J. Am. Chem. Soc. **1993,** *115,* 4823–4824

Nuclear Spin Relaxation of the Dihydrogen Ligand in Nonclassical Transition Metal Complexes

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Received December 17, 1992

Abstract: In a recent study of dihydrogen complexes of metalloporphyrins, Collman et al. (*J. Am. Chem. Soc.* **1992,** *114,* 5654) observed proton NMR spectra distinguished by marked line width differentials. These features, characteristic of relaxation-induced polarization transfer, are explained more fully in this brief essay.

Introduction

Recent studies of dihydrogen complexes of metalloporphyrins and related compounds have generated widespread interest within the scientific community.[1,2] The physicochemical probe most often used to investigate dynamic stability and electronic structure of these complexes has been nuclear magnetic resonance spectroscopy. The capacity of this potent probe is epitomized by the impressive NMR study of the bimetallic bridging dihydrogen complex $Ru_2(DPB)(^*Im)_2(H_2)$.[3]

As demonstrated in the study by Collman, Bothner-By, and co-workers,[3] the NMR spin relaxation characteristics of these dihydrogen complexes can be particularly informative. This study clearly indicated that extremely large chemical shielding anisotropies induce variants of spin polarization commonly exploited in various 2D NMR techniques. In the following presentation, we discuss in expanded detail, using established theory, these relaxation features. Hopefully, this discussion will encourage implementation of relaxation-induced polarization transfer as the methodology of choice in future investigations of dihydrogen complex formation and structure.

Theory and Discussion

The relaxation features of two identical protons have been discussed previously.[4,5] Here, we merely reproduce pertinent, illustrative expressions. We start by consideration of the dissipation and relaxation-induced transfer of single-quantum coherence which is described by the simple expression

$$(-\mathrm{d}/\mathrm{d}t)\begin{bmatrix} \langle I_+\rangle \\ \langle I_+(2I_z+1)\rangle \end{bmatrix} = \begin{bmatrix} 1/T_{2+} & 1/T_{2x} \\ 1/T_{2x} & 1/T_{2-} \end{bmatrix} \begin{bmatrix} \langle I_+\rangle \\ \langle I_+(2I_z+1)\rangle \end{bmatrix} \qquad (1)$$

In this brief presentation, it is assumed that the protons are relaxed by axially symmetric, anisotropic chemical shieldings (CS) and a mutual dipole–dipole (D) interaction. The various relaxation rate constants appearing in eq 1 are defined as

$$1/T_{2\pm} = (3/2)(J^{D}(0) + J^{D}(\omega_0)) + J^{D}(2\omega_0) + (8/3)J^{CS}(0) + 4J^{CS}(\omega_0) + 2K^{CS\cdot CS}(\omega_0) \pm \lambda$$

$$\lambda = J^{D}(\omega_0) - 2(J^{CS}(\omega_0) + K^{CS\cdot CS}(\omega_0))\exp(-i\langle \mathcal{H}_D\rangle t)$$

$$1/T_{2x} = -4K^{D\cdot CS}(0) - 2K^{D\cdot CS}(\omega_0) \qquad (2)$$

The different autocorrelated (J) and cross-correlated (K) spectral densities introduced in these expressions are defined in greater detail elsewhere.[5] However, normalizations and terminology are summarized adequately, without ambiguity, by the expressions $J^{D}(0) = (3/10)\gamma^4\hbar^2\langle 1/r^3\rangle^2\tau_2^{D}$, $J^{CS}(0) = (1/30)(\omega_0\Delta\sigma)^2\tau_2^{CS}$, $K^{CS\cdot CS}(0) = (1/30)(\omega_0\Delta\sigma)^2\tau_2^{CS\cdot CS}$, and $K^{D\cdot CS}(0) = (1/10)\gamma^2\hbar\langle 1/r^3\rangle\omega_0(\Delta\sigma)\tau_2^{D\cdot CS}$. τ_2^{i} is the appropriate rank two spherical harmonic correlation time, and ω_0 is the characteristic Larmor frequency. In the absence of molecular ordering induced by external electric/magnetic fields or liquid-crystalline solvents, $\langle \mathcal{H}_D\rangle = 0$ whereas in the limit, henceforth assumed, $\langle \mathcal{H}_D\rangle \gg 1/T_{2\pm}$, the rapid oscillation of λ effectively averages this term to zero, resulting in $1/T_{2+} = 1/T_{2-} = 1/T_2$. Notice that the appearance of a residual dipolar coupling *reduces* the efficiency of dipolar relaxation and *enhances* the efficiency of shielding anisotropy relaxation.

