Modeling through-space magnetic shielding over ethynyl, cyano, and nitro groups

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Abstract

In a strong magnetic field, covalently bonded hydrogen nuclei located over a π bonded functional group experience magnetic shielding (or deshielding) that results from the combined effect of the magnetic anisotropy of the π bond and various other intramolecular shielding effects. Gauge including atomic orbital (GIAO)-HF in *Gaussian 98* was employed to calculate isotropic shielding values and to predict the net through-space proton NMR shielding increment for a simple model system: the proximate proton of methane held in various positions over simple molecules that contain a carbon–carbon triple bond, a carbon–nitrogen triple bond, or a nitro group. These net shielding increments of the proximate proton of methane, plotted against their Cartesian coordinates, led to the development of a single empirical equation for predicting the NMR shielding experienced by a covalently bonded proton over each group. The predictive capability of each equation has been validated by calculating shielding increments of protons over the functional group in known structures. These shielding increments are then used to adjust predicted chemical shifts for through-space shielding effects, and the adjusted values are compared to experimentally observed chemical shifts. The algorithms for predicting the shielding increment for a proton over these functional groups can be used in a spreadsheet or incorporated into software that estimates chemical shifts using additive substituent constants or a database of structures. Their use can substantially improve the accuracy of the estimated chemical shift of a proton in the vicinity of these functional groups, and thus assist in spectral assignments and in correct structure determination. © 2002 Elsevier Science Inc. All rights reserved.

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1. Introduction

Protons held over functional groups having π electrons typically experience a shift in the NMR spectrum due to through-space diamagnetic or paramagnetic shielding [1,2]. Pauling [3] described this characteristic in benzene as originating from the Larmor precession of electrons in orbits containing many nuclei. Subsequently, Pople [4] estimated this effect in hydrocarbons using a point dipole calculation.

McConnell [5] developed Eq. (1) to predict the shielding experienced by a nucleus near an anisotropic functional group that results from its magnetic anisotropy ($\Delta \chi$):

$$\Delta \sigma = \frac{1}{3} \Delta \chi \left(\frac{1 - 3\cos^2 \theta}{4\pi R^3} \right) \tag{1}$$

This equation leads to the currently held 'shielding cone model' (Fig. 1) commonly found in NMR spectroscopy textbooks [1,2]. The McConnell equation deals only with the anisotropy of the magnetic susceptibility of the functional group and its geometrical relationship to the nucleus in question. It ignores other factors that affect the chemical shift,

such as electric field effects, dipole effects, dispersion, and orbital interactions that might lead to distortion of the electron cloud.

Pople [6] used molecular orbital theory to estimate the anisotropy of the carbon–carbon triple bond. Reddy and Goldstein [7] determined diamagnetic anisotropy contributions to chemical shifts of protons near the nitrile group and the carbon–carbon triple bond. This determination was based on a linear relationship between chemical shifts and the ^{13}C–^1H coupling constant. The values obtained by their study agreed with the anisotropic effects on methyl and methylene protons in all the acetylenic and nitrilic compounds studied.

Agarwal and McGlinchey [8] evaluated proton shifts near a carbon–carbon triple bond by combining the simple classical model of circulating currents around the alkyne carbon atoms with experimentally derived ^{13}C magnetic shielding values. Their calculated shifts agreed well in both sign and magnitude to the experimental data.

Alkorta and Elguero [9] used ab initio hybrid DFT-gauge including atomic orbital (GIAO) calculations to compute the proton chemical shifts of a methane molecule positioned at selected points collinear and perpendicular to carbon–carbon single, double, and triple bonds in simple

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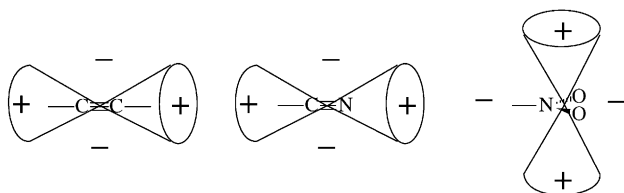
Fig. 1. Traditional NMR shielding cones for ethynyl, cyano, and nitro groups. Positive regions are shielding and negative regions are deshielding.

