

oxide<sup>17-19</sup>). A consideration of redox potentials indicates electron transfer from triplet protoporphyrins to oxygen should be slightly exothermic. However, the observation that porphyrins behave as "normal" sensitizers in other oxidations<sup>18</sup> may suggest that singlet oxygen is the predominant intermediate.

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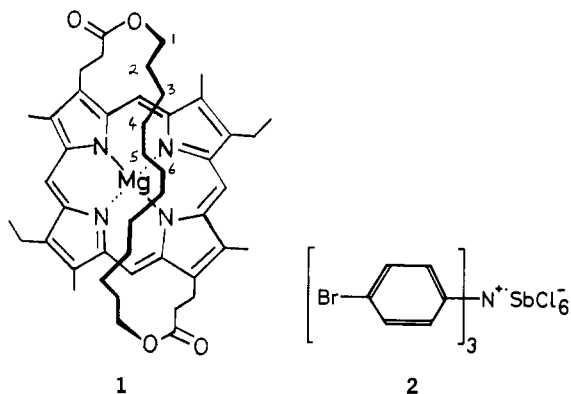
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### Radical-Induced Pseudocontact Shifts

Sir:

Paramagnetic species can induce two kinds of NMR chemical shift.<sup>1</sup> Contact shifts arise directly from delocalization of unpaired spin density and are useful probes of covalent bonding. Pseudocontact shifts are geometrically determined by dipolar field effects and are therefore probes of stereochemistry. Contact shifts caused by metal ions<sup>2</sup> and by organic free radicals<sup>3</sup> are well known, as are metal-induced pseudocontact shifts,<sup>4</sup> but radicals are generally thought not to cause significant pseudocontact effects.<sup>5</sup> We now report results which appear to disprove this last belief.

The bridged metalloporphyrin **1** (prepared from the free base<sup>6</sup> with  $\text{Mg}(\text{ClO}_4)_2$  in pyridine) can be oxidized to its radical cation  $\mathbf{1}^+$  by the crystalline aminium salt **2**.<sup>7</sup> Slight ox-



idation ( $\ll 1\%$ ) leads to NMR exchange broadening of the peripheral, hyperfine-coupled protons in the usual way.<sup>8,9</sup> The relative broadenings of these signals agree with those observed for normal disaggregated metalloporphyrin radical cations.<sup>8b</sup> Further oxidation causes downfield shifts of the resonances of the alkyl methylene bridge protons (Figure 1). The ring current shifted resonance at  $\delta -0.72$  is paramagnetically shifted downfield by an amount corresponding to at least 20 ppm in pure  $\mathbf{1}^+$ . Other alkyl bridge resonances are similarly shifted downfield by an amount proportional to the original upfield aromatic shift (see Table I).

We conclude that in the radical cation  $\mathbf{1}^+$ , the protons of the alkyl bridge experience a magnetic field which has effectively the same geometrical properties as the aromatic ring current<sup>10</sup> but which is 10 times larger and has the opposite sense.<sup>11,12</sup> The magnesium ion carries no unpaired spin, and therefore we suggest that this is due to  $g$ -tensor anisotropy of the unpaired electron, i.e., a pseudocontact shift. The expected temperature dependence of this shift cannot be readily mea-

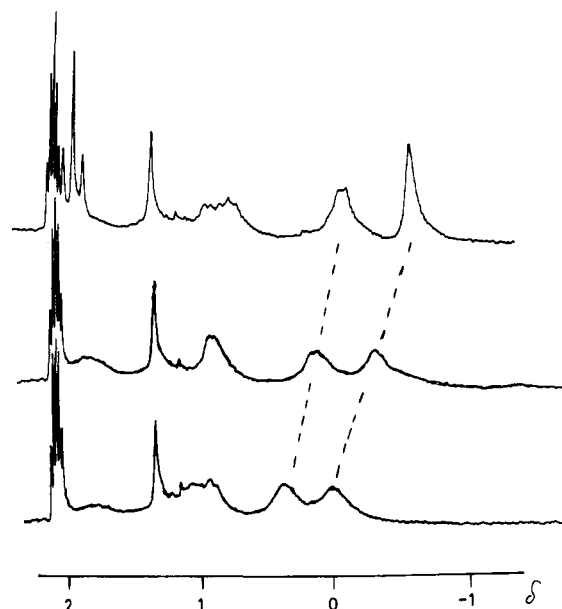


Figure 1. 100-MHz  $^1\text{H}$  NMR spectra of **1** in acetone- $d_6$ . Top: in absence of  $\mathbf{1}^+$ . Below: after partial oxidation (middle,  $\sim 1.5\%$ ; bottom,  $\sim 3.0\%$ ) to  $\mathbf{1}^+$ . The triplet at  $\delta$  2 is due to the ethyl group of the porphyrin; other protons of the periphery are more severely broadened on oxidation and are not shown. Impurity at  $\delta$  1.3.