If the residual dipolar coupling, $\gamma^2\hbar\langle(1 - 3\cos^2\theta)/r_{HH}^3\rangle$, is positive, then the high-field single-quantum coherence of the dipolar split doublet is associated with the operator $\langle I_+\rangle + \langle I_+(2I_z + 1)\rangle$ whereas the low-field component is associated with the operator $\langle I_+\rangle - \langle I_+(2I_z + 1)\rangle$. From eq 1, it is seen that the relaxation rates of these two coherences are $(1/T_2) + (1/T_{2x})$ and $(1/T_2) - (1/T_{2x})$, respectively. Therefore, the difference in relaxation rates (high-field minus low-field widths) normalized by the sum of relaxation rates yields $(1/T_{2x})/(1/T_2)$. Of course, if the residual dipolar coupling is negative, the normalized high-field minus low-field relaxation rate is $-(1/T_{2x})/(1/T_2)$. In the limit of extreme narrowing with complete, positive correlation between all interactions ($\tau_2^{D} = \tau_2^{CS} = \tau_2^{CS\cdot CS} = \tau_2^{D\cdot CS} = \tau_2$), the ratio $(1/T_{2x})/(1/T_2)$ equals $27\chi/(54 + 13\chi^2)$. The relative strengths of the anisotropic shielding and dipolar couplings are defined by $\chi = (\omega_0\Delta\sigma)/(\gamma^2\hbar\langle 1/r^3\rangle)$. It is important to appreciate that the shielding anisotropy, $\Delta\sigma$, and hence χ, is not necessarily positive. Situations where the shielding tensor is not axially symmetric are easily accommodated in more general formalisms. In the limit where adiabatic or zero-frequency terms dominate, this ratio is given by the expression $72\chi/(81 + 61\chi^2)$. In Figure 1, these two normalized relaxation differentials are plotted as a function of χ (curve A′, $\omega_0\tau_2 \gg 1$; curve B′, $\omega_0\tau_2 \ll 1$).

Also shown in Figure 1 are relaxation rate differentials for the situation where the principal axes of the dipolar and shielding anisotropies are orthogonal, the shielding tensor is axially symmetric, and, as a result of highly anisotropic, axially symmetric motions, all interactions correlate completely. The unique motional axis is collinear with the principal axes of the shielding tensors and perpendicular to the H–H internuclear vector ($\tau_2^{D} = 4\tau_2^{CS} = 4\tau_2^{CS\cdot CS} = -2\tau_2^{D\cdot CS}$). These curves are labeled A ($\omega_0\tau_2 \gg 1$) and B ($\omega_0\tau_2 \ll 1$). Subject to the dynamic scenario described above, the dipolar-shielding anisotropy correlation factor is *negative*. Note that three signed factors, (i) the coupling

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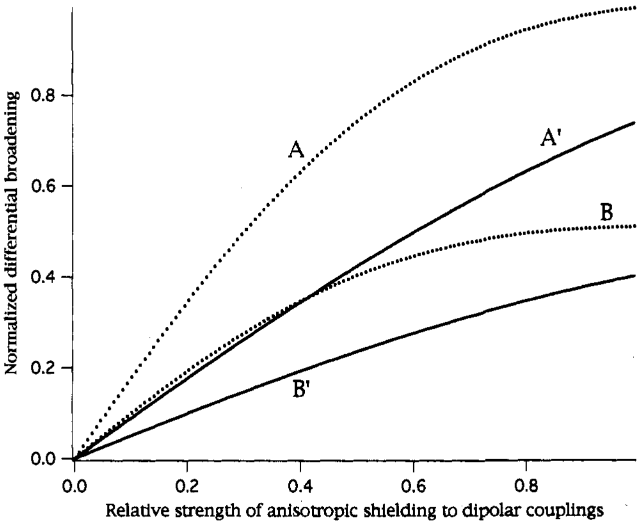