Fig. 2. Geometries of methane positioned over acetylene, HCN, and HNO$_2$ (C$_{2v}$).

structures. Comparison of the calculated data with the classical shielding cone models reversed the classical picture in the case of the carbon–carbon single bond. Their calculations reproduced deshielding in the plane of, but not shielding perpendicular to, the carbon–carbon double bond, in contrast to the classical shielding cone model. Their calculations of methane in the vicinity a carbon–carbon triple bond were consistent with the classical shielding cone model.

Abraham and Reid [10] used the CHARGE7 model to determine the two and three bonds cyano substituent chemical shift in various molecules. The CHARGE7 model theory distinguishes between substituent effects over one, two and three bonds that are attributed to the electronic effects of the substituents and longer-range effects due to the electric fields, steric effects and anisotropy of the substituents. They concluded that the anisotropic and steric effects of the cyano group were negligible in the compounds investigated and that the cyano substituent chemical shift effect was due to the electric field and electronic effects of the cyano group.

Recently, the same authors reported on anisotropic and steric effects of the acetylene group using the same approach [11]. Their calculations gave very good agreement with observed substituent chemical shifts. They concluded that steric effects generally predominate over anisotropy effects, especially when the overall substituent effect is large.

Klod and Kleinpeter [12] have calculated the anisotropy effect of multiple bonds (and aromatic rings) using nucleus independent chemical shieldings (NICS) [13] calculated using the GIAO method. Their method gives good agreement with experimental chemical shifts for protons that are not spatially near the multiple bond, but not in cases where the proton is close to the multiple bond.

We have used the GIAO method at the Hartree–Fock level of theory [14–16] to predict magnetic shielding of covalently bonded hydrogens over a carbon–carbon double bond [17–21] and aromatic rings [22,23] using methane as a probe. As predictions using that approach agree well with experimental observations and disagree with the traditional shielding cone model for alkenes, the same method was also applied to map the shielding surfaces of other anisotropic functional groups. We have also compared the results of magnetic shielding of a methane probe over a carbon–carbon double bond calculated using HF or MP2, and have shown that there is little difference in the result between the methods [24]. In that system, MP2 calculations
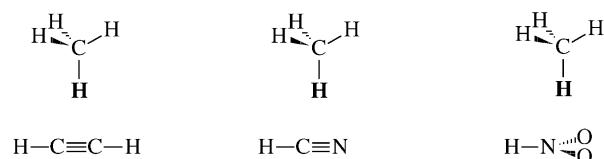
provided shielding values about 9% lower than did HF at the same 6–31G(d, p) basis set. Because this is within the limits of uncertainty of the predictions, subsequent calculations were performed at the HF level for computational efficiency.

We have recently reported a detailed analysis of the localized orbital origin of the through-space magnetic shielding effects of several common organic functional groups including the carbon–carbon double and triple bonds, the carbon–nitrogen triple bond, the carbonyl group, and the nitro group [25]. In that study, the inadequacy of absolute chemical shieldings ("ghost atom" shielding calculations) for predicting chemical shifts was noted. The reason for this is the importance of mutual perturbation of interacting orbitals at close proximity, a factor that is not included in ghost atom models. We have also investigated using other molecular probes, but have found methane to be the best simple model for predicting shielding of protons bonded to carbon [26].

In this paper, we report the results of calculating the NMR shielding surface of the proximate proton of methane held in various positions over three test structures: acetylene, HCN, and HNO$_2$ (C$_{2v}$ symmetry, Fig. 2). These structures were selected as the simplest examples that contain the functional groups to be studied: ethynyl, cyano, and nitro. HNO$_2$ was modeled in C$_{2v}$ symmetry rather than the expected C$_s$ symmetry of nitrous acid (HONO) because the C$_{2v}$ symmetry structure is a better model for an organic nitro group.

2. Computational methods

The same methodology developed for calculating the through-space magnetic shielding of protons over a carbon–carbon double bond [17–21] was used. Optimized geometries of methane and each of the test structures were determined by using Hartree–Fock theory and the 6–31G(d, p) basis set [27] in Spartan [28] on an SGI O2 graphics workstation equipped with an R4000 processor. The Cartesian coordinate file of the geometry-optimized test structure was merged with a Cartesian coordinate file of methane in various positions over the anisotropic functional group. The methane molecule was positioned over the test structure such that one proximal proton of methane was directed toward the test structure at a distance of 2.0 Å (Fig. 2). The coordinates of the test structure remained fixed while the coordinates of methane were changed incrementally

along the major axis of the test structure (Y-axis) and to the side of the test structure (X-axis) for HNO_2 (C_{2v}). In the case of acetylene and HCN, methane was moved only along the axis of the test structure (Y-axis) because of the symmetry of the test structures. The distance above the test structure (Z-axis) was held constant for a series of calculations. The displacements in the X and Y direction were made in 0.5 Å increments. This process was repeated at distances from the test structure (Z) of 2.5, 3.0, and 3.5 Å.

