Electronegative Atoms in the INDO Perturbation Theory of Carbon-13 Chemical Shifts

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Abstract: The previously reported finite perturbation INDO method for ^{13}C shieldings was directed toward characterizing the influence of electronegative substituents in simple carbon frameworks. A set of atomic INDO parameters for fluorine was chosen on the basis of a satisfactory level of agreement between calculated and experimental ^{13}C chemical shifts for the following compounds: CH_2F_2, CH_3F, CH_3CH_2F, $CH_2{=}CHF$, $CH{\equiv}CF$, and C_6H_5F. A pseudo-atom approach for simulating the influence of an electronegative substituent on ^{13}C shieldings was explored for the systems CH_3X, CH_3CH_2X, $CH_2{=}CHX$, and $CH{\equiv}CX$. Trends in ^{13}C shieldings and electronic distributions are discussed.

With the current surge in popularity of ^{13}C nmr techniques, there is a great deal of interest in the interpretation of ^{13}C chemical shifts. A substantial amount of effort has gone into characterizing and explaining the influence that electronegative substituents exert on ^{13}C shieldings.

While most of the experimental ^{13}C work reported recently utilizes the ^{13}C chemical shift in largely an empirical manner, the opinion that ^{13}C shifts should provide valuable information on electronic distributions has often been expressed. However, the justification of that assumption and the achievement of that goal has been elusive. Semiempirical approaches to the theory of ^{13}C shieldings have generally been based upon Pople's early molecular orbital theory of diamagnetism and shielding[1] or upon the simplified molecular orbital treatments,[2,3] or their valence bond counterparts,[4] that can be derived at the level of the "average excitation energy" approximation.[2,3] Semiempirical developments of these approaches, including computational treatments based on approximate wave functions such as those of the CNDO/2[5] and extended Hückel[6] methods, have perhaps provided some useful qualitative guidelines.[7-15] However, they have been of limited computational value in the sense that there is at least one arbitrary parameter that must be chosen for each molecule or each molecular type (*e.g.*, the average ΔE). The availability of a dependable and computationally economical theory that requires an input of only atomic identities and positions would be an important influence on a rapidly growing field.

Only recently have promising *computational* theories of ^{13}C chemical shifts appeared. In 1970, Ditchfield, Miller, and Pople[16] presented an *ab initio* SCF–MO perturbation theory of ^{13}C shielding. While the results were promising and provocative, they were not gauge invariant. More recently Ditchfield[17] has reported the results of a similar approach, but employing a basis set of gauge-invariant Slater AO's. The results obtained by this method have been very good.[17,18]

Also recently, Ellis, Maciel, and McIver[19] have reported a SCF–MO theory of ^{13}C chemical shifts at the INDO[20] level of MO approximation. That work also employed gauge-invariant atomic orbitals. It was confined to hydrocarbons (including carbonium ions) and gave computed shieldings that accounted semiquantitatively for the major structural relationships that have been observed experimentally for ^{13}C chemical shifts. The present paper is concerned with extending the INDO perturbation theory to include the effects of an electronegative atom or substituent. The availability of this capability in the theory would markedly enhance the scope of utility of the theory in interpretive work. The approach in this work has been to simulate the influence of an electronegative substituent in the following two ways: (1) to find a set of INDO atomic parameters that would simulate, at least qualitatively, the influence exerted by a fluorine substituent on the ^{13}C shieldings of the hydrocarbon frameworks in simple fluorocarbons; and (2) to employ the *pseudo-atom* method[21,22] in the simulation of electronegative substituents.

Results and Discussion

1. The Method of Calculation. The INDO perturbation calculations were carried out in the same manner employed by Ellis, Maciel, and McIver.[19] The

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Table I. Atomic INDO Parameters Used in Standard INDO Calculations and Those Used in ^{13}C Chemical Shift Calculations Reported Here[a]

	Standard INDO parameters[b]				Modified INDO parameters[c]			
	$(\frac{1}{2})(I+A)_s$	$(\frac{1}{2})(I+A)_p$	β_0	ξ	$(\frac{1}{2})(I+A)_s$	$(\frac{1}{2})(I+A)_p$	β_0	ξ
Hydrogen	7.176		−9.0	1.2	7.176		−12.0	1.2
Carbon	14.051	5.572	−21.0	1.625	17.051	8.572	−17.0	1.625
Fluorine	32.27	11.08	−39.00	2.60	57.50	18.60	−31.0	3.0

[a] Units are eV, except for Slater exponents. [b] Parameters taken from ref 20. [c] Parameters used in ^{13}C chemical shift calculations reported here.

