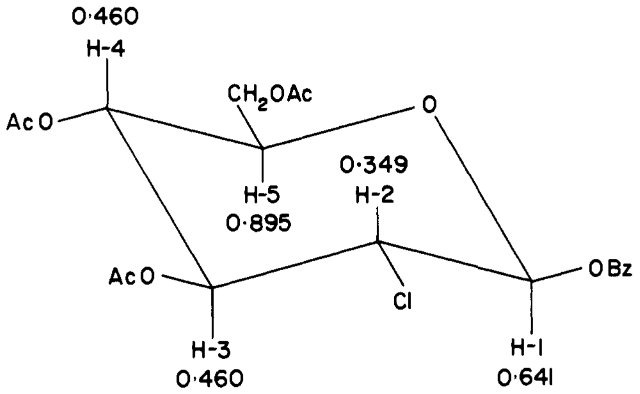

Figure 1. The structure of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose showing the initial relaxation rates R_1(NS) (in s^{-1}) for the ring protons.

sufficiently dilute solution in a magnetically inert solvent, only intramolecular dipole-dipole interactions are significant. Then the fraction of the relaxation of A arising from the IDD mechanism is

$$f^{A}(\mathrm{NS}) = \frac{2[R_1{}^{A}(\mathrm{NS}) - R_1{}^{A}(\bar{A})]}{R_1{}^{A}(\bar{A})} \tag{1}$$

Selective inversion of the nuclei, A and B, gives another value for the relaxation rate, $R_1{}^{A}(\bar{A},\bar{B})$, and now

$$f^{A}(\mathrm{B}) = \frac{2[R_1{}^{A}(\bar{A},\bar{B}) - R_1{}^{A}(\bar{A})]}{R_1{}^{A}(\bar{A})} \tag{2}$$

is the fractional contribution to the relaxation of A via dipolar interaction with B.

A practical demonstration both of the ease with which these experiments can be performed as well as of the high accuracy of the determination is afforded by the data for 0.1 M 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose in C_6D_6. For H-1 of this molecule, the deviation from exponential relaxation is sufficiently small that the initial rate could be accurately determined from measurements taken within 2 s of the perturbation. The nonselective R_1 values (in s^{-1}) are summarized in Figure 1. Selective inversion of H-1 gives a value for $R_1{}^1(\bar{1})$ of 0.427 s^{-1}. Thus the ratio $R_1{}^1(\bar{1})/R_1{}^1(\mathrm{NS})$ is 1.5, which shows that this proton receives 100% of its relaxation from the other protons in the same molecule. The estimated error in the relaxation rate measurements is $\pm 0.005\ s^{-1}$.

The measured initial relaxation rates for the selective inversion of pairs of protons are $R_1{}^1(\bar{1},\bar{2}) = 0,452$, $R_1{}^1(\bar{1},\bar{3}) = 0.487$, and $R_1{}^1(\bar{1},\bar{5}) = 0.552\ s^{-1}$. From eq 2 this gives the fractional contribution to the relaxation of H-1 from H-2, H-3, and H-5 as 0.12 ± 0.05, 0.28 ± 0.05, and 0.59 ± 0.05, respectively. The ratio of the contributions from H-3 and H-5 are in excellent agreement with a similar determination from NOE measurements.[14] Note that the relaxation measurements give a direct indication of the contribution of H-2; this contribution was masked in the NOE experiment[14] by multiple spin effects.

There are several important molecular and spectral prerequisites for the *simple* application of this type of measurement. First, it must be possible to use the initial rate approximation.[11] In this regard it should be appreciated that for complex spin systems the relaxation can never be truly exponential, but very frequently the observed relaxation behavior following single selective inversion is essentially exponential. This can happen when there are multiple relaxation pathways for all of the interacting nuclei, which is generally the case for complex organic molecules. Furthermore, essentially exponential relaxation will be observed following multiple-selective inversion if the several nuclei involved have approximately the same relaxation rates. We have studied other molecules in which the relaxation rates of the nuclei involved in the dipolar interaction are very different, and here the relaxation behavior is definitely nonexponential; however, numerical solution of the relaxation equations taking into account the different relaxation times allows the evaluation of the individual dipolar contributions.

