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Short Communication

Correlations of ^{13}C Chemical Shifts and Geometry Modifications

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The effect of geometry modifications of ^{13}C chemical shifts has been investigated in a small subset of molecules using both LO-INDO and Gaussian 70 (4-31) calculations. The Gaussian calculations, while known to give poor absolute shifts, compare well to the reparameterized semi-empirical INDO determinations in calculated shift changes. In virtually all cases the signs of the shift changes were found to be opposite to that of the changes in the calculated electronic energy.

Key words: ^{13}C chemical shifts – LO-INDO – Gaussian 4-31.

The variable-size simplex optimization technique was recently used to reparameterize the $I+A$ and β parameters of a London orbital (LO) INDO approximation to the perturbed Hartree–Fock calculation of ^{13}C chemical shifts in hydrocarbons [1]. The absolute shifts for 39 nuclei in a set of molecules containing up to four carbons were reproduced to within a standard error of 9.9 ppm for an unconstrained optimization and to a standard error of 10.0 ppm for an optimization constrained to yield Mulliken gross charges [2] in agreement with double zeta *ab initio* calculations of Snyder and Basch [3]. The parameterization gave particularly good results for doubly and triply bonded carbons but was less satisfactory for aliphatic systems.

Obtaining an understanding of the chemical shift is a complex problem since not only is it theoretically difficult to calculate accurately but it is also difficult to understand physically since even the classical picture for a molecule is complicated. In an effort to provide some additional insight into ^{13}C chemical shifts we have carried out a variety of calculations on methane, ethane, ethylene, and acetylene in which the standard geometry employed previously [1] was changed

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by CC- and CH-bond stretches and compressions and by other rotations and bends in the molecular systems. We used the LO-INDO parameters found in our earlier charge-constrained parameterization (Series 2 of Ref. 1) and have also performed calculations using the same geometries with the Gaussian 70 SCF program [4] at the 4-31 level, modified [5] to calculate chemical shifts via the non-London perturbed Hartree–Fock method [6]. Several interesting correlations have been found which we wish to report on in this brief note.

Bond-length alterations of 0.1 Å were employed in all cases to insure a significant effect; rotational studies usually used angular increments of 15°. A representative set of data is shown in Table 1 where changes in the chemical shift, σ, are indicated for resonant (C*H) and non-resonant (CH) CH- and CC-bond changes. The absolute scale of Appleman and Daily [7] for chemical shifts is used.

In all examples studied, for both C*H- *and* C*C-bond alterations and for both the LO-INDO *and* Gaussian 4-31 approaches, bond compressions yielded positive (diamagnetic) changes in σ while bond stretches effected negative (paramagnetic) changes. While Gaussian 70 absolute chemical shifts do not reproduce experimental results well compared to the semi-empirical parameter-optimized LO-INDO approach, in virtually all cases the signs and magnitudes of the shift changes in the two types of calculations agree. The calculated changes for CH-bond alterations are smaller by about 30–40% in the INDO approach but 40–60% larger for CC-bond alterations. Stretch effects in both methods yield larger shifts changes than compressions by about 30–40%. Non-resonant CH-bond effects are small and show no similar correlation, although the LO-INDO and Gaussian calculations parallel each other.

Rotational studies carried out on ethane and ethylene suggest that at small angles of rotation (less than 30°) the shift changes are small (a few ppm). The bending

Table 1. ^{13}C shift changes in ppm for CH- and CC-bond compressions (com) and stretches (str)

		C*H $\Delta\sigma$		CH $\Delta\sigma$		C*C $\Delta\sigma$	
	$\sigma^{a}_{\mathrm{calc}}$	com	str	com	str	com	str
1. LO-INDO							
CH_4	194.8	+2.7	−3.3	—	—	—	—
CH_3CH_3	189.4	+2.7	−3.5	+0.3	−0.4	+0.8	−2.2
$CH_2{=}CH_2$	70.2	+2.2	−3.0	−1.4	+1.2	+20.9	−29.5
$CH{\equiv}CH$	119.2	+0.1	−0.7	−1.7	+1.5	+17.6	−23.7
2. Gaussian 4-31							
CH_4	221.0	+3.1	−4.9	—	—	—	—
CH_3CH_3	230.1	+4.0	−6.0	+0.7	−0.8	+0.5	−2.4
$CH_2{=}CH_2$	94.6	+2.2	−4.1	−0.4	+0.7	+16.1	−21.4
$CH{\equiv}CH$	142.5	+1.3	−2.5	−1.1	+1.7	+9.1	−12.9

[a] Experimental shifts are 196.0 (CH_4), 188.0 (CH_3CH_3), 70.6 ($CH_2{=}CH_2$), and 120.0 ($CH{\equiv}CH$); see Ref. [1].

away from linearity of the hydrogens in acetylene has an effect of similar magnitude. As is the case for bond alterations, acetylene is anomalous in that a greater shift change occurs for perturbing the hydrogen attached to the non-resonant carbon. Acetylene is unique with its axial symmetry, but this nonbonded effect seems unexpected.

Simplistic pictorial associations of charge density and chemical shift often fail and, indeed, can lead to erronious physical predictions. In our calculations here it was found that while $(\Delta\sigma/\Delta\rho)$ was positive in most cases for CH-bond changes, it was uniformly negative for the CC-bond change cases. While the Mulliken gross charge classification is, admittedly, a coarse measure of charge density, systematically applied one would hope to realize definitive correlations if they were present.

Two significant results emerge from this work. First, except for the apparently unusual case of acetylene, resonant atom negative shifts changes were found in all cases to correlate with increases in electronic energy as exhibited in bond modifications and molecular rotations, while positive shift changes are associated with a lowering of the electronic energy; no such correlation is present for non-resonant atom shifts. The Gaussian energy changes are more to be accepted but both these and the LO-INDO results had similar signs. Second, while Gaussian 70 minimal basis set calculations generally yield poor absolute chemical shift values, the *changes* calculated here compare well with those obtained from the empirically adjusted LO-INDO determinations. Gaussian calculations are generally felt to provide better descriptions of the charge distribution than empirical theories and thus even at the current level may be able to provide ultimately a better understanding of the origin of certain observed shift effects.

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