Figure 1. Plot of the normalized differential broadening, $(1/T_{2x})/(1/T_2)$, as a function of the ratio $(\omega_0\Delta\sigma)/(\gamma^2\hbar\langle 1/r^3\rangle)$ for a pair of identical protons subject to a residual, direct dipolar coupling. Motional and geometrical parameters identified with each of the four specific curves, A, B, A′, and B′, are described in the text.

responsible for multiplet structure, (ii) the couplings responsible for spin relaxation, and (iii) the cross-correlation factor whose own sign depends upon both intercoupling orientation and dynamics, determine whether the high-field or low-field component is preferentially broadened or narrowed. Given this fact, in Figure 1 we make no attempt to provide the absolute sign of the normalized differential broadening and this sign should be considered on a case-by-case basis.

With the aid of Figure 1, it is possible to advance a plausible rationalization of the observations noted in ref 3. With a negative dipolar coupling, and a narrowed high-field component, the cross-correlation term must be negative. The magnitude of the differential broadening, $(1/T_{2x})/(1/T_2)$, is approximately $^1/_3$. Using the values given in ref 3, ω_0 = 620 MHz and $\gamma^2\hbar\langle 1/r^3\rangle \approx$ 70 kHz, curves A, A′, B, and B′ yield effective $\Delta\sigma$ values of 20, 40, 40, and 80 ppm, respectively. If other interactions are effective at relaxing the protons, they add to $1/T_2$ alone and quench observable differentials as does inhomogeneous broadening. Thus, these shielding anisotropies must be considered lower limits. Additional experiments such as those described in ref 3 could easily distinguish between scenarios A, A′, B, B′, or intermediate possibilities. In addition to utilization of line width differentials, cross-correlation can be explored with multiquantum or longitudinal relaxation.[6] Indeed, a methodology with this goal has been proposed.[5] It is equally important to realize that one can examine relaxation-induced multispin order even in the absence of residual couplings—the appearance of residual dipolar coupling is not prerequisite for the exploitation of the information implicit in ref 3.

Nuclear spin relaxation in HD isotopomeric complexes promises to yield even more exacting insight. The appropriate relaxation expressions for HD complexes also appear in the published literature.[7,8] For purposes of illustration, consider the three proton-single-quantum coherences $|\alpha\rangle|m\rangle \leftrightarrow |\beta\rangle|m\rangle$, $m = +1, 0, -1$. Each of these three coherences, labeled as $(I_+)^m$, can be written as a sum of product operators

$$(I_+)^m = I_+[2 + 3mS_z + (3m^2 - 2)(S_z{}^2 - S^2)]/6 \quad (3)$$

The angular momentum, S, is associated with the deuteron. It is apparent that the difference in outermost line widths monitors two-spin order, whereas the widths of the outermost lines minus twice the width of the central lines probe three-spin order.

If nuclear spin relaxation results from proton and deuteron shielding anisotropies (CSH, CSD) and axially symmetric deuteron quadrupolar (Q) and proton–deuteron dipolar (D) couplings, the time evolution of each of the operators, $(I_+)^m$ is characterized by a unique relaxation constant given as follows:

