
MNDO AND AM1 STUDY OF MOLECULAR GEOMETRIES IN EXCITED STATES

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Geometries of the singlet excited states of series of organic molecules have been calculated using MNDO and AM1 semiempirical methods with limited configuration interaction. Changes in molecular geometries after excitation are reproduced reasonably well, with AM1 being superior to MNDO, which in some cases fails. Molecules having biradical-like character in excited state are described better than classical ones.

One of the most interesting application fields of quantum chemical calculations is their using in theoretical photochemistry. In this connection methods of different level of sophistication may be used. From very simple methods based only on symmetry, to the highly sophisticated *ab initio* methods.

The best results are obtained, of course, by using *ab initio* methods with allowance for correlation energy. Such approach, however, requires involving of large basis sets and incorporating extensive configuration interaction, and is very costly in terms of computer time. Applications of high-quality *ab initio* techniques in theoretical photochemistry have therefore so far been limited to small systems only.

From this reason the field is still open for semiempirical methods. Semiempirical approaches such as CNDO/S¹, HAM², and LNDO/S³ have been successfully used for calculations of vertical excitation energies. These methods, however, fail in describing nonvertical areas of energy hypersurfaces. CNDO/INDO give good geometries of simple organic molecules in excited states⁴ but problems arise in describing conjugated or strained systems and the worst of all is unrealistic overstabilization of $\sigma\pi^*$ and $\pi\sigma^*$ excited states. MNDOC (ref.⁵) and SINDO1 (ref.⁶) methods have proved promising for calculating excited state geometries and reaction paths of some photochemical reactions^{7,8}.

The most used semiempirical methods currently are MNDO (ref.⁹) and AM1 (ref.¹⁰). Both became invaluable tools in studies of geometries, energetics, and reactivity of organic molecules.

In the last decade some applications of MNDO in theoretical photochemistry have appeared; e.g. calculations of excitation energies¹¹, chiroptical properties of organic molecules¹², photochemical hydrogen shifts¹³, electronic structure of some biradical systems¹⁴, photoisomerizations of diphenylbutadiene¹⁵, stilbene¹⁶, and pentadieniminium¹⁷.

In this work we present results of MNDO and AM1 calculations on series of organic molecules in excited states with aim to test how these methods reproduce changes in molecular geometry after excitation. Knowledge of minima on excited state energy hypersurfaces is necessary for proper understanding of photochemical reaction mechanisms.

RESULTS AND DISCUSSION

Semiempirical methods MNDO and AM1 with limited configuration interaction (CI) were used for optimizing geometries of molecules in their lowest excited singlet states. CI was based on the half-electron approximation¹⁸, with inclusion of mono-excited configurations relative to the reference open-shell singlet (i.e. also some biexcited configurations from the closed shell ground state were included). The total number of configurations used were 17. Gradient with respect to all internal coordinates was calculated numerically by finite difference method. Since the CI wavefunction is not variationally optimized the calculation of energy gradient in one point required $2n + 1$ (n is the number of optimized parameters) full SCF + CI calculations. In the case of molecules with degenerate molecular orbitals (twisted ethylene and square cyclobutadiene) a unitary transformation¹⁹ was used to obtain the most delocalized orbital sets.

Table I shows the S_1 geometries calculated in this way for 10 organic molecules of different structural types. Our results are compared with experimental ones and/or results of high-quality *ab initio* calculations.

MNDO gives reasonably good results for most molecules, in some cases, however, fails. For small molecules $\text{HC}\equiv\text{CH}$, $\text{H}_2\text{C}=\text{O}$, and HCN , MNDO retains in S_1 state the same symmetry as in the ground state. It is probably caused by hard adjusting of parameters to proper description of the ground state geometry, what results in overstabilization of these areas also on the higher energy surfaces. Small molecules are particularly sensitive to this uncounterbalance in parametrization. In the area of experimental minima MNDO gives minima too, but these are only the local ones higher in energy than unrealistic vertical minima.