Table I. Shifts of Bridge Protons in **1** and  $\mathbf{1}^+$ .

Proton	$\delta$ ( <b>1</b> ) <sup>a</sup>	$\delta$ ( $\mathbf{1}^+$ ) <sup>b</sup>	Relative aromatic shift <sup>c</sup>	Relative paramagnetic shift <sup>c</sup>
H-1	3.75, 3.69	8.3	0.19	0.23
H-2	0.72	9.1	0.38	0.42
H-3,4	-0.16	16.2	0.76	0.82
H-5	-0.65	$\sim 19$	0.98	1.0
H-6	-0.72	$\sim 19$	1.0	1.0

<sup>a</sup> 0.03 M in acetone- $d_6$ , 310 K, 270 MHz. Chemical shifts are in  $\delta$  units (parts per million) from  $\text{Me}_4\text{Si}$ . <sup>b</sup> Calculated by extrapolation from partially oxidized solutions. <sup>c</sup> Relative to H-6.

sured as  $\mathbf{1}^+$  gives a diamagnetic dimer at low temperatures.<sup>13</sup>

Although it is believed that radicals cannot induce pseudocontact shifts, we feel that they have simply not been searched for under suitable conditions for these reasons.

(i) In a pure organic radical, the long electron  $T_1$  leads to broad lines even for protons which are not hyperfine coupled. In our system which is undergoing exchange via electron transfer, the line widths can be controlled by varying the mole fraction of paramagnetic molecules.

(ii) Simple nitroxides undoubtedly do have small  $g$ -tensor anisotropies.<sup>5</sup>

(iii) Assuming axial symmetry, the pseudocontact shift,  $\Delta H_i$ , is given by

$$\frac{\Delta H_i}{H} = -\frac{\beta^2 S(S+1)}{9kT} (g_{\parallel}^2 - g_{\perp}^2) \cdot \frac{3 \cos^2 \theta - 1}{r^3}$$

where  $\theta$  is the angle between the magnetic axis and the vector connecting the unpaired spin and the proton  $H_i$ , and  $r$  is the length of that vector. For planar, delocalized radicals a proton in the plane of the  $\pi$  system is close to only a very small part of the unpaired spin density and the  $r^{-3}$  dependence renders distant centers ineffective. In order to be in the plane and close enough for a pseudocontact effect to be observable, the proton would normally be covalently bound so that hyperfine interaction dominates both shift and broadening.<sup>14</sup> However, a proton held above the plane of the radical as in  $\mathbf{1}^+$  is close to all the unpaired spin without the possibility of hyperfine in-

teraction. In addition,  $|3 \cos^2 \theta - 1| \approx 2$  above the plane and only 1 in the plane. Thus the total expected pseudocontact effect will be much larger above the plane of the  $\pi$  system.

This interpretation makes clear predictions on the geometrical dependence of radical-induced shifts which we hope to test in porphyrins and other radicals. Coupling constant and chemical shift evidence show that the bridge in **1** is flexible, but a more rigid bridge would allow measurement of  $\theta$ ,  $r$ , and hence  $g$ -tensor anisotropy.

These results reveal the possibility that, in isolated photosynthetic reaction centers, chlorophyll-protein complexes, or chlorophyll-doped membranes, the chlorophyll radical cation could act as a natural in situ spin label causing shifts as well as broadening. Other biologically important radical cations and anions presumably have the same potential, although in all cases the long electron  $T_1$  may be a problem.

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## References and Notes

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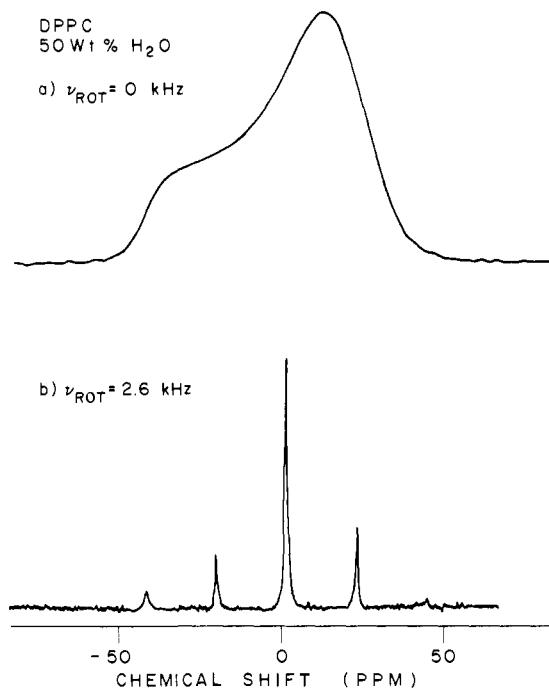
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## High Resolution $^{31}\text{P}$ and $^{13}\text{C}$ Nuclear Magnetic Resonance Spectra of Unsonicated Model Membranes

