Calculation of Excited-state Geometries using Molecular Orbital Theories

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Summary Molecular orbital theories which neglect overlap integrals underestimate geometry changes in excited states of molecules.

SEVERAL authors have reported zero-differential-overlap (ZDO) molecular orbital calculations of the geometry for excited states of unsaturated molecules.[1–3] We point out that such ZDO calculations completely discount one of the major factors influencing bond lengths and bond angles in excited molecules.

Geometries and energies calculated for ethylene

State	Twist angle	Bond length (Å) Ref. 1	Bond length (Å) This work	Excitation energy (kcal./mole)
Ground . .	0°	—	1·34	0
Singlet $\pi\pi^*$ . .	0°	1·43	1·54	147·9
	90°	1·38	1·45	126·0
Triplet $\pi\pi^*$ . .	0°	—	1·61	73·6
	90°	—	1·52	58·8

Consider the π-electron energy levels ϵ_π and $\epsilon_{\pi*}$ of ethylene. According to one-electron LCAO–MO theories which retain the overlap integrals S,

$$\epsilon_\pi = (\alpha + \beta)/(1 + S)$$

and

$$\epsilon_{\pi^*} = (\alpha - \beta)/(1 - S).$$

Since the π^* level is more antibonding than the π level is bonding, the total π-electron energy E for a $\pi\pi^*$ electron configuration is net antibonding:

$$E = 2(\alpha - \beta S)/(1 - S^2).$$

In the excited molecule, the energy can be stabilized by decreasing the magnitudes of β and of S; this is accomplished by lengthening the carbon–carbon bond and/or by twisting the p_π orbitals away from each other.[4] Any theoretical method which neglects overlap integrals predicts that the one-electron π-energy of the $\pi\pi^*$ configurations is independent of geometry (since S is neglected), and thus neglects a major driving force in the determination of the equilibrium geometry. It is difficult to see how such an error can be compensated for by any adjustment in the values of semi-empirical parameters.

According to an analysis based on first-order perturbation theory,[5] the net antibonding character of the lowest $^3\pi\pi^*$ state of an acyclic polyene containing $2m$ unsaturated carbon atoms is given approximately by

$$-8S(\beta - \alpha S)/(m + 1)^2.$$

The destabilization due to overlap effects decreases rapidly with increasing chain length, and the exothermicity associated with rotation by 90° about a C=C bond becomes zero in the longer polyenes. Hence the error in the calculated geometry due to the use of the ZDO approximation should be appreciable only for the shorter chains.

The predictions based on variations in the one-electron energy are supported by semi-empirical SCF–LCAO–MO π-electron calculations which include differential overlap between orbitals on bonded atoms.[5,6] The bond lengths and excitation energies calculated by this method for the planar and 90° twisted forms of the $^1\pi\pi^*$ and $^3\pi\pi^*$ states of ethylene are listed in the Table; these results were obtained by minimizing the total energy with respect to the carbon–carbon distance rather than *via* a bond length–bond order relationship.

Due to overlap destabilization, the bond distances calculated for the planar singlet and the planar triplet are both longer than the C(sp^2)–C(sp^2) single bond separation[6] of about 1·52 Å. Since the overlap destabilization is zero in the twisted conformation the optimum bond lengths are shorter (by 0·09 Å) than in the planar forms. In contrast, the ZDO calculations of Kirby and Miller[1] for the singlet predict that the carbon–carbon separation is shorter than the single-bond length even in the planar geometry.

The calculations predict that the 90° twisted conformations of both the excited singlet and triplet are substantially more stable than the planar forms, in agreement with the conclusions reached by Mercer and Mulliken[4] from the vibrational structure of the $\pi\pi^*$ absorption spectra. The calculated excitation energy for the 0–0 band of the triplet of 58·8 kcal./mole is in excellent agreement with the value of 57 kcal./mole extrapolated from the spectrum;[4] the agreement is poorer in the case of the singlet (126 calculated, 108 kcal./mole observed[4]).

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