Molecules having biradical character, e.g. twisted ethylene and related systems, or square cyclobutadiene are well described by using MNDO. The results for cyclobutadiene, an antiaromatic molecule with four π electrons and degenerate frontier orbitals, are particularly interesting because even *ab initio* methods often fail in describing its electronic structure correctly²⁰. MNDO, on the other hand, well gives S_0 geometry as rectangular (D_{2h} , also starting from D_{4h}), and S_1 as symmetrical square geometry.

AM1 results are given in the second column of Table I. The results are clearly better, in any case AM1 does not fail qualitatively. Correct bent geometries are given for acetylene, as well as for HCN , formaldehyde is pyramidal (although only slightly). For allene AM1 yields D_{2h} S_1 geometry. *Ab initio* calculation gives for this symmetry a local minima only of 0.1 eV less stable than absolute C_{2v} one²¹, and therefore we can AM1 result consider as at least qualitatively good.




Also changes in bond lengths and angles after excitation are better described using AM1 parametrization (e.g. ethylene, cyclobutadiene).

The results reported here suggest that MNDO and AM1 methods may be suc-

TABLE I
MNDO and AMI optimized geometries of excited states (lengths in angstroms, angles in degrees)

Molecule	Symmetry	Parameter	MNDO	AMI	Exp./ <i>ab initio</i>	Ref.
HC≡CH	C_{2h} A_u	CC	1.299	1.320	1.371	22
		CH	1.054	1.070	1.096	
		CCH	180.0	143.7	121.6	
H ₂ C=CH ₂	D_{2d} B_1	CC	1.430	1.467	1.48	23
		CH	1.085	1.081	—	
		CCH	121.2	128.4	—	
	D_{2d} A_1	CC	1.346	1.425	1.41	
		CH	1.097	1.107	—	
		CCH	125.5	128.8	—	
	D_{2d} B_2	CC	1.345	1.414	1.43	
		CH	1.094	1.112	—	
		CCH	125.4	128.3	—	
HCN	C_s A''	CN	1.288	1.236	1.297	24
		CH	1.050	1.149	1.140	
		HCN	180.0	131.9	125.0	
HNO	C_s A''	NO	1.180	1.161	1.241	24
		NH	1.026	1.010	1.036	
		HNO	121.8	129.3	116.3	
H ₂ C=O	C_s A''	CO	1.307	1.291	1.32	24
		CH	1.090	1.097	1.09	
		HCO	119.0	118.7	120.5	
		O-CH ₂	0.0	4.7	31.0	
CO ₂	C_{2v} B_2	CO	1.241	1.241	1.246	24
		OCO	136.3	128.9	122.0	
H ₂ C=C=CH ₂	D_{2h} A_g	CC	1.317	1.315	1.322	21
		CH	1.087	1.091	1.072	
		CCH	122.6	121.3	119.5	
H ₂ C=C=O	C_s A''	CC	1.414	1.404	1.419	25
		CO	1.187	1.197	1.226	
		CH _{cis}	1.075	1.092	1.071	
		CH _{trans}	1.082	1.092	1.067	
		CCO	154.4	146.9	129.3	
		CCH _{cis}	123.0	120.7	120.8	
		CCH _{trans}	119.5	119.0	119.9	

TABLE I
(Continued)

Molecule	Symmetry	Parameter	MNDO	AM1	Exp./ <i>ab initio</i>	Ref.
	D_{2h} B_{1g}	CC	1.420	1.363	1.34	26
		CC'	1.477	1.532	1.57	
		CH	1.071	1.077	—	
		CCH	134.0	138.4	—	
	D_{4h} A_{1g}	CC	1.437	1.435	1.447	
		CH	1.072	1.077	—	
	D_{6h} B_{2u}	CC	1.421	1.410	1.449	27
		CH	1.088	1.098	1.082	

^a D_{6h} symmetry was considered in benzene.

cessfully used for calculation of molecular geometries in excited states. Changes in geometry after excitation are reproduced reasonably well, with biradical-like geometries described better than "classical" ones, where MNDO in some cases fails.

On the basis of present results and previously reported calculations on vertical excitation energies¹¹ we believe that MNDO and especially AM1 with limited configuration interaction may be useful tools in studies in theoretical photochemistry.

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