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Communications to the Editor

Computational Evidence of NMR Deshielding of Protons over a Carbon−Carbon Double Bond

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Diamagnetic shielding of protons due to the anisotropy of the magnetic susceptibility of nearby groups has been known for some time. Shielding is most pronounced in aromatic compounds because of the high electron density associated with aromatic rings. Pauling[1] explained the phenomenon in benzene in terms of abnormally large magnetic moments caused by the Larmor precession of the six π electrons in orbits containing multiple nuclei. Pople[2] estimated this shielding effect using a point dipole calculation. McConnell[3] proposed an equation to predict the directional dependence of the NMR shielding tensor experienced by a nucleus because of its proximity to an anisotropic group. Evaluation of the sign of the shielding effect calculated by this equation gives rise to the familiar "shielding cone" (Figure 1) found in most textbooks on NMR spectroscopy.[4] An empirical function was developed by Johnson and Bovey[5] to predict the shielding increment of a proton held over the face of a benzene ring. Schneider[6] applied the program SHIFT, employing a ring current model to the calculation of diamagnetic shielding in cyclophanes. More recently, Martin, Allen, Moore, and Vo[7] developed an empirical equation for predicting the NMR shielding of a proton over benzene based on ab initio calculations of a simple model system, methane over a benzene ring.

The magnitude of the shielding effect in alkenes is smaller than that observed in aromatic systems, but the effect is significant enough to be of consequence in structural assignments based on NMR spectra. In the traditional textbook representation (Figure 1) based on the McConnell[3] equation, protons positioned over a carbon−carbon double bond are considered to be in the "shielding cone" of the carbon−carbon double bond. However, analysis of the NMR spectra of compounds which appear to possess the necessary structural features to exhibit such shielding reveals that in many instances protons so oriented experience *deshielding* instead (Figure 2). In this paper we report preliminary results of ab initio calculations which predict *deshielding* of protons above the face of a carbon−carbon double bond, as is observed experimentally in structures **1** and **2**. These results are diametrically opposed to the long-held notion of a "shielding cone" above and below the face of a carbon−carbon double bond and call into question the validity of chemical shift predictions based solely on that model.

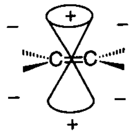

Figure 1. Traditional NMR shielding cone for a carbon−carbon double bond.

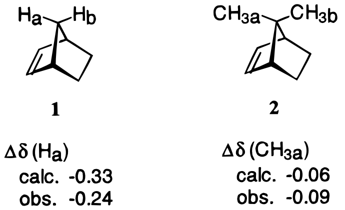

Figure 2. GIAO-predicted and observed NMR shielding increments in structures having protons over a carbon−carbon double bond.

Input geometries of structures **1** and **2** were generated using Spartan[8] molecular modeling software running on an SGI Indigo2 R4000 computer and were optimized at an ab initio level using Hartree−Fock theory, with a basis set of 6-31G(d,p).[9] The geometry-optimized structures were saved as Brookhaven protein databank (.pdb) files which were transferred to a Cray T-916 supercomputer. Using the same theory and basis set employed in the geometry optimization calculations of the individual structures, each of these input files was submitted for a single point computation using Gaussian 94.[10] The NMR isotropic shielding tensors were calculated using the utility GIAO (gauge invariant atomic orbital), developed by Ditchfield[11] and later modified by Chesnut.[12] GIAO calculates an isotropic shielding value for each atom. Differences in these values may be used to predict chemical shift differences (in ppm).