The isotropic shielding value of the proximal proton of methane in various positions over the test structure was determined by performing single-point calculations in Gaussian 98 [29] using GIAO-HF/6-31G(d, p) on a Cray T90. The isotropic shielding value was corrected for basis set superposition error (BSSE) using the counterpoise method of Boys and Bernardi [30]. The correction for BSSE was typically 0.01 ppm or less, and thus, is negligible. Through-space shielding increments ($\Delta\sigma$) were determined for the proximal proton of methane by subtracting the isotropic shielding value calculated for the protons of isolated methane from the isotropic shielding value calculated for the proximal proton of methane at various positions over the test structures. The shielding increment is a measure of the net through-space NMR shielding (or deshielding) influence of the functional group. The shielding increment ($\Delta\sigma$) was plotted against position in the X (or Z) and Y Cartesian coordinates of the hydrogen relative to the anisotropic group to determine the shielding surface. TableCurve3D [31], a statistical modeling package, was used to obtain a mathematical equation that fit the surfaces.

The shielding surface above HNO_2 was described well by the same form of equation for each of several distances of the proximal proton of methane above the test structure. Quadratic equations relating the constants and coefficients in the equation for each surface and the distance (Z) above HNO_2 were determined using MSExcel [32].

To test the accuracy of each shielding equation, the function was used to calculate shielding increments of protons in similar proximity to the functional groups in known structures. This provides an estimate of the through-space shielding effect of the functional group. The shielding increments were subtracted from the chemical shift predicted using appropriate additive substituent effects [33] (the latter gives an estimate of electronic through-bond effects, but do not generally consider through-space effects) to provide "adjusted" chemical shifts. The adjusted chemical shifts were compared to the experimentally observed chemical shifts.

3. Results and discussion

Magnetic shielding surfaces for each functional group were determined by plotting the magnetic shielding increment ($\Delta\sigma$) of the proximal proton of methane against its position in Cartesian coordinates (Figs. 3–5). Because of the cylindrical symmetry of acetylene and HCN, their shielding
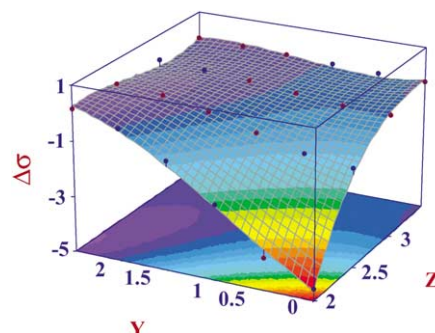

Fig. 3. Calculated shielding increment ($\Delta\sigma$) surface for methane over acetylene; Y and Z values are in Å; $\Delta\sigma$ values are in ppm. The center of the C–C bond is at $Y = 0$.
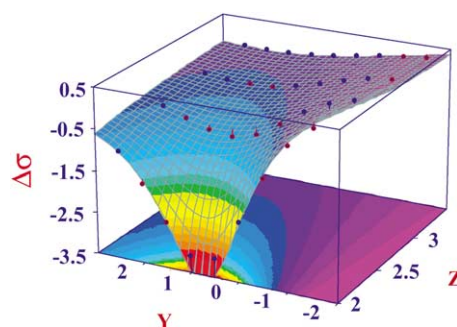

Fig. 4. Calculated shielding increment ($\Delta\sigma$) surface for methane over HCN; Y and Z values are in Å; $\Delta\sigma$ values are in ppm. The center of the C–N bond is at $Y = 0$.

surfaces were mapped in the Z and Y directions only. The best-fit equation (Table 1) for the shielding surface of acetylene was found to have the form of Eq. (2):

$$\Delta\sigma = a + bZ + cY + dZ^2 + eY^2 + fZY + gZ^3 + hY^3 + iZY^2 + jZ^2Y \tag{2}$$