shielding is represented as a sum of contributions as follows.

$$\sigma_{\alpha\beta}(\mathrm{M}) = \sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M,M}) + \sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M,M}) + \sum_{\mathrm{K}\neq\mathrm{M}}^{\mathrm{atoms}} [\sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M,K}) + \sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M,K})] \quad (1)$$

In eq 1, $\sigma_{\alpha\beta}(\mathrm{M})$ is the $\alpha\beta$ element of the shielding tensor for nucleus M; $\sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M,M})$ and $\sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M,M})$ are the local diamagnetic and paramagnetic contributions, respectively, to that element of the tensor; and $\sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M,K})$ and $\sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M,K})$ represent the contributions to that tensor element due to diamagnetic and paramagnetic currents on the Kth other atom. The two-center terms, $\sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M,K})$ and $\sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M,K})$, were evaluated using the long-range approximation given by McConnell[23] and Pople.[1] The one-center contributions were calculated according to the following equations given by Ellis, Maciel, and McIver.[19]

$$\sigma_{\alpha\beta}{}^{\mathrm{d}}(\mathrm{M,M}) = 2\sum_{\mu}^{\mathrm{M}}\sum_{\nu}^{\mathrm{M}} R_{\mu\nu}(0)\,\langle\chi_\mu{}^0|h_{\alpha\beta}{}^{11}(\mathrm{M})|\chi_\nu{}^0\rangle \quad (2)$$

$$\sigma_{\alpha\beta}{}^{\mathrm{p}}(\mathrm{M,M}) = 2\sum_{\mu}^{\mathrm{M}}\sum_{\nu}^{\mathrm{M}} \left(\frac{\partial R_{\mu\nu}}{\partial B_\alpha}\right)_0 \langle\chi_\mu{}^0|h_\beta{}^{10}(\mathrm{M})|\chi_\nu{}^0\rangle \quad (3)$$

In eq 2 and 3, $R_{\mu\nu}(0)$ is the value of the $\mu\nu$ element of the density matrix (**R**) in the absence of a perturbation, and the definitions of the operators $h_{\alpha\beta}{}^{11}(\mathrm{M})$ and $h_\beta{}^{10}(\mathrm{M})$ have been given as[19]

$$h_{\alpha\beta}{}^{11}(\mathrm{M}) = \frac{e^2}{2mc^2}(\mathbf{r}_\nu\mathbf{r}_\mathrm{M}\delta_{\alpha\beta} - \mathbf{r}_{\nu\alpha}\mathbf{r}_{\mathrm{M}\beta})/|\mathbf{r}_\mathrm{M}|^3 \quad (4)$$

$$h_\beta{}^{10}(\mathrm{M}) = -\frac{e\hbar}{mc^{i}}\frac{(\mathbf{r}_\mathrm{M}\times\nabla)_\beta}{|\mathbf{r}_\mathrm{M}|^3} \quad (5)$$

As in the previous work on hydrocarbon systems,[19] the London overlap approximation[24] and a modified set of atomic INDO parameters for carbon and hydrogen were employed. As in the previous work, Slater's screening rules[25] were used in the evaluation of integrals of the $\langle r^{-3}\rangle$ and $\langle r^{-1}\rangle$ type, in order to take into account the different molecular environments of nonequivalent carbon atoms. In the INDO method, this approach is manifested in the following expression for the Slater experiment, ξ, where P stands for the total valence-shell electron density on the carbon atom in question.

$$\xi = [3.25 - 0.35(P - 4)]/2 \quad (6)$$

2. Choosing the Parameters for Fluorine. The approach was to search for a set of atomic INDO parameters for fluorine that would yield INDO perturbation calculations of ^{13}C shifts that are in reasonable agreement with experimental patterns for a selected set of fluorocarbons. The fluorocarbon set consisted of CH_3F, CH_2F_2, CH_3CH_2F, $CH_2{=}CHF$, $CH{\equiv}CF$, and fluorobenzene. Although the main emphasis in choosing this set was on comparing computed ^{13}C shifts with the experimental values, another constraint was to eliminate any parameter set that gave computed fluorine substituent effects on the electron distributions that did not compare at least qualitatively with those obtained by a more conventional method, *e.g.*, CNDO/2.

