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α -SUBSTITUENT EFFECTS IN ^{13}C NMR OF HYDROCARBONS. QUANTUM CHEMICAL CALCULATIONS

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The ^{13}C NMR α -substituent effects within the series methane to neopentane and ethene to isobutene have been calculated using Hartree–Fock perturbation theory with MINDO/3. The sign and order of magnitude of the calculated α -effects are in agreement with new experimental values, including effects of multiple substitution.

Recently, the ^{13}C chemical shifts of small hydrocarbons have been measured in the gas phase [1]. The resulting α -substituent effects, without disturbing differences in solvent effects, are given in table 1. The largest discrepancy with the previous experimental α -effects [2] is the difference between methane and ethane: 14.1 ppm instead of 8.0 ppm. The new α -effects show that the consequences of multiple terminal methyl substitution become progressively smaller, analogous to the well-known downfield shifts of C_2 in the series butane, 2-methylbutane and 2,2-dimethylbutane, measured as neat liquids [2]. In table 1 a survey is given of α -substituent effects from known theoretical ^{13}C shift calculations [3–7]. It should be realized, however, that not all of these calculations were aimed explicitly on the effects of multiple methyl substitution. The difference between methane and ethane can be reasonably reproduced in sign and order of magnitude with a finite perturbation, a coupled Hartree–Fock^{*} or a Pople method. Serious discrepancies between calculations and experiments, however, occur whenever effects of multiple substitution are considered. Calculations with the Pople method [6,7] do not reproduce the observed decrease of the α -effects within the series methane to neopentane. The difference between ethane and C_2 of propane calculated by means of finite perturbation calculations is equal to or larger than the difference between methane and ethane, in contrast with the experiments. Sometimes, C_2 of propane is calculated even upfield from ethane. Ellis [4] ascribes this to the set of INDO parameters used or the basic approach employed. The shielding results of Ditchfield et al. [3] are dependent on the origin of the vector potential describing the magnetic field, which is taken at the center of mass.

We calculated ^{13}C shifts with the concept of Strong et al. [9]. Only the second order paramagnetic term was calculated. The expression for the xx component of the screening tensor of atom A is given by (eq. (16) of Strong et al. [9]):

$$(\sigma_A)_{xx} = -\frac{2e^2\hbar^2}{m^2c^2} \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \sum_B^{\text{atoms}} \frac{1}{\Delta E_{ij}} (c_{iy_A}c_{jz_A} - c_{iz_A}c_{jy_A}) \langle R_{y_A} | 1/r_A^3 | R_{z_A} \rangle \\ \times (c_{iy_B}c_{jz_B} - c_{iz_B}c_{jy_B}) \langle R_{y_B} | R_{z_B} \rangle.$$

^{*} α -effects, calculated by coupled Hartree–Fock perturbation theory [8–10] were not included in table 1, because only the shift difference between methane and ethane is available for comparison with experimental values.

Table 1
Experimental and calculated α -substituent effects (positive numbers relate to downfield shifts in ppm)

*C	$C-^*C$	$C-C-^*C$	$C-^*C-C$	$C-C-^*C-C$	$C-^*C-C-C$	$C=^*C$	$C=^*C-C$	$C-^*C-C$	Ref.
$\rightarrow^*C-C$	$\rightarrow C-^*C-C$	$\rightarrow C-C-^*C-C$	$\rightarrow C-^*C-C-C$	$\rightarrow C-C-^*C-C-C$	$\rightarrow C-^*C-C-C$	$\rightarrow C=^*C-C$	$\rightarrow C=^*C-C-C$	$\rightarrow C-^*C-C-C$	
8.0a)	10.2	9.4	9.1	2.7	10.3	8.1	14.6	b)	
14.1	11.8	10.8	7.8	3.2	12.7	9.2	-	c)	
13.2	18.5	-	-	-	11.3	-	-	d)	
23.8	25.5	-	-	-	25.3	-	-	e)	
15.6	23.4	-	-	-	27.3	-	-	f)	
1.5	-1.7	-	-	-	9.5	-	-22.1	g)	
3.0	-0.3	-	-	-	11.2	-	-21.0	h)	
7.7	7.7	-	-	-	9.9	-	-	i)	
4.0	3.4	-	3.5	-	-	-	-	j)	
13.7	13.4	14.1	13.3	13.6	-	-	-	k)	
14.2	12.4	12.5	10.5	6.5	15.7	13.8	15.0	l)	
3.6	3.4	3.5	3.4	4.4	4.8	5.0	9.7	m)	
-23.3	-9.4	-2.6	0.2	8.9	-20.2	-2.2	25.3	n)	

a) A shift difference of 11.2 ppm, obtained by Pugmire, is also quoted by Strong et al. [9]. The experimental conditions are, however, not given. The commonly accepted value was 8.0 ppm.

b) Experimental [2]. c) Experimental from gas phase measurements [1].

d) Calculated; finite perturbation method with ab initio with different basis sets [3], σ_p . (The use of $\sigma_p + \sigma_d$ results in upfield α -effects.) LEMAO-5G standard scale.

e) As in d), but with LEMAO-5G optimized scale.

f) As in d), but with 4-31G.

g) Calculated; finite perturbation method with INDO [4], σ_p .

h) Calculated; finite perturbation method with INDO [4], $\sigma_p + \sigma_d$.

i) Calculated; finite perturbation method with INDO [5], $\sigma_p + \sigma_d$.

j) Calculated; Pople method with a constant $\Delta E = 10$ eV with an LCAO MO theory [6], σ_p .

k) Calculated; Pople method with a constant $\Delta E = 10$ eV with EHT [7], σ_p .

l) Approach (1), see text. m) Approach (2), see text. n) Approach (3), see text.

(The effective nuclear charges were calculated without a β -correction parameter, i.e. $\beta = 1$, eq. (35) of Strong et al. [9].) We used the MINDO/3 procedure [11]. All geometries were optimized with MINDO/3. For the energy difference between a ground and an excited state molecular wavefunction, three approaches were used:

(1) $\Delta E_{ij} = 10$ eV, without invoking the closure rule.

(2) $\Delta E_{ij} = -(\epsilon_i - \epsilon_j)$, the energy difference between an occupied MO_i and an unoccupied MO_j .

(3) $\Delta E_{ij} = -(\epsilon_i - \epsilon_j) + 2K_{ij} - J_{ij}$, the singlet transition energy.

Results of calculated α -effects are given in table 1†.

Approach (1) shows remarkably good results. The sign and order of magnitude of the calculated α -effects is in agreement with the experimental values, including the effects of multiple substitution. We realize that approach (1) can only yield approximate results. In this concept refinements of one single aspect like ΔE_{ij} are not warranted as can be seen from the results of approaches (2) and (3). For calculation of β -substituent effects approach (1) is inadequate. All β -effects calculated were smaller than 1.5 ppm. This could be due to the neglect of two-center one-electron terms (eq. (17) of Strong et al. [9]). Presumably approach (1) is also applicable for calculating α -substituent effects in heterosubstituted hydrocarbons.

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† For butane σ_P calculated = 0.64 σ_P (trans) + 0.36 σ_P (gauche).

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