Theoret. chim. Acta (Berl.) 21, 211—214 (1971)

Nuclear Spin Coupling Constants from the Extended Hückel Method

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Received January 4, 1971

The ability to calculate directly bonded X–H nuclear spin coupling constants from molecular parameters obtained from the extended Hückel model has been studied as a function of the following calculational details: (1) the atomic orbital basis set; (2) the off-diagonal Hamiltonian matrix element approximation; and (3) charge iteration. It has been found that although variations such as these have a significant effect on the magnitudes of the observed coupling constants, none is capable of fitting the experimentally observed trends in X–H coupling constants.

Introduction

In spite of its well-recognized crudeness, the extended Hückel molecular orbital (EHMO) model, when used correctly, has provided a great deal of insight into various chemical problems. As part of a program to further define the limits of usefulness of the EHMO method, we report here the calculation of X–H nuclear spin coupling constants for a number of heteroatoms directly bonded to hydrogen.

This problem is of interest because it has been recently demonstrated [1] that values of $J_{^{13}C-H}$ which show excellent agreement with experimental results can be calculated using wave functions and energies obtained from EHMO calculations. Of even greater interest is the fact that the calculated coupling constants appear to be quite sensitive to the details of the calculational procedure, i.e., the approximation used for the off-diagonal Hamiltonian matrix elements, whether iteration to charge self-consistency is carried out, the atomic basis set employed, etc. Polezzo, Cremaschi, and Simonetta [1], using Clementi [2] atomic orbitals (CAO's), the Cusachs [3] approximation for the off-diagonal elements and iteration to self-consistent atomic charges, were able to obtain values of $J_{^{13}C-H}$ in quantitative agreement with the experimental values. On the other hand, Fahey *et al.* [4] had shown earlier that the EHMO technique using a Slater-type orbital (STO) basis set, the Wolfsberg-Helmholz [5] (WH) approximation and no charge iteration, yielded molecular parameters which gave values of $J_{^{13}C-H}$ $\sim 50\%$ smaller than the experimental values.

Thus, it appears that the calculation of nuclear spin coupling constants provides an opportunity to examine the effects of the details of the calculational procedure on the validity of the results obtained from the EHMO method. Also, if this method can be shown to be capable of producing quantitatively correct X–H nuclear spin coupling constants, it might prove to be a useful tool for furnishing information about molecular structure.

To explore these possibilities we have calculated directly bonded ^{11}B–H coupling constants for a series of L : BH$_3$ adducts as a function of variations in the EHMO method.

Results

The extended Hückel calculations have been carried out using a standard computer program [6]. Both Slater-type orbitals (using exponents obtained by Clementi *et al.* [7]) and Clementi orbitals [2] (linear combinations of STO's) have been employed as basis sets. Off-diagonal Hamiltonian matrix elements were calculated using both the Wolfsberg-Helmholz arithmetic mean formula [5] and the Cusachs [3] approximation. Diagonal Hamiltonian matrix elements were approximated by the valence orbital ionization potentials obtained by Basch *et al.* [8]. Calculations were performed both with and without iteration to self-consistent atomic charges which were determined from a Mulliken population analysis [9]. The nuclear spin coupling constants were calculated by use of the following equation developed by Pople and Santry [10]:

$$J_{\mathrm{AB}} = -\left(\frac{16\pi\beta\hbar}{3}\right)^2 \frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}}{h} \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{unocc}} \frac{1}{E_j - E_i} \cdot \sum_{\lambda,\mu,\nu,\sigma} c_{i\lambda} c_{j\mu} c_{j\nu} c_{i\sigma} \langle \phi_\lambda | \delta(r_{\mathrm{A}}) | \phi_\mu \rangle \langle \phi_\nu | \delta(r_{\mathrm{B}}) | \phi_\sigma \rangle .$$

A computer program was written to perform these calculations.

The ^{11}B–H coupling constants for the series of L : BH$_3$ adducts based on four variations of the EHMO method are reported in Table 1.

Also in order to explore the applicability of the method of Polezzo, Cremaschi, and Simonetta [1] for the calculation of other X–H coupling constants, calculations have been performed on a series of simple molecules and the results are reported in Table 2.