By varying each of the INDO parameters individually in calculations on CH_3F and CH_2F_2, some useful guidelines were obtained for the directions in which the various INDO parameters should be moved to achieve a desired effect. Then, utilizing these guidelines, several parameter sets were explored for all of the test compounds except fluorobenzene. The two parameter sets that were most promising on the basis of the two criteria stated above were then used in calculations on fluorobenzene; and the relative levels of agreement in that case were used to make the choice of a parameter set on which calculations are reported in this paper. This is strictly an empirical approach, the implementation of which was largely intuitive. It cannot be claimed that the fluorine parameter set is "optimized" in any true statistical sense, but, then, such a claim has not been made for the carbon and hydrogen INDO parameters either.[19] No attempt was made in this study to find a set of carbon and hydrogen INDO parameters that optimize the ^{13}C shifts calculated for fluorocarbons; the set of hydrogen and carbon parameters used by Ellis, Maciel, and McIver was employed in this work,

While, as expected, a fluorine parameter set that gives *quantitative* agreement with respect to the two criteria stated above was not found, a set was chosen that gave a level of qualitatively successful results that is considered satisfactory for the purposes of this study. Table I lists the INDO parameters chosen and gives the standard INDO values for comparison.

Table II contains the ^{13}C shifts computed for the selected set of fluorocarbons. For comparison, the calculated shift values reported earlier for the parent hydrocarbons,[19] repeated in this work, are also given, as are the corresponding experimental results.[18,26–28] It is seen that most of the important experimental trends and patterns are reproduced. For example, the general decrease in shielding of the α carbon resulting from fluorine substitution is accounted for,

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Table II. ^{13}C Chemical Shifts and Electron Density Elements Calculated by the INDO Perturbation Method

	Calculated shift[a]		Experimental shift[b]		Calculated valence-shell atom or orbital electron density							
	$\delta_{c\alpha}$	$\delta_{c\beta}$	$\delta_{c\alpha}$	$\delta_{c\beta}$	$P_{c\alpha}$[c]	$P_{\pi\alpha}$[d]	$P_{\sigma\alpha}$[e]	$P_{c\beta}$[c]	$P_{\pi\beta}$[c]	$P_{\sigma\beta}$[e]	P_H	P_F
CH_3F	59.7		77.5	(26)	3.892	1.105	2.787				0.888	7.441
CH_2F_2[f]	121.6		111.3	(28)	3.357	1.092	2.265				0.890	7.431
CH_4	0		0	(26)	4.480	1.118	3.362				0.880	
$C^{\beta}H_3C^{\alpha}H_2F$[g]	65.0	6.4	81.4	16.7 (26)	3.729	1.061	2.668	4.362	1.132	3.230	0.923α[j]	
											0.860β[j]	7.487
CH_3CH_3[h]	3.0		8.0	(26)	4.274	1.083	3.191				0.909	
$C^{\beta}H_2{=}C^{\alpha}HF$	161.1	100.8	150.5	91.3 (18)	3.644	0.959	2.685	4.334	1.062	3.272	0.906α[j]	
											0.824β[j]	7.467
$CH_2{=}CH_2$	115.0		125.4	(18)	4.204	1.000	3.204				0.897	
$C^{\beta}H{\equiv}C^{\alpha}F$	82.6	63.6	92.9	18.4 (18)	3.549	0.948	1.653	4.296	1.070	2.156	0.772	7.384
$CH{\equiv}CH$	80.6		76.0	(18)	4.152	1.000	2.152				0.848	
C_6H_5F[i]	162.2	115.2	165.9	116.5 (27)	3.555	0.952	2.603	4.172	1.046	3.126	0.865[k]	
	126.3	121.8	131.7	126.4 (27)	4.029	0.980	3.049	4.104	1.015	3.089	0.903[k]	7.501
											0.901[k]	
C_6H_6	120.7		130.8	(27)	4.078	1.000	3.078				0.921	

[a] Calculated from eq 1–5, ppm relative to methane. Larger values correspond to lower shielding. [b] Ppm with respect to methane. Literature references indicated in parentheses. [c] Valence-shell atomic density of a carbon = $P^2_{2s2s} + P^2_{p_xp_x} + P^2_{p_yp_y} + P^2_{p_zp_z}$ for that carbon. [d] The carbon π orbital is taken to be $2p_y$, where the xz plane is designated as the plane of symmetry of the molecule. For acetylenic compounds, both $2p_y$ and $2p_x$ are designated as π orbitals. [e] The σ electron density is the total atomic density minus the π orbital density. [f] The plane containing the carbon and fluorine atoms is taken as the xz plane. [g] The calculation was carried out for a conformation with a trans-planar H–C$^{\beta}$–C$^{\alpha}$–F arrangement in the xz plane. [h] The calculation was carried out for the trans H–C$^{\alpha}$–C$^{\beta}$–H arrangement in the xz plane. [i] Carbon position designations (replacing α,β): first line, substituted carbon, ortho; second line, meta, para. [j] The two numbers represent α and β hydrogens, the latter being the average of two nearly identical values. [k] The three numbers represent ortho, meta, and para hydrogens, in that order.

