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π-Electron Hyperconjugation in Organic Molecules and Ions

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The extent of energetic stabilization by alkyl groups with π-electron systems via hyperconjugation is investigated theoretically by MINDO molecular orbital calculations. In neutral hydrocarbons, this stabilization represents about 4% of the effective $C-C$ bond energy, and is additive in the number of alkyl groups present. Calculations for conjugated, polar, and ionic molecules are also discussed.

Das Ausmaß der energetischen Stabilisierung von π-Elektronen-Systemen mit Alkylgruppen durch Hyperkonjugation wird theoretisch durch MINDO-MO-Berechnungen untersucht. In neutralen Kohlenwasserstoffen beträgt diese Stabilisierung etwa 4% der effektiven $C-C$ Bindungsenergie und ist additiv entsprechend der Zahl der vorhandenen Alkylgruppen. Berechnungen für konjugierte, polare und ionische Moleküle werden ebenfalls diskutiert.

La méthode des orbitales moléculaires MINDO est utilisée pour calculer le degré de stabilisation par hyperconjugaison entre des groupements alkyles et des systèmes d'électrons π. Dans des hydrocarbures neutres cette stabilisation représente environ 4% de l'énergie effective de la liason C–C; elle est additive par rapport au nombre de groupements alkyles. On discute aussi des calculs effectués pour des molécules conjuguées polaires ou ioniques.

Introduction

There has been continuing interest and controversy regarding the extent to which π-electron hyperconjugation between alkyl groups and a conjugated network of π-electrons energetically stabilizes unsaturated organic molecules [1–4]. A typical example of the hyperconjugation phenomenon is the resonance interaction of the 1s orbitals of the (methyl) hydrogen atoms and the $2p_z$ orbital of the methyl carbon atom with the π-electrons of the unsaturated carbon atoms in the propene molecule, $CH_3(H)C=CH_2$. Various authors have attempted to investigate the energies involved in such effects by using π-electron theories appropriately modified to allow for the conjugative interaction of alkyl groups R with π-electron networks [1–5].

We have reinvestigated this problem by using a modern semiempirical SCF-LCAO molecular orbital theory (MINDO) which considers *all* the valence electrons of organic molecules [6]. These calculations were undertaken in order to answer the following questions: i) What is the magnitude of energy involved in π-hyperconjugation in alkenes? ii) Does this stabilization depend on the polarity or length of the conjugated network? iii) If more than one R group is bonded to the π-electron network, is the total stabilization simply additive? iv) Does the magnitude of the stabilization vary with the nature of the alkyl group R?

Method of Calculation

The calculations were executed by using the Modified Intermediate Neglect of Differential Overlap (MINDO) theory [6]. This method is a variant of the INDO theory of Pople *et al.* [7], and is parameterized to fit the ground-state bonding energies of organic compounds containing carbon, hydrogen, nitrogen, and oxygen. In contrast to most π-electron theories, both bonded and nonbonded interactions between all valence orbitals (1*s* on H; 2*s* and 2*p* on C, N, O) are included in the calculations.

Two calculations were done for each molecule considered. In the first, the usual hyperconjugative interaction between the AO's of the alkyl group and the p_π AO's of the unsaturated atoms was included. Hence all resonance integrals β_{uv} between AO's ϕ_u and ϕ_v were evaluated from the formula

$$\beta_{uv} = S_{uv}(I_u + I_v) f(R_{uv})$$

where S_{uv} is the overlap integral between ϕ_u and ϕ_v, I_u and I_v represent the valence-state ionization potentials of ϕ_u and ϕ_v, and $f(R_{uv})$ is an empirical function of both the type of atom pair involved and the internuclear separation [6a].

