CNDO/2 Molecular Orbital Calculations and the Existence of an Electric Field Effect upon Proton Chemical Shifts

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Summary A comparison of vinyl proton chemical shifts for 4-substituted styrenes and 1-vinylbicyclo[2,2,2]octanes obtained from CNDO/2 calculations and from the Buckingham equation demonstrates the existence of an electric dipolar field effect

THE relative importance of the many factors which can contribute to proton chemical shifts is not yet completely understood.[1,2] We have used the CNDO/2 MO approach,[3] which has been applied to chemical shift calculations,[4—6] to investigate the importance of one factor, the direct electric field effect due to a polar substituent. Evidence for the existence of a significant field effect is presented below.

According to Buckingham,[7] the effect a polar substitutent on proton chemical shifts is given by $\Delta\delta = AE_Z + BE^2$. The second term can be ignored for remote substituents. A is a constant of the order of $(2—4) \times 10^{-12}$ esu^{-1} for C–H bonds and E_Z is the component of the dipolar field acting along the C–H bond, *i.e.*, the magnitude of the field effect depends upon the orientation of the C–H bond. The bond is polarized, altering the electron density near hydrogen. This should be detected by CNDO/2 calculations of hydrogen 1*s* electron density.

4-Substituted styrenes were chosen for this investigation to allow isolation of through space or field effects. Any electronic effects transmitted through bonds should be equally felt at the two protons bonded to the β carbon, H_B and H_C (see Figure 1) but the field effect should be much greater at H_C than at H_B since the field is approximately parallel to C_β–H_C but perpendicular to C_β–H_B. Therefore, differences between H_C and H_B should reflect field effects.

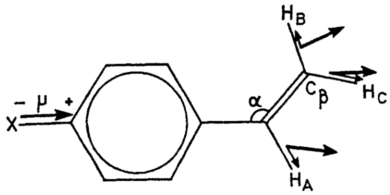

FIGURE 1. *Labelling of vinyl protons and electric field (heavy line) and component of electric field along* C–H *bond (light line) due to a polar group in a* 4-*substituted styrene.*

CNDO/2 calculations were performed using normal parameters[8] and geometries.[9] The geometry of the vinyl group was optimized by varying the angle α and by rotating the phenyl group up to 30°. The most stable form had $\alpha = 130°$ with the two groups coplanar, similar to *trans*-stilbene.[9] Charge densities for H_B, H_C and C_β, relative to styrene, are reported in Table 1. $\Delta(H_C - H_B)$ parallels the expected field effect of the substituent, even for $-OCH_3$ where the field effect is opposite in sign to the overall effect of the substituent. For comparison, CNDO/2 results for $\Delta(H_C - H_B)$ have been converted to chemical shifts using a factor of 26·6 p.p.m./H 1*s* electron.[1] Chemical shifts according to the field effect model were estimated using the Buckingham equation. Previously reported procedures[10] were used, except that A was changed from $3{\cdot}1 \times 10^{-12}$ to $4{\cdot}0 \times 10^{-12}$ because of the change in α from 120° to 130°.† The latter value is in good agreement with the value of $4{\cdot}2 \times 10^{-12}$ found by Zürcher.[11] Experimental chemical shifts were measured in cyclohexane and extrapolated to infinite dilution. Values for 4-cyano- and 4-ethynyl-styrene were corrected for substituent anisotropic magnetic susceptibility, using an average value[12] of $\Delta\chi = -25 \times 10^{-6}$ cm^3 mol^{-1} in each case. There is nearly quantitative agreement between the two independent calculations of the field effect and experimental data (see Table 1) although the CNDO/2 calculations underestimate the effect of $-CN$ and overestimate the effect of $-NO_2$, as reported by others.[5] We believe that the good agreement is conclusive evidence for the existence of an electric field effect upon proton chemical shifts. This conclusion is reinforced by the observation of an excellent correlation between the field substituent parameter, F[13] and $(\delta_C - \delta_B)$ for a large number of 4-substituted