Table III. Calculated Substituent Effects on Electronic Distributions[a]

	INDO perturbation theory							CNDO/2						
Molecule	$\Delta P_{c\alpha}$	$\Delta P_{\pi\alpha}$	$\Delta P_{\sigma\alpha}$	$\Delta P_{c\beta}$	$\Delta P_{\pi\beta}$	$\Delta P_{\sigma\beta}$	ΔP_H	$\Delta P_{c\alpha}$	$\Delta P_{\pi\alpha}$	$\Delta P_{\sigma\alpha}$	$\Delta P_{c\beta}$	$\Delta P_{\pi\beta}$	$\Delta P_{\sigma\beta}$	ΔP_H
CH_3F	−588	−13	−575				8	−237	−11	−226				13
CH_2F_2	−1123	−26	−1097				10	−451	−24	−427				20
$C^{\beta}H_3C^{\alpha}CH_2F$	−545	−22	−523	88	49	39	14, −49[b]	−222	−14	−208	39	18	21	15, −19[b]
$C^{\beta}H_2{=}C^{\alpha}HF$	−560	−41	−519	130	62	68	9, −73, −72[c]	−239	−26	−213	81	75	6	20, −27, −21[c]
$C^{\beta}H{\equiv}C^{\alpha}F$	−603	−52	−499	144	70	4	−76	−264	−19	−225	94	61	−29	−29
C_6H_5F[d]	−523	−48	−475	94	45	49	−56, −18[e]	−323	−31	−292	56	48	8	−24, −5[e]
	−49	−20	−29	26	15	11	−20	−20	−21	1	19	26	−7	−4

[a] ΔP_i stands for the calculated electron density of the ith atom, or the ith σ or π atomic orbital, in a fluorine-substituted hydrocarbon minus the corresponding electron density in the parent hydrocarbon. Molecular conformations and σ, π specifications are given in Table I. Values given are actual values times 1000. [b] The two numbers represent α and β hydrogens, the latter being the average of two nearly identical values. [c] The three numbers represent, in order, α, β-cis and β-trans hydrogens, the cis, and trans designation relative to the fluorine atom. [d] Position designations (replacing α, β): first line, substituted carbon, ortho; second line, meta, para. [e] The three numbers represent ortho, meta, and para hydrogens, in that order.

as well as (with a reversal of the two sp^2 cases) the decreasing magnitude of this effect through the series $CH_2F_2 > CH_3F \approx CH_3CH_2F > C_6H_5F > CH_2{=}CHF > CH{\equiv}CF$. The experimental order of the ^{13}C chemical shifts for α carbons in the fluorocarbons, $C_6H_5F > CH_2{=}CHF > CH_2F > CH{\equiv}CF > CH_3CH_2F > CH_3F$, is reproduced in the calculated values of the α-carbon shifts. Also the experimentally observed order of the β-carbon shifts, $C_6H_5F > CH_2{=}CHF > CH{\equiv}CF > CH_3CH_2F$, is reproduced by the calculation. With the exception of fluoroacetylene,[29] the chemical shift difference $\delta_{c\alpha} - \delta_{c\beta}$ is accounted for within a few per cent. All of the calculated fluorine substituent effects on C_α and C_β chemical shifts are of the correct sign.

Table II also includes information on the computed density matrices, which in the INDO framework give atomic and orbital electron densities directly. The electron densities summarized in Table II served as guidelines for choosing the fluorine parameter set, the guideposts being the corresponding electron densities calculated by the CNDO/2 method.[5] While it is not claimed that CNDO/2 provides accurate wave functions, the density matrices computed by this method have proved to be quite successful in accounting for a variety of experimental measurements and in comparison with *ab initio* calculations.[30]

As the emphasis in this paper is on substituent effects, it is convenient to compare density matrix elements for fluoro-substituted hydrocarbons with the corresponding elements obtained in calculations on the parent hydrocarbons. Such comparisons are given in Table III for both INDO perturbation calculations and CNDO/2 calculations. The results are given as the differences between specific electron density elements, total carbon, π carbon, σ carbon, and hydrogen for the corresponding fluorocarbons and hydrocarbons (scaled by a factor of 1000). Inspection of the numbers in Table III reveals that the calculated fluorine substituent effects are of the same sign for both MO calculations

(29) Professor P. D. Ellis (private communication) has obtained some evidence that the neglect of certain two-center terms in the Hamiltonian of the INDO perturbation method may cause serious problems for cylindrically symmetric molecules, *e.g.*, fluoroacetylene.

