CALCULATION OF ENERGIES OF EXCITED STATES WITH MNDO CI METHOD

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The energies of the lowest singlet excited states of eighteen molecules have been calculated by the MNDO half-electron method with configuration interaction. The method overall overestimates the stability of excited states, but the actual values depend on the character of the particular chromophore. The best agreement with experiment was obtained for the conjugated systems.

Theoretical studies of reaction paths of photochemical reactions require a realistic description of both ground and excited state energy hypersurfaces. Reliable *ab initio* estimations of such processes can be obtained only if large basis sets are used and extensive configuration interaction (CI) is included, and these calculations become very costly in terms of computer time. Therefore, *ab initio* studies of excited state processes have been limited so far to small systems only. For this reason the theoretical photochemistry is still the convenient field for application of semiempirical methods.

Currently the widest used semiempirical method is MNDO (ref.[1]), which was shown as very useful in the study of ground state reactions[2]. The use of MNDO for studying the excited state chemistry is, however, quite rare. Some photochemical reactions were studied[3,4] and energies of excited states[5] and chiroptical properties of organic molecules[6] were calculated. In our previous paper[7] we studied singlet and triplet excitation energies of thirty molecules using MNDO CI method with mono and biexcited configurations with closed shell molecular orbitals (MO's).

In the course of photochemical reaction the bonds are often broken and diradicals play the role as intermediates, and such systems are described better by half-electron (HE) MO's than by closed shell MO's, although with CI.

Therefore in present study the HE version of MNDO with CI is tested for calculation of excited state energies.

RESULTS AND DISCUSSION

The HE version[8,9] of MNDO (ref.[1]) augmented with subroutines for calculation of CI were used. In CI twenty-four monoexcited configurations relative to the

reference open shell singlet were included (i.e. also some biexcited configurations from the closed shell ground state). These configurations were formed by transitions from the four highest occupied to the four lowest unoccupied orbitals. Transition energies were calculated for the ground state optimized geometries.

TABLE I

Vertical excitation energies (eV) calculated with MNDO method

Molecule	State		SDCI[a]	HECI	Exp.[a]
$H_2C=CH_2$	$^1B_{1u}$	$\pi\pi^*$	6·05	6·21	7·65
	$^1A'$	$\pi\pi^*$	5·78	5·98	7·19
	$^1A_1$	$\pi\pi^*$	5·59	5·80	6·74
	^1B_u	$\pi\pi^*$	5·53	5·77	7·08
	$^1B_2$	$\pi\pi^*$	4·92	5·44	7·19
	$^1B_2$	$\pi\pi^*$	5·44	5·67	7·03
$H_2C=CHF$	$^1A'$	$\pi\pi^*$	5·64	5·76	7·19
$H_2C=CF_2$	$^1A_1$	$\pi\pi^*$	5·43	5·51	7·59
	^1A_g	$\pi^2\pi^{*2}$	3·88	4·59	—[b]
	^1B_u	$\pi\pi^*$	5·20	5·13	5·92
	$^1B_2$	$\pi\pi^*$	4·31	4·23	5·20
	$^1B_2$	$\pi\pi^*$	3·14	2·69	3·44
$H_2C=O$	$^1A_2$	$n\pi^*$	3·13	2·81	4·2
$CH_3CH=O$	$^1A''$	$n\pi^*$	2·98	2·70	4·28
$(CH_3)_2C=O$	$^1A_2$	$n\pi^*$	3·08	2·57	4·48
$NH_2CH=O$		$n\pi^*$	3·91	3·33	5·7
$H_2C=CH—CH=O$	$^1A''$	$n\pi^*$	3·10	4·02	3·21
$HC≡C—CH=O$	$^1A''$	$n\pi^*$	3·13	2·81	3·56
$O=CH—HC=O$	^1A_u	$n\pi^*$	2·39	2·81	2·73

[a] See ref.[7]; [b] not observed.

In Table I results of our calculations (denoted HECI) are compared with the experimental data and previously reported results[7] of CI calculations with singly and doubly excited configurations using closed shell MO's as the basis (denoted SDCI).

Molecules under study may be divided into four groups, according to the type of their lowest transition, namely ethylene and its derivatives with $\pi\pi^*$ transition of the isolated $C=C$ bond, conjugated hydrocarbons, simple carbonyl compounds with the lowest transition of $n\pi^*$ character and finally conjugated carbonyl compounds. The MNDO method overall overstabilizes the energies of excited states, but the results depend strongly on the character of chromophore. Conjugated systems both of $\pi\pi^*$ and $n\pi^*$ types are described more realistic than unconjugated molecules.

The results of HECI and SDCI are about of the same quality, the average absolute errors for all eighteen transition energies are 1·27 and 1·20 eV, respectively.

The overstabilization of excited state energies in MNDO approximation is already known. It is caused by overestimation of correlation effects in the HECI approximation[5] and also by underestimation of antibondingness of antibonding molecular orbitals[10]. Our results, that the reliability of excited state energies depends on the chromophore type, is consistent with previous findings of Dewar[5].

On the basis of our calculations it can be said, that the MNDO method overall overestimates the stability of excited states, the results, however, depend strongly on the character of the particular chromophore. The best agreement with experiment was obtained for the conjugated systems. The HE MO's as the basis for CI provide the results approximately of the same quality as the closed shell MO's.

It is known, that MNDO was parametrized for reproduction of ground state properties, and therefore it cannot yield results for excited states of the same quality as semiempirical methods specially designed for spectroscopic studies. The great advantage of MNDO is, however, the possibility to study the ground as well as the excited state hypersurfaces with the same level of approximation, what is the necessary condition for the proper description of photochemical reactions. With regard to our previous study[7], which confirmed that MNDO CI reproduces the ordering of states and their relative distances quite well, we believe that this method may serve as a useful tool for study of excited state processes.

We are currently examining the adequacy of MNDO CI approximation for obtaining geometries of organic molecules in excited states.

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