From a practical standpoint the spectrum itself should be sufficiently dispersed that the 180° perturbation can be applied selectively to the chosen resonances.[10]

It is interesting to note that the conditions most favorable for these relaxation experiments include those for which the NOE experiment is, unfortunately, complicated by multiple spin effects;[6] therefore, the measurement of selective relaxation rates provides a useful alternative approach for the quantitative evaluation of dipole-dipole interactions in complex organic molecules.

In a rigid molecule, the *ratio* of the dipole-dipole interactions between pairs of nuclei is related to the *ratio* of their separations by an inverse sixth power dependence. An independent measurement of the molecular correlation times, for example, from a temperature-dependent study of the relaxation, would allow a determination of the internuclear distances themselves.

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Chemical Shift Elements for the Aromatic Nitrogen from Nuclear Magnetic Resonance Measurements on Solutions

Sir:

Determination of the components of the chemical shielding tensor, $\sigma_{\parallel}$ and $\sigma_{\perp}$, for a nucleus has been possible in the past by obtaining the NMR spectrum of the compound in which the free rotation of the molecule is restricted so that a particular orientation of the molecule with respect to the external field is maintained during the time of the NMR measurements. These measurements on solids and nematic phases have yielded useful information; however, there are many instances where the values of $\sigma_\parallel$ and $\sigma_\perp$ in a solution are desired. We have derived some equations which permit one to obtain $\sigma_\parallel$, $\sigma_\perp$, and, additionally, the correlation time τ from NMR measurements on solutions. This communication will use these equations on ^{15}N NMR data obtained on the molecule pyridine which has an aromatic nitrogen of the type found in porphyrin and related compounds (hemes, chlorophyll, and vitamin B_{12}) in order to obtain the molecular level information.

The nuclei for which the derived equations are applicable are those nuclei whose observed spin-lattice relaxation time, $T_{1\mathrm{obs}}$, has components from the chemical shift anisotropy (csa) and spin-rotational (sr) modes of relaxation and therefore is a function of six parameters: $\sigma_\parallel$ and $\sigma_\perp$ which are the $\parallel$ and $\perp$ components of the chemical shift tensor, $C_\parallel$ and $C_\perp$ which are the $\parallel$ and $\perp$ components of the spin rotational tensor, and τ_c and τ_j which are the rotational angular position and velocity correlation times. Six constraints can be placed on the relations between the various parameters so analytic expressions can be obtained for the various parameters. The six constraints are as follows: the definition of $T_{1\mathrm{csa}}{}^{-1}$, the definition of $T_{1\mathrm{sr}}{}^{-1}$, Hubbard's equation relating τ_c and τ_j,[1] Ramsey's relation between $\sigma_\parallel$ and $C_\parallel$ and between $\sigma_\perp$ and $C_\perp$,[2] and the definition of σ, i.e., $\sigma = \frac{1}{3}\sigma_\parallel + \frac{2}{3}\sigma_\perp$. When these expressions are combined, closed equations for all the parameters can be determined three of which are shown below.

$$\sigma_\perp = \sigma - \tfrac{1}{3}\Delta\sigma \text{ and } \sigma_\parallel = \sigma + \tfrac{2}{3}\Delta\sigma \text{ where}$$

$$(\Delta\sigma)^2 = -\frac{9}{4}(\sigma^{\mathrm{sr}})^2 \times \left\{1 \pm \sqrt{1 + 20\left(\frac{\beta_e}{\hbar H_0}\right)^2 \frac{T_{1\mathrm{sr}}{}^{-1} T_{1\mathrm{csa}}{}^{-1}}{(\gamma\sigma^{\mathrm{sr}})^4}}\right\}$$

$$\tau_c{}^{-1} = -\frac{3}{10}\frac{(\gamma H_0 \sigma^{\mathrm{sr}})^2}{T_{1\mathrm{csa}}{}^{-1}} \times \left\{1 \pm \sqrt{1 + 20\left(\frac{\beta_e}{\hbar H_0}\right)^2 \frac{T_{1\mathrm{sr}}{}^{-1} T_{1\mathrm{csa}}{}^{-1}}{(\gamma\sigma^{\mathrm{sr}})^4}}\right\}$$