(30) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

for nearly all of the electron density elements that are summarized (the ΔP_σ values for the β carbon of fluoroacetylene and for the meta and para carbons of fluorobenzene being the only exceptions). The characteristic CNDO/2 pattern of alternation of the sign of substituent effects on the total, π, and σ electron densities of the α carbons and β carbons is also evident in the numbers obtained by the INDO perturbation method. Another pattern of note is that for many of the electron density elements given in Table III the magnitudes of the polarizations (deviations from hydrocarbon densities) obtained by INDO perturbation theory are approximately twice as large as those given by CNDO/2. Thus, the INDO perturbation theory in its present form requires roughly twice the CNDO/2 level polarizations in order to give a reasonable qualitative agreement between calculated and experimental ^{13}C chemical shifts. Which level of polarization is more realistic is somewhat difficult to decide, say, by direct comparison with *ab initio* methods, because there is a considerable degree of arbitrariness involved in partitioning electron densities in MO calculations and, therefore, in comparing the results of substantially different MO approaches.[31,32]

Another factor of interest in the results given in Table II is the importance of the Slater-exponent correlations, embodied in eq 6 in the success of calculating substituent effects by the INDO perturbation approach. Such corrections have been included in the results given in Table II. Earlier work on hydrocarbons[19] indicated that the inclusion of these factors was not very important in accounting for the relationship between ^{13}C shielding and gross structural variations in a series of hydrocarbons. However, in the presence of the strong polarizing influence of electronegative substituents, such corrections might be expected to assume a greater importance. This expectation is borne out in Table IV, in which the calculated fluorine substituent effects on the ^{13}C shieldings are given for each system studied, both for the case of including the Slater-exponent correction and for the case of leaving it out of the calculation, and are compared with the corresponding experimentally determined fluorine substituent effects.

Table IV. Role of Slater Exponent Corrections in Calculation of Fluorine Substituent Effects on ^{13}C Chemical Shifts[a]

	Calculated without Slater correction[b]		Calculated with Slater correction[c]		Experimental[d]	
	$\Delta\delta_{c\alpha}$	$\Delta\delta_{c\beta}$	$\Delta\delta_{c\alpha}$	$\Delta\delta_{c\beta}$	$\Delta\delta_{c\alpha}$	$\Delta\delta_{c\beta}$
CH_2F_2	88.9		121.6		111.3	
CH_3F	50.5		59.7		77.5	
$C^\beta H_3C^\alpha H_2F$	50.7	5.1	62.0	3.4	73.4	8.7
$C^\beta H_2{=}C^\alpha HF$	15.6	−9.0	46.0	−14.3	25.1	−33.1
$C^\beta H{\equiv}C^\alpha F$	−17.5	−13.0	2.0	−17.0	16.9	−57.6
C_6H_5F[e]	12.4	−0.9	41.5	−5.5	35.1	−14.3
	3.1	2.5	5.6	1.1	0.9	−4.4

[a] $-\Delta\delta_c$ represents the shielding of the *i*th carbon of a fluorine-substituted hydrocarbon minus the shielding of the corresponding carbon in the parent hydrocarbon. [b] Calculated without using eq 6. [c] Calculated with the correction embodied in eq 6 included, *i.e.*, corresponding to the results of Table I. [d] Experimental data referenced in Table I. [e] Carbon position designations (replacing α, β): first line, substituted carbon, ortho; second line, meta, para.

It should be noted that, with only three exceptions (the α carbon of vinyl fluoride, the β carbon of ethyl fluoride, and the meta carbon of fluorobenzene), the level of agreement between calculated and observed $\Delta\delta_c$ values is improved by the application of eq 6 in the calculation.

It is noteworthy that the order of the ^{13}C chemical shifts calculated for fluorobenzene, *i.e.*, substituted carbon > meta > para > ortho, agrees with the experimental data.[27] However, the sign of the substituent effect (fluorobenzene shift minus benzene shift) at the para position is not of the correct sign. It is intetsting that there are monotonic relationships between the calculated (or experimental) chemical shifts and any one of the classes of atomic electron density elements, total, π, or σ.