The best-fit equation for the shielding surface of HCN has the form of Eq. (3):

$$\Delta\sigma = \frac{a + bZ + cY + dY^2}{1 + eZ + fY + gY^2 + hY^3} \tag{3}$$

The numerical values of the constant (a) and coefficients for the best-fit equation for the shielding surface of these two functional groups are given in Table 2. The r^2 values for the

Table 1
The form of the best-fit function for the shielding surfaces as a function of proton coordinates

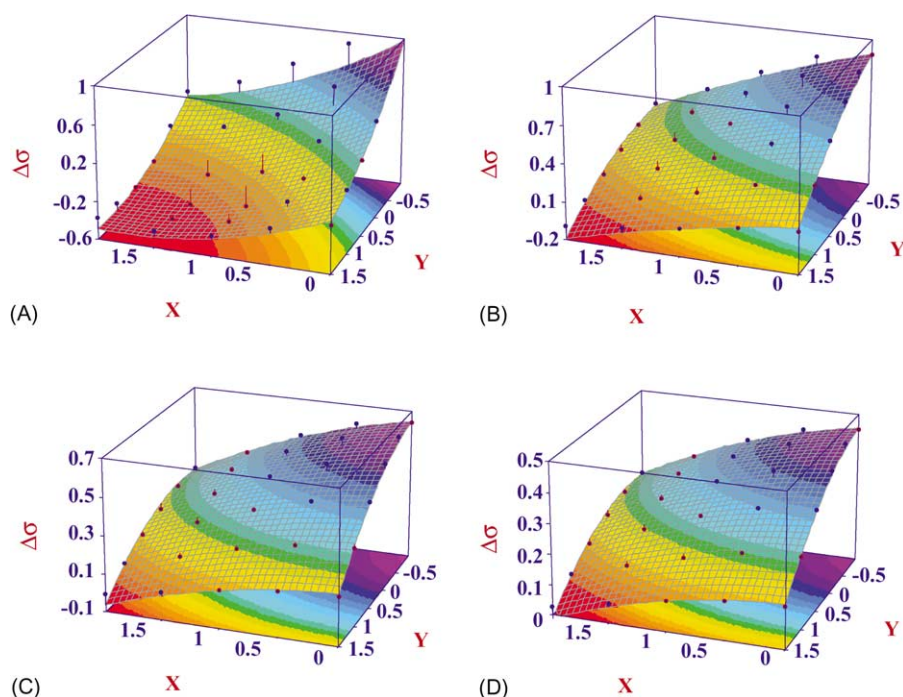| Functional group	Equation
Ethynyl	$\Delta\sigma = a + bZ + cY + dZ^2 + eY^2 + fZY + gZ^3 + hY^3 + iZY^2 + jZ^2Y$
Cyano	$\Delta\sigma = (a + bZ + cY + dY^2)/(1 + eZ + fY + gY^2 + hY^3)$
Nitro	$\Delta\sigma = a + bX + cY + dX^2 + eY^2 + fXY$

Fig. 5. Calculated shielding increment ($\Delta\sigma$) surface for methane over HNO_2 (C_{2v}) at distances (Z) of: (A) 2.0 Å; (B) 2.5 Å; (C) 3.0 Å; (D) 3.5 Å; X and Y values are in Å; $\Delta\sigma$ values are in ppm. The N atom is at $Y = 0$.

best-fit equations for acetylene and HCN are 0.99 and 0.98, respectively.

Three dimensions (X, Y and Z) had to be mapped for the shielding surface (Fig. 5) over HNO_2, our model for the nitro group, because it lacks cylindrical symmetry. The constant (a) and coefficients of the best-fit Eq. (4) of the shielding surface for the nitro group at each of several distances above the plane of the nitro group are shown in Table 3:

$$\Delta\sigma = a + bX + cY + dX^2 + eY^2 + fXY \qquad (4)$$

Simple quadratic equations were found using MSExcel to relate the constant (a) and coefficients of the best-fit equation to the distance above the test structures (Table 4).