Discussion

As mentioned above, it has been shown from previous results [1, 4] that ^{13}C–H nuclear spin coupling constants calculated from molecular parameters obtained from the EHMO method are quite sensitive to the details of calculational procedure. This is substantiated by the results given in Table 1, which show that the effects of charge iteration and the off-diagonal element approximation upon the values of the ^{11}B–H coupling constants in a series of L : BH$_3$ adducts are quite significant. In fact note that in general the magnitudes of the coupling constants vary in the order: Cusachs approximation plus iteration > experimental values > Cusachs approximation with no charge iteration ∼ Wolfsberg-Helmholz approximation plus iteration > Wolfsberg-Helmholz approximation without charge iteration.

In attempting to explain these trends one must examine the effect of the calculational procedures on the two major contributors to the coupling constant, e.g., the *s*-character of the B–H bond and the separations of the energy levels

Table 1. ^{11}B–H *coupling constants in* L : BH$_3$ *adducts*

Molecule	$J_{^{11}B-H}$ (Hz) Cusachs	Cusachs + Iteration	Wolfsberg-Helmholz	Wolfsberg-Helmholz + Iteration	Experimental
BH_4^-	76	137	54	84	82
$H_3B:CO$	63	83	49	51	113
$H_3B:CN^-$	64	108	49	65	87
$H_3B:GeH_3^-$	59	100	48	59	81
$H_3B:PH_3$	57	103	49	63	104
$H_3B:NH_3$	60	107	51	65	91

Table 2. X–H *coupling constants*

Molecule	X	J_{X-H} (Hz) Calculated[a]	Experimental
$B_2H_6(H_b)$	^{11}B	106	46
$B_2H_6(H_t)$	^{11}B	187	135
CH_4	^{13}C	130	125
C_2H_2	^{13}C	246	249
CH_3F	^{13}C	108	149
NH_3	^{15}N	− 32	− 61
PH_3	^{31}P	166	182
NH_4^+	^{15}N	− 62	− 73
PH_4^+	^{31}P	287	548
H_2O	^{17}O	66	74
HF	^{19}F	−948	±615

[a] Using the Cusachs approximation, CAO's and charge iteration.

corresponding to occupied and unoccupied molecular orbitals. Analysis of the results shows that iteration to self-consistent charge, regardless of which off-diagonal element approximation is used, always has the effect of decreasing the energy gaps between occupied and unoccupied molecular orbitals in the L : BH$_3$ adducts. This should lead to increased coupling constants as is observed. In addition the *s*-character [11] of the B–H bond increases significantly upon charge iteration when the WH approximation is used. On the other hand the *s*-character of the B–H bond remains constant or decreases slightly upon iteration of the calculation employing the Cusachs approximation. (Also, it is interesting that the total B–H bond strength was found to increase in every case when charge iteration was carried out independently of the off-diagonal element approximation used). Since the increases in $J_{^{11}B-H}$ upon iteration of the calculation using the Cusachs approximation are greater or equal to those observed for the W–H calculation, this suggests that the lowering of energy level differences between filled and unfilled molecular orbitals produces the most significant effect on $J_{^{11}B-H}$.

In comparing the results from the Cusachs approximation to those using the W–H method for off-diagonal elements it is observed that the generally larger values of $J_{^{11}B-H}$ obtained by the former method arise from both smaller energy gaps between occupied and unoccupied orbitals and a significantly larger *s*-character in the B–H bond.

Finally, in order to determine the effect of the atomic orbital basis set calculations were performed on acetylene using the Cusachs approximation, charge iteration and Clementi and Raimondi [7] STO's (inserting the proper contact integrals) and compared to the same calculation but with a CAO basis set. The calculated values of $J_{^{13}C-H}$ were found to agree within 3%. Thus it appears that the basis set is not critical as long as the correct contact integrals are inserted when STO's are employed.

Thus, there are important differences in the magnitudes of the coupling constants obtained from these variations in EHMO method but unfortunately the trends in $J_{^{11}B-H}$ cannot be fit by any of the variations in the way that is possible for ^{13}C–H coupling constants.

In order to determine if these boron compounds presented unusually difficult problems, the X–H coupling constants for a series of simple molecules containing other heteroatoms were also calculated. Note from Table 2 that although the results are generally good on an absolute scale, the accuracy is not nearly that obtained for the $J_{^{13}C-H}$ values in hydrocarbons.

Thus it appears that, although the EHMO model is capable of producing surprisingly accurate values of J_{X-H} in all cases, the method is not good enough to provide structural information. Further, this work supports the general validity of the wave functions and energies obtained from EHMO calculations but emphasizes that the choices of the basis set, off-diagonal element approximation or charge iteration are not important for most qualitative uses of the method such as exploring trends in the bonding in a series of similar molecules.

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