The overall picture that emerges from the results summarized in Tables II–IV is that the parameter set chosen here for the INDO perturbation calculation of ^{13}C chemical shifts in fluorocarbons is capable of qualitatively reproducing the main features of the fluorine substituent effects on both ^{13}C shifts and electronic distributions. This method should provide a useful basis for exploring the relationships between empirically determined substituent effects on ^{13}C shielding and the electronic effects that are responsible for them.

3. Pseudo-Atom Calculations. As an auxiliary approach to developing MO methods for studying the effects of electronegative substituents on ^{13}C shieldings, we have employed the INDO perturbation method in a "pseudo-atom" format.[21,22] In the pseudo-atom approach one chooses a basic substrate system, (*e.g.*, methyl) and introduces a substituent pseudo-atom for which the atomic (INDO) parameters are considered variable. By variation of these parameters a variety of substituent electronic effects can be simulated by the pseudo-atom. This approach has proved to be rather successful in simulating substituent effects on spin–spin coupling constants.[21,22]

The cases treated in this study were the CH_3X, CH_3CH_2X, $CH_2{=}CHX$, and $CH{\equiv}CX$ systems, where formally the pseudo-atom X was assigned a Z value (nuclear charge minus inner-shell-electron charge) of 4 and allotted three valence electrons. The pseudo-atom parameter variations were carried out to reproduce known experimental trends in ^{13}C chemical shift calculations *via* the INDO perturbation method. The particular parameter sets employed were chosen because they resulted in computational convenience and experimentally reasonable ranges of chemical shifts. The specific parameters that were varied are $(^1/_2)(I + A)_{2s}$, $(^1/_2)(I + A)_{2p}$, β_0, and ξ, where $(^1/_2)(I + A)$ is a sort of electronegativity term used in the evaluation of the diagonal elements of the core Hamiltonian, and β_0 is a bonding parameter used in the formation of the off-diagonal elements of the core Hamiltonian. The parameter sets employed were those corresponding to *standard* INDO parameters of (1) boron, (2) carbon, and (3) a set intermediate between standard nitrogen and carbon values (16.60, 6.30, −23.00, and 1.78 eV, respectively, for the parameters listed above). The carbon and hydrogen parameters employed are those listed on the right side of Table I.

The results of INDO perturbation calculations of

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(31) P. Lowdin, *J. Chem. Phys.*, 18, 365 (1950).
(32) R. S. Millikin, *ibid.*, 23, 1841 (1955).

^{13}C shieldings for these four pseudo-atom systems for each of the three parameter sets are given in Tables V–VIII. In addition to the calculated ^{13}C shieldings, these tables present pertinent information on the computed electron density distributions for these systems.

Table V summarizes results for the CH_3X system.

Table V. Results of Pseudo-Atom INDO Perturbation Calculations on the CH_3X System[a]

Parameter set[b]	Carbon oribtal densities[c] P_{2s2s}	$P_{p_zp_z}$	$P_{p_yp_y}$	$P_{p_zp_z}$	Atomic densities[d] P_c	P_X	^{13}C shieldings[e] $-\sigma_c$
1	1.087	1.114	1.114	1.302	4.617	3.251	88.3
2	1.131	1.134	1.134	1.098	4.497	3.378	123.1
3	1.149	1.141	1.141	1.012	4.443	3.427	145.3

[a] Calculations performed with the C–X bond along the *z* axis. [b] Parameter sets described in text. [c] INDO density matrix elements. [d] Total valence-shell electron density of the carbon atom. [e] σ_c is the calculated shielding constant.

As would be expected for the pseudo-atom parameter sets chosen, it is seen that atomic electron densities of the pseudo-atom and the carbon atom increase and decrease, respectively, as one progresses from set 1 to set 2 to set 3. The decrease in computed ^{13}C shielding associated with that parameter variation parallels what one expects, on the basis of experimental data,[26] for a series of substituted methanes (*e.g.*, halomethanes) with increasing substituent electronegativity. It is interesting to note that, while the total carbon atom density decreases with decreasing shieldng and increasing X atom density, the orbital electron densities, P_{2s2s}, $P_{p_xp_x}$, and $P_{p_yp_y}$, show *increasing* values through the 1 → 2 → 3 progression of parameter sets. The decrease in total carbon valence-shell electron density, P_c, is due to the p_z orbital, which is directed along the C–X bond.