We define the shielding increment ($\Delta\sigma$) as the difference in the isotropic shielding value calculated by GIAO for the proton(s) over the double bond (H_a) versus that for comparable protons not over a double bond (labeled H_b). Structures such as **2** in which a methyl group is held over an alkene double bond pose a special problem. Rapid rotation of the methyl group results in the NMR chemical shift representing the average environment of the three protons, yet GIAO utilizes a specific geometry (single conformation) for computation of the isotropic shielding values. Therefore, in an attempt to estimate an average shielding increment two conformers were used, the lowest energy conformer (which had one methyl proton directed toward the alkene double bond) and one differing from it by a 60 degree rotation. The shielding increments of the six proton environments were averaged

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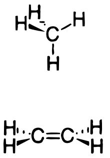

Figure 3. Initial geometry of the methane−ethene pair.

to provide an "effective shielding increment." The GIAO-calculated shielding increments are found in Figure 2. Also in Figure 2 are the experimentally observed shielding increments, defined here as the chemical shift difference between two proton types in similar environments except for their relationship to a carbon−carbon double bond; $\Delta\sigma = \delta H_b - \delta H_a$ or $\Delta\sigma = \delta CH_{3b} - \delta CH_{3a}$, where the protons labeled a are located over the carbon−carbon double bond. Thus a negative value of $\Delta\sigma$ suggests that H_a or CH_{3a} is deshielded relative to H_b or CH_{3b}. Both the GIAO calculations and the experimental observations concur that structures **1** and **2** display deshielding (a downfield, or paramagnetic shift) for the protons (H_a) over the carbon−carbon double bond. This is in sharp contrast to the predicted shielding (upfield, or diamagnetic shift) according to the traditional shielding cone model based on the McConnell equation.[3]

A simple model system was constructed to test the generality of deshielding over a carbon−carbon double bond. Input geometries of methane and ethene were generated separately using Spartan[10] molecular modeling software running on an SGI Indigo2 R4000 computer, and each was optimized at an ab initio level using Hartree−Fock theory using a 6-31G(d,p) basis set.[11] The optimized structures were exported to a Brookhaven protein databank file format (.pdb) file at which point two files were textually merged to create the geometry indicated in Figure 3, in which one proton of the methane molecule is 2.0 Å above the plane of ethene directly over the center of the carbon−carbon double bond with the proximal C−H bond oriented normal to the plane of ethene. The other three protons project away from ethene. Similar data files were created in which the methane molecule was located up to 5 Å away from the plane of ethene. Using the same theory and basis set as employed previously, each of these input files was submitted to a single point GIAO computation using Gaussian 94. The isotropic shielding values for each proton on the methane molecule over ethene were transformed into the calculated shielding increment ($\Delta\sigma$) by subtracting from each data point the isotropic shielding value calculated similarly for methane alone. The shielding increment $\Delta\sigma$ was graphed against the distance from the center of the carbon−carbon double bond (solid circles, Figure 4). Positive values of $\Delta\sigma$ represent shielding; negative values represent deshielding. A similar series of calculations was performed with methane located approximately over[13] one hydrogen atom of ethene; a similar, but less dramatic deshielding curve was obtained (open circles, Figure 4). In contrast to the traditionally employed shielding cone model, our results demonstrate *deshielding* for protons above the center of a carbon−carbon double bond within 3 Å of the plane of the alkene, as is observed experimentally in several systems. A detailed computational analysis of the (de)-shielding surface above a carbon−carbon double bond is in progress.

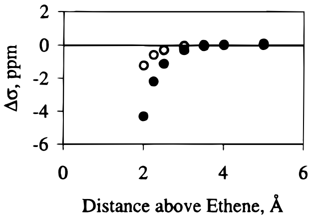

Figure 4. Graph of the GIAO-calculated shielding increment ($\Delta\sigma$) of a proton of methane (a) oriented as in Figure 3 vs distance above the center of ethene (solid circles) and (b) oriented as in Figure 3 but positioned approximately over[13] one hydrogen of ethene (open circles) vs. distance above ethene.

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(13) The Cartesian coordinates of ethene placed all atoms in the *XY* plane with the carbon−carbon double bond along the *Y* axis, centered at the origin. The two series of calculations had the proximal proton of methane at $X,Y =$ 0,0 and 1,1, respectively. For reference, one hydrogen of ethene was located at $X,Y = 0.915, 1.225$.