TABLE 1

Comparison of calculated charge densities $(\times 10^4)$ *and chemical shifts in p.p.m.* (δ *scale*) *for* 4-*substituted styrenes relative to styrene*

	Relative charge densities				$\Delta(\delta_C - \delta_B)$[a]		
Substituent	$\Delta C\beta$	ΔH_B	ΔH_C	$\Delta(H_C - H_B)$	CNDO/2	Field	Exp.
$—C(Me)_3$	−46	−11	−12	−1	−0·003	−0·010	−0·009
—Me	−38	−8	−9	−1	−0·003	−0·008	−0·006
$—C{\equiv}CH$	+7	+2	+7	+5	+0·013	+0·011	+0·017[b]
—OMe	−82	−17	−12	+5	+0·013	+0·018	+0·022[c]
—F	−17	−2	+16	+18	+0·048	+0·049	+0·066[c]
—Cl	+76	+18	+36	+18	+0·048	+0·047	+0·052[c]
$—CF_3$	+105	+26	+48	+22	+0·059	+0·042	+0·047
$—C{\equiv}N$	+53	+13	+27	+14	+0·037	+0·042	+0·057[b]
$—NO_2$	+159	+39	+74	+35	+0·093	+0·081	+0·073[c]

[a] Chemical shift difference between H_C and H_B for 4-substituted styrenes relative to styrene. [b] Corrected for anisotropic magnetic susceptibility of triple bonds. The uncorrected values are 0·017 p.p.m. larger. [c] Experimental values from ref. 10.

TABLE 2

Comparison of calculated vinyl proton chemical shifts in p.p.m. (δ *scale*) for 4-X-1-*vinylbicyclo*[2,2,2]*octanes* (*relative to* $X = H$)

Substituent	CNDO/2				Electric Field			
	$\Delta\delta_A$	$\Delta\delta_B$	$\Delta\delta_C$	$\Delta(\delta_C - \delta_B)$	$\Delta\delta_A$	$\Delta\delta_B$	$\Delta\delta_C$	$\Delta(\delta_C - \delta_B)$
F	+0·045	+0·027	+0·067	+0·040	+0·059	+0·005	+0·052	+0·047
NO_2	+0·109	+0·056	+0·128	+0·072	+0·088	+0·005	+0·081	+0·076

† The value of A was estimated from the slope of a plot of chemical shift, δ, *versus* calculated electric field component, E_z, along the C–H bond (calculated at the midpoint of the bond).[10] Alteration of the bond angle, α, alters E_z and consequently A.

styrenes [$\Delta(\delta_C - \delta_B) = 0{\cdot}065F$, correlation coefficient 0·989].[14]

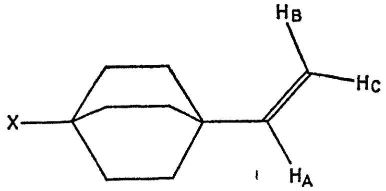

FIGURE. 2. *Labelling of vinyl protons for 4-substituted 1-vinylbicyclo*[2,2,2]*octanes.*

The calculated charge densities for individual styrenes reflect through bond as well as through space substituent effects. $\Delta C_\beta(\pi)$ is typically 2—3 × $\Delta C_\beta(\sigma)$, indicating that through bond effects are primarily transmitted through the π system. In order to estimate substituent effects in the absence of conjugation, we have performed calculations for the geometrically similar 1-vinylbicyclo[2,2,2]octane (Figure 2) and its 4-fluoro- and 4-nitro-derivatives. Results are given in Table 2. While no experimental results are available for comparison, the CNDO/2 results are consistent with the electric field model and inconsistent with any inductive model. This strongly suggests that the field effect is the predominant substituent effect in these compounds, in agreement with previous conclusions from acid dissociation constants of 4-substituted bicyclo[2,2,2]octane carboxylic acids.[15] Thus the CNDO/2 approach can be used to investigate the mechanism of transmission of substitutent effects, including the detection of geometrically dependent effects.

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