Substitution of these quadratic equations for the constant (a) and the coefficients in the best-fit equation gave one equation (Eq. (5)) for predicting the magnetic shielding increment due to through-space shielding arising from the

Table 3
Values of the constant and coefficients at each distance Z above HNO_2 (C_{2v}) and the r^2 values for the best-fit equation as a function of proton coordinates

Parameter	2.0 Å	2.5 Å	3.0 Å	3.5 Å
a	0.4195	0.6915	0.5493	0.3929
b	−0.6403	−0.1966	−0.0732	−0.0367
c	−0.4617	−0.2558	−0.1578	−0.1023
d	0.1417	−0.0345	−0.0482	−0.0346
e	0.0995	−0.0644	−0.0625	−0.0417
f	0.0902	0.0583	0.0335	0.0181
r^2	0.94	0.97	0.98	0.99

Table 2
Values of the constant and coefficients in the equations for the shielding surface over acetylene and HCN, and the r^2 value of each equation

Parameter	Value (acetylene)	Value (HCN)
a	−48.5805	0.395022
b	39.63832	−0.101658
c	14.17498	0.16666
d	−10.7655	−0.025583
e	−0.00907	−0.545363
f	−8.54178	0.051383
g	0.968578	−0.040123
h	−0.18083	−0.016614
i	0.216983	–
j	1.230514	–
r^2	0.99	0.98

Table 4
Equations relating the constant and coefficients to the distance Z above the plane of HNO_2 (C_{2v}) and their r^2 values

Equation	r^2
$a = -0.4284Z^2 + 2.3119Z - 2.4706$	0.86
$b = -0.4072Z^2 + 2.6265Z - 4.2528$	0.99
$c = -0.1504Z^2 + 1.0626Z - 1.982$	1.00
$d = 0.1897Z^2 - 1.1517Z + 1.6797$	0.96
$e = 0.1847Z^2 - 1.1002Z + 1.5537$	0.94
$f = 0.0165Z^2 - 0.139Z + 0.3023$	1.00

Table 5
The rms deviation (in ppm) of the shielding increment calculated by the shielding equation and that calculated by GIAO as a function of the distance (Z) above the test structure

Distance above test structure (Å)	rms deviation (acetylene)	rms deviation (HCN)	rms deviation (HNO_2)
2.0	0.12	0.14	0.08
2.5	0.09	0.09	0.05
3.0	0.07	0.03	0.05
3.5	0.07	0.01	0.02

proximity to the nitro group:

$$\Delta\sigma = -0.4284Z^2 + 2.3119Z - 2.4706$$
$$+ (-0.4072Z^2 + 2.6265Z - 4.2528)X$$
$$+ (-0.1504Z^2 + 1.0626Z - 1.982)Y$$
$$+ (0.1897Z^2 - 1.1517Z + 1.6797)X^2$$
$$+ (0.1847Z^2 - 1.1002Z + 1.5537)Y^2$$
$$+ (0.0165Z^2 - 0.139Z + 0.3023)XY \tag{5}$$

The shielding increment for each position of a proximal proton of methane in each input data file was also calculated using the appropriate shielding increment equation. These values were compared with the GIAO-calculated shielding increments by calculating the root mean square (rms) deviation (Table 5). The rms deviation provides an indication of the precision of the shielding increment function in reproducing the GIAO-calculated shielding values. The rms data shows greater deviation for protons closer to the functional group. This is due in part to the fact that larger shielding increments are encountered at closer distances than at farther distances. Another possible explanation is that a different mathematical function might better fit the data and give better predictions at closer distances.

