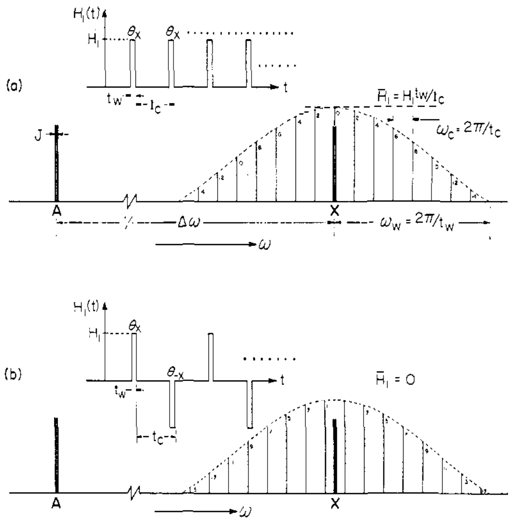

Figure 1. Pulsed version of spin decoupling in AX spectrum. The rf field is applied at the X frequency and modulated by the pulse trains (corresponding to (a) constant phase and (b) phase alternated rf) of duty factor t_w/t_c (here = 1/8). Only the A peak is sampled and $\gamma H_1 \ll \Delta\omega$. Shown schematically are also the AX spectrum and the side bands (absolute amplitudes) in the first $(\sin \omega t)/\omega t$ lobe from the Fourier decomposition of the pulse trains. The case of interest is that of $t_w, t_c \rightarrow 0$. In (a), even though $\bar{H}_1 \neq 0$ and $\gamma\bar{H}_1 \gg J$, there is essentially no spin decoupling (here $^7/_8$) for $\theta = 2n\pi$. In (b), even though $\bar{H}_1 = 0$, there can be complete spin decoupling for $\theta \sim (2n + 1)\pi$ [here $\theta = (2n + 1 + [0.06/(2n + 1)])\pi$].

To make this more concrete, consider the simple examples of heteronuclear spin decoupling described in Figure 1. The approach described above would argue that for $t_c \rightarrow 0$ there should be spin decoupling of X in the constant-phase case (a), since $\bar{H}_1 \neq 0$ (if $\gamma\bar{H}_1 \gg J$), and no spin decoupling in the phase alternated case (b), since $\bar{H}_1 = 0$, *i.e.*, there is no center band! In fact, it is easy to verify that $\bar{H}_1 \neq 0$ *is neither a necessary nor a sufficient condition for spin decoupling;* this is made quite transparent by the following observations: (1) in Figure 1a, $\bar{H}_1 \neq 0$, but there will be essentially no spin decoupling for $\theta = 2n\pi$; and (2) in Figure 1b, $\bar{H}_1 = 0$, yet there can be full spin decoupling for $\theta \sim (2n + 1)\pi$.

Similar remarks apply to the case of homonuclear spin decoupling described in this journal recently by Jesson, *et al.*[3a] The claim that their problem reduces to one in which $\bar{H}_1$ is applied continuously (we replace their H_2, $\bar{\mathcal{H}}'$ by H_1, $\bar{H}_1$) fails outright; consider the fact that *so long as* $\gamma H_1 \gg \Delta\omega$ ($\Delta\omega = \delta_A - \delta_B$) *there will be no spin decoupling no matter what the value of* H_1. At most a uniform collapse of the chemical shift can occur.[2] Thus it is not always possible to compensate for long dwell times by indiscriminately increasing H_1. Normally, examples such as 1 and 2 above will be not encountered in the homonuclear case, as $\gamma H_1 \ll \Delta\omega$ is adjusted experimentally, and since $t_c < \pi/\Delta\omega$ (to satisfy the Nyquist condition so that the whole spectrum is sampled) it follows that $\theta \ll \pi$. Details will be presented separately.

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