Table VI. Results of Pseudo-Atom INDO Perturbation Calculations on the $C^\beta H_3C^\alpha H_2$–X System[a]

Parameter set[b]	Carbon orbital densities[c]								Atomic densities[d]			^{13}C shieldings[e]	
	C_α				C_β								
	P_{2s2s}	$P_{p_xp_x}$	$P_{p_yp_y}$	$P_{p_zp_z}$	P_{2s2s}	$P_{p_xp_x}$	$P_{p_yp_y}$	$P_{p_zp_z}$	$P_{c\alpha}$	$P_{c\beta}$	P_X	$-\sigma_{c\alpha}$	$-\sigma_{c\beta}$
1	1.056	1.239	1.069	1.055	1.071	1.143	1.141	0.869	4.419	4.224	3.291	61.6	−11.1
2	1.099	1.060	1.086	1.052	1.093	1.147	1.145	0.838	4.297	4.223	3.439	101.8	5.2
3	1.118	0.985	1.093	1.048	1.101	1.147	1.145	0.832	4.244	4.225	3.491	129.4	12.7

[a] Calculations performed with the C^β–C^α bond along the *z* axis. [b] Parameter sets described in text. [c] INDO density matrix elements. [d] Total valence-shell electron density of the α carbon atom. [e] $\sigma_{c\alpha}$ is the calculated shielding constant for the α carbon.

Table VII. Results of Pseudo-Atom INDO Perturbation Calculations on the $C^\beta H_2{=}C^\alpha H$—X System[a]

Parameter set[b]	Carbon orbital densities[c]								Atomic densities[d]			^{13}C shieldings[e]	
	C_α				C_β								
	P_{2s2s}	$P_{p_xp_x}$	$P_{p_yp_y}$	$P_{p_zp_z}$	P_{2s2s}	$P_{p_xp_x}$	$P_{p_yp_y}$	$P_{p_zp_z}$	$P_{c\alpha}$	$P_{c\beta}$	P_X	$-\sigma_{c\alpha}$	$-\sigma_{c\beta}$
1	1.093	1.173	1.071	1.014	1.143	1.118	0.636	1.029	4.351	3.926	3.282	114.1	128.4
2	1.120	1.049	1.079	0.990	1.157	1.126	0.629	1.008	4.238	3.920	3.426	144.2	122.6
3	1.134	0.995	1.079	0.979	1.162	1.127	0.630	1.000	4.187	3.928	3.478	166.9	116.2
1′	1.115	0.958	1.111	0.960	1.161	1.135	0.656	0.996	4.144	3.948	3.522	164.0	141.9
2′	1.116	0.959	1.106	0.961	1.161	1.135	0.658	0.996	4.142	3.950	3.523	171.0	139.2
3′	1.116	0.960	1.102	0.962	1.161	1.135	0.662	0.995	4.140	3.953	3.525	176.6	135.9

[a] Calculations performed with C^β–C^α bond along the *z* axis and all atoms in the *xz* plane. [b] Parameter sets described in the text. [c] INDO density matrix elements. [d] Total valence-shell electron density of the α-carbon atom. [e] $\sigma_{c\alpha}$ is the calculated shielding constant for the α carbon.

Table VI summarizes analogous results for the $C^\beta H_3C^\alpha H_2X$ system, including electron density data for both carbons. For the α carbon, it is seen again that the 1 → 2 → 3 parameter set progression leads to a decrease in electron density and a sharp decrease in ^{13}C shielding, effects that one associates with experimental trends for C_α in substituted ethanes as substituent electronegativity is increased.[26,33] As in the CH_3X case, the only carbon orbitals that reflect the trend in $P_{c\alpha}$ are the 2p orbitals involved directly in the C–X bond; the density matrix elements of the other C_α atomic orbitals show the reverse trend. Focusing on the β carbon, one sees a negligible change in $P_{c\beta}$ throughout the pseudo-atom variation. Nevertheless, there is a substantial variation in the computed ^{13}C shielding, $\sigma_{c\beta}$. That variation is in the opposite sense to the $\sigma_{c\alpha}$ variation, in agreement with the experimentally established gross trend for substituted ethanes.[26,33]

For the $C^\beta H_2{=}C^\alpha HX$ case summarized in Table VII, trends similar to those described in Table VI are observed for the 1 → 2 → 3 parameter variation. Qualitatively, the $\sigma_{c\alpha}$ and $\sigma_{c\beta}$ trends, which are of opposite sense, are in agreement with the gross pattern of substituent effects on experimentally determined ^{13}C chemical shifts in substituted ethylenes.[11,13,34]