$$\begin{aligned}(1/T_2)_m = {} & (8/3)[m^2J^{\mathrm{D}}(0) + J^{\mathrm{CSH}}(0) - 2mK^{\mathrm{D\cdot CSH}}(0)] + \\ & (2 - m^2)((1/3)J^{\mathrm{D}}(\omega_{\mathrm{H}} - \omega_{\mathrm{D}}) + J^{\mathrm{D}}(\omega_{\mathrm{D}}) + 2J^{\mathrm{D}}(\omega_{\mathrm{H}} + \omega_{\mathrm{D}})) + \\ & 2m^2(J^{\mathrm{D}}(\omega_{\mathrm{H}}) + J^{\mathrm{CSH}}(\omega_{\mathrm{H}})) + 2J^{\mathrm{CSD}}(\omega_{\mathrm{D}}) + \\ & 4(2 - m^2)J^{\mathrm{Q}}(\omega_{\mathrm{D}}) + 8m^2J^{\mathrm{Q}}(2\omega_{\mathrm{D}}) + 2mK^{\mathrm{Q\cdot CSD}}(\omega_{\mathrm{D}}) - \\ & 4mK^{\mathrm{D\cdot CSH}}(\omega_{\mathrm{H}}) \quad (4)\end{aligned}$$

where $J^{\mathrm{Q}}(0) = (3/160)(e^2qQ/\hbar)^2\tau_2{}^{\mathrm{Q}}$ and $K^{\mathrm{Q\cdot CSD}}(0) = (1/40)(\omega_0\Delta\sigma)_{\mathrm{D}}(e^2qQ/\hbar)\tau_2{}^{\mathrm{Q\cdot CSD}}$. The relevant relaxation differentials reduce to

$$\begin{aligned}(1/T_2)_{+1} - (1/T_2)_{-1} = {} & -(32/3)K^{\mathrm{D\cdot CSH}}(0) + 4K^{\mathrm{Q\cdot CSD}}(\omega_{\mathrm{D}}) - \\ & 8K^{\mathrm{D\cdot CSH}}(\omega_{\mathrm{H}}) \quad (5a)\end{aligned}$$

and

$$\begin{aligned}(1/T_2)_{+1} + (1/T_2)_{-1} - 2(1/T_2)_0 = {} & (16/3)J^{\mathrm{D}}(0) - \\ & 2((1/3)J^{\mathrm{D}}(\omega_{\mathrm{H}} - \omega_{\mathrm{D}}) + J^{\mathrm{D}}(\omega_{\mathrm{D}}) + 2J^{\mathrm{D}}(\omega_{\mathrm{H}} + \omega_{\mathrm{D}})) + \\ & 4(J^{\mathrm{D}}(\omega_{\mathrm{H}}) + J^{\mathrm{CSH}}(\omega_{\mathrm{H}})) + 8(2J^{\mathrm{Q}}(2\omega_{\mathrm{D}}) - J^{\mathrm{Q}}(\omega_{\mathrm{D}})) \quad (5b)\end{aligned}$$

Once again, in the study by Collman et al.,[3] the observation that the central component ($m = 0$) was narrowest can be rationalized if either $(16/3)J^{\mathrm{D}}(0)$ *or* $16J^{\mathrm{Q}}(2\omega_{\mathrm{D}})$ is the dominant contribution to loss of single-quantum coherence. However, it is important to recognize if extreme narrowing fails, deuteron quadrupolar relaxation is more efficient at relaxing the central component rather than the outer components of the proton triplet. Obviously, this simple fact can help unravel the complex nuclear spin relaxation characteristics in these novel chemical systems. Furthermore, it was observed[3] that the highest field component is broadened relative to the lowest field component. Assuming the proton–deuteron scalar coupling is positive, the high-field component will be broadest if the (proton–deuteron) dipolar (proton) shielding anisotropy cross-correlation is negative, as for the protium isotopomer. Conversely, if the quadrupolar deuteron shielding anisotropy dominates, the deuteron shielding anisotropy quadrupolar cross-correlation is positive.

Conclusion

It should be apparent from this brief commentary that a wealth of pertinent information is available if relaxation-induced polarization is correctly identified and subsequently utilized in the study of these dihydrogen complexes. Undoubtedly, successful application of these ideas will promote our understanding of the electronic, structural, and dynamic features of these intriguing chemical species.

Acknowledgment. Valuable and illuminating discussions with Professor A. A. Bothner-By are respectfully acknowledged.

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