The extent of energetic stabilization by alkyl groups with \( \pi \)-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.


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 \( \pi \). Dans des hydrocarbures neutres cette stabilisation représente environ 4% de l'énergie effective de la liaison 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 \( \pi \)-electron hyperconjugation between alkyl groups and a conjugated network of \( \pi \)-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 2\( p_z \) orbital of the methyl carbon atom with the \( \pi \)-electrons of the unsaturated carbon atoms in the propene molecule, \( \text{CH}_3(\text{H})\text{C} = \text{CH}_2 \). Various authors have attempted to investigate the energies involved in such effects by using \( \pi \)-electron theories appropriately modified to allow for the conjugative interaction of alkyl groups \( R \) with \( \pi \)-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 \( \pi \)-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 \( \pi \)-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 $\pi$-electron theories, both bonded and nonbonded interactions between all valence orbitals (1s on H; 2s and 2p 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 $p_{\pi}$ AO's of the unsaturated atoms was included. Hence all resonance integrals $\beta_{uv}$ between AO's $\phi_u$ and $\phi_v$ were evaluated from the formula

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

where $S_{uv}$ is the overlap integral between $\phi_u$ and $\phi_v$, $I_u$ and $I_v$ represent the valence-state ionization potentials of $\phi_u$ and $\phi_v$, 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 $\pi$-hyperconjugative interaction between all AO's of the alkyl group $R$ and the $p_{\pi}$ orbitals of the unsaturated atoms was “cut off” by setting to zero all the resonance integrals $\beta_{uv}$ corresponding to such conjugation. Hence in the second calculation, the molecular orbitals associated with the $\pi$-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 $\pi$-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.  

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 $C_{sp^3}-C_{sp^3}$ 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

---

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