In the second calculation for each system, the π-hyperconjugative interaction between all AO's of the alkyl group R and the p_π orbitals of the unsaturated atoms was "cut off" by setting to zero all the resonance integrals β_{uv} corresponding to such conjugation. Hence in the second calculatiom, the molecular orbitals associated with the π-electron system proper are not "contaminated" by contributions from the AO's of the alkyl groups, and vice-versa. For a given molecule, the difference between the total bonding energies in the two calculations represents the energy by which π-electron hyperconjugation is effective in stabilizing the system, and is termed the *Hyperconjugation Energy.*

The standard bond angles and bond lengths developed previously [6] were used in all cases. The calculations were performed on the University of Western Ontario IBM 7040 computer using the MINDO program described elsewhere[1].

Results and Discussion

The Hyperconjugation Energies for the various molecules and ions of interest are listed in the Table. In all cases, the hyperconjugative interaction was found to energetically stabilize the molecule.

The stabilization energies for all the neutral hydrocarbons considered are small but significant, and account for approximately 4% of the total effective $C_{sp^3}-C_{sp^2}$ bond energy. Since the Hyperconjugation Energies for propene and 1-butene are identical to within 0.1 kcal/mole (Table), there is no significant difference in the capacity to hyperconjugate between a methyl group and an ethyl group for neutral species. The calculations for iso-butene yield a total Hyperconjugation Energy for the two methyl groups which is only slightly less than twice that in propene, which indicates that hyperconjugation in such systems is

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[1] See Ref. [6a] and the notes avaible from the Quantum Chemistry Program Exchange. Chemistry Department, Indiana University, Bloomington, Indiana 47401, USA.

almost additive (i. e. within 5 – 10%). These two findings support Dewar's contention that the effects of π-electron hyperconjugation in neutral hydrocarbons can be absorbed into a constant, *effective* $C_{sp^3}-C_{sp^2}$ single bond energy [3].

Table. *Hyperconjugation energies (in kcal/mole)*

System	Hyperconjugation energy		π-system
	Total	Per Alkyl group	Net charge (e.)
Propene	3.7	3.7	–0.0039
l-Butene	3.6	3.6	–0.0053
iso-Butene	7.0	3.5	–0.0050
1,3-Pentadiene	3.8	3.8	–0.0048
Acetaldehyde	5.6	5.6	–0.0283
Ethyl cation	12.8	12.8	–0.1186
iso-Propyl cation	22.3	11.2	–0.1772

The calculation on 1,3-pentadiene, in which a methyl group is bonded to a terminal carbon of trans-butadiene, indicates that extended conjugation per se within the unsaturated network has no significant effect on the Hyperconjugation Energy. In contrast, the value of 5.6 kcal/mole for acetaldehyde (compared to 3.7 kcal/mole for propene) illustrates the response of hyperconjugation to polar effects, since in the former system the π-electrons of the carbonyl group are polarized toward oxygen and away from the unsaturated carbon atom. A more dramatic increase in Hyperconjugation Energy is found for the carbonium ions (Table), where the unsaturated carbon atoms bear a formal positive charge of +1-electron, which is initially localized in the p_π orbital. The values of 12.8 and 22.3 kcal/mole for the ethyl and iso-propyl cations respectively represent lower limits to the Hyperconjugation Energy; since the actual $C_{sp^3}-C_{sp^2}$ bonds in these species are probably significantly shorter than those in neutral alkenes [8]. Hyperconjugation in carbonium ions is not a weak interaction as it is in neutral systems, and for this reason it is not surprizing that the additivity of Hyperconjugation Energies in going from the ethyl to the iso-propyl ion is not as exact as that found for alkenes (Table).

In the last column of the table, the net charge of the p_π orbitals associated with the unsaturated carbon atoms is reported for each molecule. In all cases considered, the π-system gains electron density at the expense of the alkyl groups, although the transfer of charge is extremely small for the neutral hydrocarbons. Newton and Lipsomb found a somewhat larger transfer of electron density of 0.013 e. from the methyl group to each pair of π molecular orbitals in an *ab initio* calculation for methylacetylene [9]. It is interesting to note that the vertical hyperconjugation energy per π-electron pair of 3.81 kcal/mole obtained in the latter calculation [9] is in excellent agreement with that of 3.7 kcal/mole found here for propene, even though slightly different methods of "localization" were used in the two methods.

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