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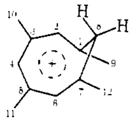

i

the protic impurities which are always present in the SbF_5, despite careful purification.[9] Cation i is not an intermediate in the formation of **3** and was prepared independently by protonation of **2** with FSO_3H in SO_2ClF solution at −78°.

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$$\Delta\sigma = -\frac{e^2a^2}{2mc^2R^3}$$

where $\Delta\sigma$ = the ring-current contribution to the mean screening constant of the proton, a = the radius of the aromatic ring, and R = the distance from the center of the aromatic ring to the proton. For the calculation, the MINDO/2 optimized geometry of **1** from ref 4a was utilized. The C–H bond lengths in 1 were assumed to be the same as in cyclooctatetraene (1.09 Å).

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Spin-Lattice Relaxation of Protons. A General, Quantitative Evaluation of Contributions from the Intramolecular Dipole-Dipole Mechanism

Sir:

The demonstration[1-4] of several chemically useful stereospecific dependencies for the spin-lattice relaxation times (T_1 values) of the protons of organic molecules provides a compelling need for the development of methods for the accurate measurement of the relaxation contributions between individual protons via the intramolecular dipole-dipole (IDD) mechanism. Although such measurements can be made via nuclear Overhauser enhancement (NOE)[5,6] experiments, a number of difficulties somewhat limit the overall scope of that approach. We now describe an alternative method, based on the selective measurement of T_1 values, which appears to have a wide generality.

For a coupled spin system,[7] the relaxation is, in general, nonexponential but the *initial* rate of relaxation, R_1, is a function of the initial perturbation. The conventional two-[8] or three-pulse[9] Fourier transform methods, in which a 180° pulse inverts the populations of all transitions, provide a routine source of the nonselective R_1 value, $R_1{}^A$(NS). A different value, $R_1{}^A(\tilde{A})$ is obtained by selective[10-13] inversion of the spin states of a single nuclear species (A). The ratio $R_1{}^A(NS)/R_1{}^A(\tilde{A})$ then gives the extent to which that particular species is relaxed via dipole-dipole interaction *with other spins inverted by the nonselective pulse.* For complete proton dipolar relaxation, this ratio is[6] 1.5. For a

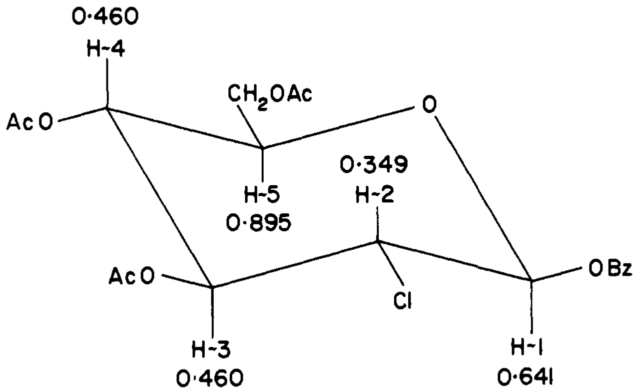

Figure 1. The structure of 3,4,6-tri-*O*-acetyl-1-*O*-benzoyl-2-chloro-2-deoxy-β-D-glucopyranose showing the initial relaxation rates R_1(NS) (in s^{-1}) for the ring protons.

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

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

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

$$f^A(B) = \frac{2[R_1^A(\tilde{A},\tilde{B}) - R_1^A(\tilde{A})]}{R_1^A(\tilde{A})} \quad (2)$$

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 $R_1^1(\tilde{1})$ of 0.427 s^{-1}. Thus the ratio $R_1^1(\tilde{1})/R_1^1(\mathrm{NS})$ 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 $R_1^1(\tilde{1},\tilde{2}) = 0.452$, $R_1^1(\tilde{1},\tilde{3}) = 0.487$, and $R_1^1(\tilde{1},\tilde{5}) = 0.552\ s^{-1}$. 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