A Molecular Orbital Treatment of ^{13}C–H Spin-Spin Coupling Constant

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The correlation between the ^{13}C–H spin-spin coupling constant, J_{C-H}, and the degree of hybridization of the carbon atom has been investigated both experimentally and theoretically by several authors.[1-7]

Here we will present a semi-quantitative approach to an interpretation of the values of the coupling constant, J_{C-H}, for some saturated and unsaturated compounds; the approach uses an extended Hückel treatment which has recently been proposed by Hoffmann.[8] In this method, a molecular orbital is expressed by a linear combination of valency atomic orbitals, that is, the 1s orbitals of a hydrogen atom, the 2s, 2px, 2py and 2pz orbitals of a carbon atom, and so on. The orbital energy is then given by solving the secular equation:

$$det\,|H_{ij}-S_{ij}\varepsilon|=0 \qquad (1)$$

where H_{ij} is a matrix element and S_{ij} is the overlap integral between the ith and jth atomic orbitals. These are evaluated by a procedure similar to those previously reported.[8,9]

When we assume that J_{C-H} is exclusively determined by the contact term, it is expressed by the equation:[10]

$$J_{C-H}=(1/h)(2\beta\hbar)^2\gamma_C\gamma_H(1/\Delta E)$$
$$\times[(2\pi^2/3)P^2(2s_C|\delta|2s_C)(1s_H|\delta|1s_H)] \qquad (2)$$

where $P=2\sum_{i}^{occ}a^i_{1s_H}b^i_{2s_C}$, and where $a^i_{1s_H}$ and $b^i_{2s_C}$ are coefficients of the hydrogen 1s and carbon 2s orbitals in the ith molecular orbital respectively. ΔE is the mean excitation energy, which is assumed to be a constant throughout this treatment. Equation 2 is then simply written as:

$$J_{C-H}=AP^2 \qquad (3)$$

It may be seen that J_{C-H} is proportional to the square of the bond order, P^2. The values of the calculated P^2 and the observed J_{C-H} are cited in Table I. Since cyclobutane is nonplanar and has two groups of a nonequivalent C–H bond, their mean value is indicated in the table. For the sake of simplicity, the calculation of J_{C-H} is carried out with respect to only one configuration, the chair form for cyclohexane, and the staggered form for ethane.

TABLE I. CALCULATED VALUES OF P^2 AND OBSERVED J_{C-H}

Compound	P^2	J_{C-H}, c. p. s.
Group a Cycloalkanes and epoxide		
C_2H_4O	0.324	175
C_3H_6	0.270	161
C_4H_8	0.240	134
C_5H_{10}	0.209	128
C_6H_{12}	0.206	124
Group b Halomethanes and ethane		
$CHCl_3$	0.240	209
CH_2Cl_2	0.206	178
CH_3Cl	0.178	150
C_2H_6	0.176	126
CH_4	0.152	125
Group c Unsaturated compounds		
$HC\equiv CH$	0.377	248
$C_6H_5{}^{13}CHO$	0.336	174
Benzene	0.268	159
$CH_2{=}CH_2$	0.248	157

In each group, a, b and c, one can find a linear relationship between the values of P^2 and J_{C-H}, with a few discrepancies. These discrepacies may partly be attributed to the parametrization of the matrix element in an extended Hückel method, and partly also to the fact that only the contact term is taken into account as contributing to the coupling constant.

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