INVESTIGATION OF GEOMETRY OF MOLECULES
IN ELECTRONICALLY EXCITED STATES BY CNDO/2 METHOD

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Equilibrium geometry of molecules in the lowest excited singlet state has been studied by the semi-empiric method CNDO/2 with configuration interaction. The results agree well with experimental data, and the used method reproduces well the geometry changes due to electronical excitation of molecules.

Changes in physico-chemical properties and reactivity of molecules accompanying their electronic excitation are often quite considerable. Smaller molecules change their equilibrium geometry fundamentally, bond lengths, bond angles and even symmetry being changed. Not negligible changes in geometry are encountered also with greater molecules; not only their functional groups, but also molecular skeleton is changed. Experimental determination of these changes is connected with considerable complications, and, therefore, suitable theoretical methods can give useful information in this field. Even in the case of greater molecules the theoretical methods are the only source of data about their properties in the excited states.

Successful qualitative predictions about shapes of simple molecules in their ground and excited states were made on the basis of the Walsh diagrams[1]. Development of quantum-chemical methods made it possible to replace the empirical approach by precise quantum-chemical calculations at various levels. With respect to the electronically excited states of molecules predominant number of calculations concerned UV spectra interpretation. Far less calculations dealt with geometry of molecules in excited states. The best results were obtained by the method *ab initio*[2]. Due to limited possibility of application of non-empirical calculations for greater systems, it turns out that semi-empirical methods must be used for this purpose. Out of them the CNDO/2 method[3] proved to be the best for calculation of equilibrium geometry of molecules in the ground state. This method, still without the configuration interaction, was used for bond angles calculation of excited molecules, too[4]. The half-electron method in CNDO approximation was used also for automatic optimization of formaldehyde excited state geometry[5].

The present paper deals with application of CNDO/2 method with configuration interaction for calculation of equilibrium bond lengths and bond angle in a number of molecules of "closed shell" type in their lowest excited singlet states. The results are compared with the known experimental data and with available non-empirical calculations. Various modifications and parametrizations of the method were tested for small molecules in our previous paper[6].

CALCULATIONS

The ground state wave function is approximated by the Slater determinant. The excited state is obtained by an electron transfer from the occupied to the virtual molecular orbital. The excited singlet state energy is given by the relation:

$$E_{i-j} = E_g + \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij},$$

where E_g is the ground state energy, ε_i and ε_j are energies of the respective molecular orbitals, J_{ij} and K_{ij} are the Coulomb and the exchange integrals, respectively.

A better approximation of the excited state is obtained by including the configuration interactions of mono-excited states. The lowest excited singlet energy obtained in this way is minimized with respect to the bond lengths and bond angles.

The equilibrium geometry parameters were obtained by cyclic optimization. One parameter was varied with a certain accuracy, the others being fixed. After obtaining the optimum value of the first parameter (minimum energy) the second parameter was varied *etc.* In a next cycle again the first parameter was optimized with a higher accuracy, the other parameters being fixed at their optimum values. The procedure was repeated until minimum energy was obtained with the accuracy of 0·001 Å and 1° for the bond lengths and bond angles, respectively. The geometry parameters changes in the individual cycles were 0·05, 0·01, 0·005, 0·001 Å and 10°, 5°, 1° for the bond lengths and the bond (or dihedral) angles, respectively.

The semi-empirical method CNDO/2 was used for the calculations. Various modifications of this method[6] were tried, and the original parametrization by Pople, Santry and Segal[3] turned out to be the most suitable one, being completed by configuration interaction of the mono-excited states. In most cases all mono-excited states were considered for the configuration interaction (up to the maximum number of 25 configurations; otherwise only 5 highest occupied and 5 lowest virtual orbitals were considered). In the case of compounds containing elements of the 3. period the $3s$, $3p$, $3d$ orbitals were considered[7].

As the excited state geometry is often different from the ground state geometry, and the simple determinant approximates the ground state of the molecule, difficulties were encountered in some cases of SCF calculation convergency due to non-real geometry. These difficulties were removed by introduction of the density matrix extrapolation according to Howland and Flurry[8], which made the convergency far faster.

RESULTS AND DISCUSSION

Those molecules (or their structural analogues) were chosen for the investigation for which experimental results or non-empirical calculation results are available. The results obtained are given in Table I along with experimental values of geometry parameters of the investigated compounds. Known experimental values are given for those structural parameters which were not optimized. From Table I it is obvious that the calculated values agree very well with experimental data, in some cases the results are better than non-empirical calculations. For some compounds the calculated geometry parameter value does not agree with experiment quite precisely, however, the calculation reproduces correctly the geometry parameters change during excitation. Also the molecular symmetry change due to the electronic excitation is well represented by the calculation (HCN, NH_3, C_2H_2 *etc.*).