Table VIII summarizes the results of ^{13}C shielding calculations on the $C^\beta H{\equiv}C^\alpha X$ system. The results for the 1 → 2 → 3 parameter set variation parallel qualitatively the trends found experimentally,[35] and the patterns discussed above for the CH_3CH_2X and $CH_2{=}CHX$ systems, with one interesting exception. The exception is that, in the $CH{\equiv}CX$ case, *all* of the

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Table VIII. Results of Pseudo-Atom INDO Perturbation Calculations on the $C^{\beta}H{\equiv}C^{\alpha}{-}X$ System[a]

Parameter set[b]	Carbon orbital densities[c]								Atomic densities[d]			^{13}C shieldings[e]	
	C_{α}				C_{β}								
	P_{2s2s}	$P_{p_xp_x}$	$P_{p_yp_y}$	$P_{p_zp_z}$	P_{2s2s}	$P_{p_xp_x}$	$P_{p_yp_y}$	$P_{p_zp_z}$	$P_{c\alpha}$	$P_{c\beta}$	P_X	$-\sigma_{c\alpha}$	$-\sigma_{c\beta}$
1	1.153	1.050	1.050	1.009	1.225	0.751	0.751	1.039	4.262	3.766	3.183	85.9	51.8
2	1.139	1.046	1.046	0.919	1.217	0.760	0.760	1.016	4.150	3.753	3.317	102.3	44.9
3	1.137	1.043	1.043	0.875	1.216	0.767	0.767	1.004	4.098	3.754	3.370	113.0	36.5
1′	1.114	1.023	1.053	0.857	1.222	0.735	0.788	0.107	4.047	3.762	3.424	118.7	46.7
2′	1.114	1.025	1.047	0.858	1.222	0.729	0.800	1.017	4.044	3.768	3.422	122.1	43.7
3′	1.114	1.027	1.043	0.858	1.222	0.725	0.808	1.016	4.042	3.770	3.422	124.6	41.5

[a] Calculations performed with the C^{β}–C^{α} bond along the *z* axis. [b] Parameter sets described in the text. [c] INDO density matrix elements. [d] Total valence-shell electron density of the α carbon. [e] $\sigma_{c\alpha}$ is the calculated shielding constant for the α carbon.

C_{α} orbital electron densities parallel the trend of decreasing $P_{c\alpha}$.

The parameter set variations 1 → 2 → 3 were designed to be *isotropic*, in the sense that all four of the orbitals of the pseudoatom experienced consistent parameter variations (*e.g.*, $2p_x$, $2p_y$, and $2p_z$ parameters were varied identically). Because of the importance of π systems in the $CH_2{=}CHX$ and $CH{\equiv}CX$ cases, it was of interest to alter the pseudo-atom in a manner that affects primarily the π system. This was accomplished, at least qualitatively, by choosing three additional parameter sets, 1′, 2′ and 3′, which differed from each other only in that the $2p_y$ orbitals were assigned parameter values defined by sets 1, 2, and 3, respectively, for 2p orbitals (except that β_0 was fixed, at −47.00 eV); the INDO parameters for the 2s $2p_x$, and $2p_z$ orbitals were held fixed at the carbon values given in Table I. It is interesting that, for these parameter variations, the change in $\delta_{c\beta}$ for a given change in $\delta_{c\alpha}$ is larger than for the 1 → 2 → 3 parameter sequence. Inspection of the 1′ → 2′ → 3′ parameter progression in Tables VII and VIII reveals that these variations bring about very small changes in P_x, $P_{c\alpha}$, and $P_{c\beta}$. Small decreases in $P_{c\alpha}$ occur, coupled with small increases in $P_{c\beta}$, and these changes are largely due to parallel effects in the P_{p_y}'s for each of these two carbons. The small size of the variation in these density matrix elements, coupled with the reasonably large variations in the corresponding coupled ^{13}C shielding values, leads one to conclude that rather minor alterations in the π-electron system can lead to significant changes in ^{13}C shielding, especially at the β carbon.

Conclusions

The results of finite perturbation INDO calculations of ^{13}C shifts by the method described for hydrocarbons by Ellis, Maciel, and McIver indicate that this theoretical framework is capable of qualitatively accounting for the effects of electronegative substituents. Computer experiments in which a set of atomic INDO parameters for fluorine were obtained led to a reasonable accounting of fluorine substituent effects on simple hydrocarbon frameworks. A pseudo-atom method is also capable of simulating experimentally established substituent effects in ^{13}C shielding calculations. These approaches should prove useful in the interpretation of a rapidly growing body of experimental ^{13}C studies.

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