Sir:

Nuclear magnetic resonance has been used extensively in the last decade to study the structure and dynamics of model and biological membranes.<sup>1</sup> However, the complexity of these systems, which should manifest itself in a corresponding richness of their NMR spectra, has in most cases not been observed because of the substantial breadth of the NMR lines. It is now understood that this breadth is due primarily to residual chemical shift anisotropy and dipole-dipole interactions. For dilute spins, such as  $^{13}\text{C}$  and  $^{31}\text{P}$ , the dipolar broadening can be removed by sufficiently intense rf irradiation at the proton resonance frequency.<sup>2-4</sup> Nevertheless, a substantial broadening due to the anisotropy of the chemical shift remains. In order to obtain "high resolution" NMR spectra, it has become customary to subject multilamellar dispersions to pro-



**Figure 1.** Proton decoupled  $^{31}\text{P}$  spectra of DPPC in 50 wt %  $\text{H}_2\text{O}$  ( $T = 21^\circ\text{C}$ ): (a) axially symmetric powder spectrum,  $\Delta\sigma = -60$  ppm (7.2 kHz),  $\nu_{\text{rot}} = 0$ ; (b)  $\nu_{\text{rot}} = 2.6$  kHz. In (b) the side bands are spaced at the spinning frequency and the full width of the centerband is 95 Hz. Shifts are referenced to external 85%  $\text{H}_3\text{PO}_4$ .

longed ultrasonic irradiation.<sup>5</sup> This process, which results in particles of reduced size with reduced reorientational correlation times, does indeed improve the resolution of the NMR spectra; however, its exact physical and chemical consequences are a subject of much debate.<sup>6</sup> We report an approach which avoids sonication.

Almost 2 decades ago Lowe<sup>7</sup> and Andrew et al.<sup>8</sup> suggested that rapid spinning of a sample about an axis inclined at the "magic angle",  $54^\circ 44'$ , with respect to  $H_0$  would suffice to narrow dipolar broadened NMR lines. The criterion to achieve complete narrowing is that the rotation rate,  $\nu_R$ , must be greater than the dipolar line width.<sup>9</sup> For this reason  $^1\text{H}$  spinning experiments on phospholipids have not been very successful.<sup>10</sup> With the development of pulse methods for obtaining high resolution NMR spectra in solids,<sup>11-14</sup> there has been renewed interest in this technique because chemical shift tensors, like dipolar tensors, are of rank two, and can be averaged to their trace by magic angle spinning. Recently Schaefer and Stejskal<sup>15</sup> demonstrated that high resolution  $^{13}\text{C}$  spectra of several polymeric samples could be obtained by combining dilute spin double resonance and sample spinning.<sup>16</sup> However, it was thought that  $\nu_R$  must be greater than the breadth of the shift powder spectrum,  $\Delta\sigma$ , in order to achieve substantial narrowing. Thus, it appeared that this approach would be of utility only at relatively low magnetic fields—i.e.,  $<2.0$  T.

Recently we and others<sup>17-19</sup> have observed that even at  $\nu_R < \Delta\sigma$  one still obtains a narrow centerband.<sup>18</sup> However, this line is accompanied by sidebands spaced at intervals equal to the spinning frequency, as is illustrated by the  $^{31}\text{P}$  spectra of dipalmitoylphosphatidylcholine (DPPC), dispersed in excess water, shown in Figure 1. Here motional averaging narrows the rigid lattice axially asymmetric  $^{31}\text{P}$  spectrum of  $\sim 190$ -ppm breadth<sup>4</sup> to an axially symmetric one of  $\sim 60$  ppm,<sup>3</sup> which amounts to 7.2 kHz at our  $^{31}\text{P}$  frequency of 119.05 MHz. Upon spinning this sample in an Andrew<sup>20</sup>-type rotor at 2.6 kHz, we observe a single line of 95-Hz full width at half-height flanked by two sets of sidebands. The residual line width is essentially