TABLE I

Calculated and Experimental Values of Geometry Parameters

Compound	Geometry parameter[a]	Experiment (ref.[9])	CNDO/2-CI	ab initio STO-basis	(ref.[2]) G-basis
HCN	R_{CN}	1·297	1·300	1·373	1·300
	$\measuredangle$ HCN	125	127	112·4	127·8
		$^1A''$, C_s^b	$^1A''$, C_s		
HCF	R_{CF}	1·297	1·294	1·318	1·338
	$\measuredangle$ HCF	127·2	129	127·1	128·1
		$^1A''$, C_s	$^1A''$, C_s		
HCCl	R_{CCl}		1·525		
	$\measuredangle$ HCCl	134	163		
		$^1A''$, C_s	$^1A''$, C_s		
CH_2	R_{CH}	1·05[c]	1·095	1·06[d]	
	$\measuredangle$ HCH	140 ± 15[c]	142	151	
		$^1B_1$, C_{2v}	$^1B_1$, C_{2v}		
NH_3	R_{NH}	1·08	1·100		
	$\measuredangle$ HNH	120	120		
		$^1A_2''$, D_{3h}	$^1A_2''$, D_{3h}		
CO_2	R_{CO}	1·246	1·265		
	$\measuredangle$ OCO	122 ± 2	132		
		$^1B_2$, C_{2v}			
HNO	R_{NO}	1·241	1·188	1·256	
	$\measuredangle$ HNO	116·3	123	114·7	
		$^1A''$, C_s	$^1A''$, C_s		
SO_2	R_{SO}		1·541	1·492[e]	
	$\measuredangle$ OSO		140	123·5[e]	
			$^1B_1$, C_{2v}	$^1B_1$, C_{2v}	
H_2CO	R_{CO}	1·323	1·280	1·307	1·273
	$\measuredangle$ α^f	31	31	28·4	15
		$^1A''$, C_s	$^1A''$, C_s		
HFCO	R_{CO}	1·36	1·289		
	R_{CF}		1·331		
	$\measuredangle$ HCF		120		
	$\measuredangle$ α^f	~40[g]	36		
		^1A, C_1	^1A, C_1		

Table I
(Continued)

Compound	Geometry parameter[a]	Experiment (ref.[9])	CNDO/2-CI	ab initio STO-basis	(ref.[2]) G-basis
SiH$_2$	R_{SiH} ∢ HSiH		1·600 115 $^1B_1$, C_{2v}		
PH$_3$	R_{PH} ∢ HPH		1·529 120 $^1A_2''$, D_{3h}		
Acetylene-*trans*	R_{CC} ∢ HCC	1·388 120 ^1A_u, C_{2h}	1·333 136 ^1A_u, C_{2h}	1·371 121·4	1·367 125·1
Acetylene-*cis*	R_{CC} ∢ HCC		1·273 128 $^1B_2$, C_{2v}	1·332 134·4 $^1A_2$, C_{2v}	1·335 136·2
Ethane	R_{CC} ∢ ω^i	1·39^h	1·401 60 $e_g \rightarrow e_u$, D_{3d}		
Propynal	$R_{C\equiv C}$ R_{C-C} $R_{C=O}$	1·238 1·325 $^1A''$, C_s	1·208 1·400 1·289 $^1A''$, C_s		
Ketene	$R_{C=O}$ $R_{C=C}$ ∢ CCO		1·257 1·315 147 $^1A''$, C_s		1·24^j 1·37^j 130^j $^1A''$, C_s
1,2,5-Thiadiazol	∢ β^k	$\neq 0^l$	14 $^1A''$, C_s		

^{a} Bond lengths in Å, bond angles in degrees; ^{b} character of the excited state, point group of symmetry; ^{c} ref.[10]; ^{d} ref.[11]; ^{e} ref.[16]; ^{f} angle between C=O bond and the plane of the molecule; ^{g} ref.[12]; ^{h} ref.[13]; ^{i} rotation angle of CH$_3$ groups around C—C bond; ^{j} ref.[14]; ^{k} see Scheme 1; ^{l} ref.[15].

In the case of triple bond the calculated bond length values are low (acetylene, propynal). For acetylene the used method prefers *cis*-configuration, which is encountered only in complexes. Similarly, too great bond angle values are in compounds containing Cl and S (HCCl, SO_2).

In the case of CO_2 the lowest calculated excited state corresponds to $a_2 \rightarrow a_1$ transition, in contrast to the experimentally found $b_2 \rightarrow a_1$ transition.

Influence of configuration interaction on the results is very important[6]. Compounds with a carbonyl group (H_2CO, HFCO) change fundamentally their symmetry on excitation, going from planar to pyramidal form. If configuration interaction is not used in the calculation, then the optimum structure of the excited state results to be planar. First the introduction of configuration interaction gives the correct pyramidal structure with a very precise value of the non-planar angle α. Fig. 1 gives the course of the overall energy of the lowest formaldehyde excited singlet depending on the non-planar angle obtained with and without involving the configuration interaction.
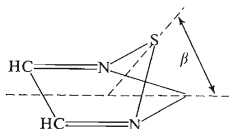
SCHEME 1

The heterocyclic compound 1,2,5-thiadiazol loses its aromatic character on excitation, becoming non-planar[15] (Scheme 1). The calculation reflects this fact well.
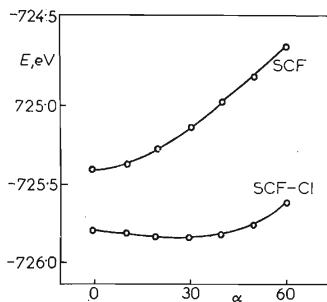

FIG. 1

Dependence of Total Energy of the Lowest Excitated Formaldehyde Singlet on the Angle α

C=O distance is 1·280 Å.

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