The validity of these equations to predict the chemical shifts of protons near these functional groups was tested by using the predicted shielding increment results in conjunction with additive substituent effects to predict a chemical shift "adjusted" for through-space (de)shielding effects. This value was compared to experimentally observed chemical shifts. The "adjusted" chemical shift predictions were obtained by using standard additive substituent increments [33] (which consider through-bond effects, but not through-space effects) and subtracting the through-space shielding increment ($\Delta\sigma$) predicted by the best-fit equation. The Cartesian coordinates of the proximal hydrogen used in the best-fit equations to obtain the shielding increment were determined by applying simple trigonometry to distances and angles measured using Spartan. In the case of phenanthrene derivatives (Fig. 6), it is known that substituents on one terminal ring have little through-bond electronic effect on the chemical shift of protons on the other terminal ring. For example, in 1-, 2-, or 3-nitrophenanthrene, the chemical shifts of H5, H6, and H7 are little changed (less than 0.1 ppm) from their counterparts in the parent phenanthrene [34]. Therefore,
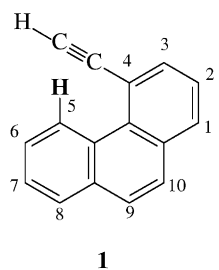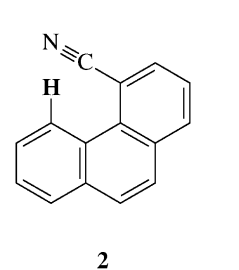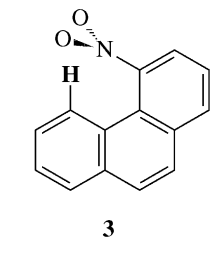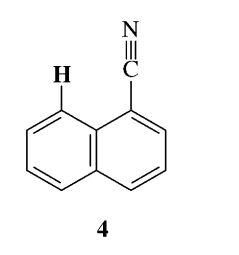

1	**2**
(0.000, 0.385, 2.285)	(0.000, 0.333, 2.213)
Predicted: 8.7 δ	Predicted: 8.7 δ
Adjusted: 10.9 δ	Adjusted: 9.8 δ
Observed: 10.3 δ [34]	Observed: 9.9 δ [34]
3	**4**
(0.000, 0.227, 2.289)	(0.000, –0.435, 2.543)
Predicted: 8.7 δ	Predicted: 8.1 δ
Adjusted: 8.2 δ	Adjusted: 8.3 δ
Observed: 8.1 δ [35]	Observed: 8.2 δ [10]

Fig. 6. Cartesian coordinates (X, Y, Z) in Å of the affected proton (shown bold) relative to the origin, chemical shift values (ppm) predicted by additive substituent constants (predicted), chemical shift predictions (ppm) adjusted by subtracting the through-space shielding increment (adjusted), and experimental values of chemical shifts in ppm (observed) [35,36].

for the 4-substituted phenanthrene derivatives, the predicted value (ignoring through-space effects) is the chemical shift of H5 on the parent phenanthrene (8.7 ppm). Examples of the application of our "adjustment" for through-space shielding effects on predicted chemical shifts are shown in Fig. 6.

Comparison of the adjusted predictions to the experimental data shows that substantial improvement over chemical shifts predicted using standard additive substituent increments is obtained by adjusting for through-space shielding effects. Each adjustment was made in the correct direction (shielding or deshielding). Adjustment of the predicted chemical shift of 4-ethynylphenanthrene (**1**) by more than 2 ppm led to a slight overestimation of the chemical shift. However, the correction was made in the proper direction and the resulting adjusted chemical shift was in error by only 0.6 ppm. Results for 4-cyanophenanthrene (**2**), 4-nitrophenanthrene (**3**), and 1-naphthalenecarbonitrile (**4**) gave excellent agreement with observed chemical shifts.

Direct GIAO-HF calculations were performed on several of the test structures to compare the results of the methane-probe method to direct calculation of shielding effects. GIAO-HF calculations of shielding values on geometry-optimized structures using the 6–31G(d, p) basis set gave a shielding difference of 1.9 ppm for H5 between phenanthrene and 4-ethynylphenanthrene (**1**); our methane-probe model gives 2.2 ppm; the experimental chemical shift difference is 1.6 ppm. Much of the small difference between these approaches can be attributed to differences in the angle of incidence of the C–H bond relative to the π bond in the methane-probe model versus the test structure, as noted previously [22].

4. Conclusions

A series of ab initio GIAO-HF calculations was performed to determine the through-space magnetic shielding increment ($\Delta\sigma$) of one proton of a methane-probe molecule at various positions over several test molecules (acetylene, HCN, and HNO_2). These test structures were selected as simple examples of the ethynyl group, the cyano group, and the nitro group. The shielding increment was plotted against the distance in the X (or Z) and Y direction from the origin of the test molecule to give a magnetic shielding surface. An equation was fitted to each of the shielding surfaces. Shielding increments calculated by these equations were used to adjust the chemical shifts predicted by additive substituent constants. Comparison to experimental data for the chemical shifts of protons that experience such through-space (de)shielding effects demonstrates the predictive utility of the equations.

Acknowledgements

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