The experimental measurements which are required for these expressions are as follows: $T_{1\mathrm{obsd}}(H_A)$ the observed T_1 at one field strength, $T_{1\mathrm{obsd}}(H_B)$ the observed T_1 at a second field strength, and σ, the chemical shift on the absolute chemical shift scale. The first two measurements are used to separate the csa component of the observed T_1. If only csa and sr modes are present, then $T_{1\mathrm{sr}}$ is obtained by difference. If dipolar relaxation is present as well, then additional experimental data are required to resolve $T_{1\mathrm{sr}}{}^{-1}$ and $T_{1\mathrm{csa}}{}^{-1}$. The ^{15}N chemical shift scale has been referenced by molecular beam measurements on $^{15}N_2$ so the value of σ can be determined by difference from the $\sigma(^{15}N_2)$ which is −101 ppm.[3]

Experimental measurements of the pyridine ^{15}N T_1 values at two different field strengths have been made[4] and at −41 °C a $T_{1\mathrm{csa}}{}^{-1}$ of $1.3 \times 10^{-2}\ \mathrm{s}^{-1}$ is calculated. In this molecule both dipolar (inter- and intramolecular) and sr modes of relaxation are present. At −41 °C a minimum in the observed T_1 exists and the customary procedure of assuming $T_{1\mathrm{sr}} = T_{1\mathrm{csa}}$ at the minimum gives a $T_{1\mathrm{sr}}{}^{-1}$ of $4.4 \times 10^{-3}\ \mathrm{s}^{-1}$. For liquid pyridine σ is found to be −93 ppm of which +324 ppm is the free atom part of the diamagnetic contribution and −417 ppm is the spin-rotational part of the paramagnetic contribution. When these values are used in the previously given equations, one obtains a $\sigma_\parallel$ of 565 ppm, a $\sigma_\perp$ of −422 ppm, and a τ_c of 2.8 ps. This $\Delta\sigma$ value is 987 ppm which is larger than that observed in the solid state. It is possible that the ring currents from the immobilized solid may contribute more to the chemical shift of one element of the tensor than to the other producing a smaller $\Delta\sigma$ in the solid than in the rotationally averaged solution molecules. However, the difference between the solid and solution values may have its origin in the fact that the method for determining the relative amounts of $T_{1\mathrm{dd}}$ and $T_{1\mathrm{sr}}$ was not the Overhauser enhancement approach but instead the minimum in the temperature dependence of T_1 method. This method is valid only if the activation energies for both the dipolar and sr processes are the same which is not generally the case. When $T_{1\mathrm{sr}}{}^{-1}$ is taken to be $2.0 \times 10^{-3}\ \mathrm{s}^{-1}$, then $\Delta\sigma$ becomes 758 ppm, and τ_c is 4.8 ps.

This communication demonstrates the fact that for aromatic nitrogens it is possible to obtain a measure of the chemical shielding of the nitrogen atom along different axes of the molecule and of the mobility of the molecule in solution from NMR data. Thus, the means are now available to treat problems such as the dimerization of chlorophyll a which may involve changes in the directional shielding of the aromatic nitrogen of the porphyrin. More details on the derivation of the equations will appear elsewhere.[5]

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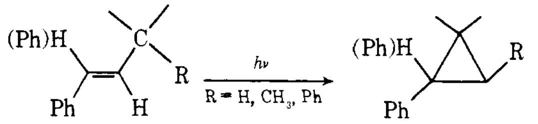
Relative and Absolute Rate Constants for Photochemical 1,2-Migration of Hydrogen, Methyl, and Phenyl in *trans*-β-Substituted-Styrenes

Sir:

Appropriately substituted styrenes or diphenylethylenes undergo photochemical 1,2-shifts of γ-hydrogen, methyl, and phenyl groups to form arylcyclopropanes (eq 1).[1]



(1)

The rates of these migrations are markedly and similarly affected by para substitution in the styrene or diphenylethylene chromophores.[2] Until now no direct comparison of the migratory aptitudes of the three groups—methyl, phenyl, and hydrogen—in the processes shown in eq 1 has been made, nor to our knowledge has a quantitative measure of the photochemical migratory abilities of these three fundamentally different moieties been carried out in any system.[3] In this communication we present a study of the relative and absolute rates of photochemical 1,2-migration of the three groups in β-substituted styrenes. Importantly, we make use of compounds which are identical but for the migrating species. We also show how substitution at the migration origin can markedly affect the migration process.