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CALCULATION OF THE $\pi\sigma^*$ AND $\sigma\pi^*$ STATES OF PLANAR UNSATURATED MOLECULES BY THE CNDO CI METHOD

B. F. Minaev and A. F. Terpugova

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The present work is devoted to investigating the luminescent properties of planar unsaturated molecules and to calculating the spectrum of their excited states by the CNDO (complete neglect of differential overlap) method [1]. Attention is paid mainly to the energies and oscillator forces of the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions, since the phosphorescence lifetime of molecules with π electrons depends on these to a considerable extent. Since the calculation was carried out by a semiempirical method and the expected results have not been established experimentally, it is necessary to validate the system of parameters used in the calculation.

PARAMETER PROBLEM

The CNDO method has been used for studying electronic spectra in [2-6]. In [3], calculations were carried out taking into account singly and doubly excited configurations to study the role of σ electrons in the spectra of planar unsaturated molecules. The authors used the unchanged parameters of the CNDO/2 method [7], considering them to be optimal since the method of [7] gives satisfactory dipole moment values for the ground state of the molecules.

It should be noted that, in contrast to the energies of single-electron states, the wave functions depend only slightly on the variation of the parameters within reasonable limits. The CNDO parameters, therefore, should be chosen first of all so as to reproduce the correct sequence of these states, as obtained in nonempirical calculations, and also the experimental photoionization data. It can be seen from Table 1 that the parameters of [7] are completely unsuitable for calculating the ground state of the benzene molecule.* The difference between the calculated and measured ionization potential (Table 1) is about 50% of the value of the latter. The energies of the highest filled σ and π orbitals ($3e_{2g}$ and $1e_{1g}$) are found to be almost degenerate, which contradicts the results of calculations ab initio [8, 10, 11] and experiment [12]. In addition, the $1a_{2u}$ orbital appears to be more stable than four of the σ orbitals, whereas in nonempirical calculations [10, 11], it follows right after the $3e_{2g}$ orbital. It is no wonder that calculation of the spectrum with the parameters of [7] gives absurd results (Table 2). Two of the $\sigma\pi^*$ and $\pi\sigma^*$ states ($^1A_{2u}$ and $^1A_{2u}$) appear to be lower than the $^1B_{2u}$ state. When applied to other planar unsaturated molecules, the parameters of [7] also give greatly overestimated ionization potentials and incorrect ratios between the energies of the π and σ molecular orbitals.

We have calculated the molecules C_2 , C_2H_2 , C_2H_4 , C_4H_6 , and C_6H_6 (Tables 2 and 3) by the CNDO method while varying the parameters β_A^0 and γ_{AB} (Table 4). In doing this, we used averaged atomic parameters I_μ and A_μ (ionization potential and electron affinity of the μ -th valence state) and the one-center coulombic integrals γ_{AA} proposed in [13]. The two-center coulombic integrals were varied according to the formula:

$$\gamma_{AB} = C_1 \gamma_{AB}^0 + C_2 \gamma_{AB}^{MN}, \quad C_2 + C_1 = 1,$$

*The problem of interpreting the first three ionization potentials in benzene can be regarded as solved [8,9].

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TABLE 1. Molecular Orbital Energies in Benzene, eV

Orbital	S-CNDO	[7]	[10]	[2]	[4]	Expt. [12]
$2a_{1g}$	-42,82	-51,4	-32,02	-31,18	-32	
$2e_{2u}$	-32,88	-27,8	-28,4	-24,81	-29,6	
$2e_{2g}$	-25,22	-30,2	-23,0	-20,10	-25,23	
$3a_{1g}$	-22,91	-29,0	-20,2	-19,64	-21,07	
$2b_{1u}$	-17,78	-21,5	-18,31	-14,26	-21,87	
$1b_{2u}$	-16,81	-19,46	-17,93	-13,81	-16,8	
$3e_{1u}$	-15,61	-18,92	-16,03	-12,99	-18,7	
$1a_{2u}(\pi)$	-13,31	-23,61	-14,65	-15,15	-18,1	12,2
$3e_{2g}$	-12,57	-13,96	-14,30	-9,79	-15,23	11,49
$1e_{1g}(\pi)$	-10,31	-13,95	-10,31	-9,4	-13,3	9,25

TABLE 2. Energies of the Excited States of Benzene, eV

State	S-CNDO	[7]	[2]	[3] ^a	Expt. [20]
$^3B_{1u}$	3,43	8,29	3,66	7,26	3,66
$^3E_{1u}$	4,47	9,18	8,18	9,10	4,5-4,7
$1,3B_{2u}(\pi\pi^*)$	4,97	10,07	5,50	10,15	4,72
$1B_{1u}(\pi\pi^*)$	5,91	10,26	5,88	10,37	6,2
$1E_{1u}$	7,40 (1,2)	14,14	10,72	12,44	7,05 (0,7)
$1A_{2u}(\sigma\pi^*)$	5,82 (0,002)	9,8	5,5	—	—
$1,1A_{2u}(\pi\sigma^*)$	9,11 (0,06)	—	8,3	—	—

^aCalculation by the method of [21] taking into account CI (configuration interaction) for single excitation.

TABLE 3. Energies of Single-Electron States in Ethylene, eV

Orbital	S-CNDO	[7]	[8]	[17]	[2]	Expt. [13]
$2a_g$	-33,06	-39,06	-25,43	-28,1	-26,01	
$2b_{3u}$	-25,68	-27,49	-19,14	-21,71	-19,48	
$1b_{2u}$	-21,16	-25,11	14,73	-17,58	-17,15	
$3a_g$	-16,40	-19,15	-11,63	-15,91	-13,01	14,39
$1b_{1g}$	-13,79	-15,82	-11,10	-13,77	-10,98	12,5
$1b_{1u}(\pi)$	-11,84	-16,6	-10,30	-10,0	-10,93	10,5

The axes were chosen in accordance with [2]; $R_{CC} = 1.34 \text{ \AA}$; $R_{CH} = 1.07 \text{ \AA}$.

where the superscripts indicate the approximations of Ohno and Mataga-Nishimoto [14, 15]. The results were compared with accurate calculations of this series of molecules in a Gaussian basis [8, 16, 17]. Increasing the resonance parameter β_C^0 to -10 eV proved to improve the numerical MO values (they became closer to the MO values obtained in the accurate calculations), but did not lead to a correct ratio between the energies of the π and σ orbitals. Comparison of the MO energies (see Tables 2 and 3) shows that the energy diagrams obtained in [8, 16, 17] cannot be reproduced without introducing different parameters β_C^0 for the π and σ atomic orbitals. We selected the following values: $\beta_C^0(\pi) = -10 \text{ eV}$ and $\beta_C^0(\sigma) = -15 \text{ eV}$, which led to qualitatively correct ratios between the energies of the π and σ molecular orbitals. Variation of the coefficients c_1 and c_2 did not lead to any preferential recommendations, and we subsequently used the values $c_1 = 0.79$ and $c_2 = 0.21$.

TABLE 4. Parameter Systems in the CNDO Method for Carbon and Hydrogen Atoms, eV

Parameter	[7]		[5]		[13,18]*		[2]	
	H	C	H	C	H	C	H	C
β_A^0	-9	-21	-12	-17	-5,4	-8,2	-9	-11,15
V_{AA}	20,4	16,06	12,85	11,11	12,85	10,33	20,4	16,06
$I+A$	7,18	14,05	7,18	14,05	7,18	14,96	7,18	10,89
$\frac{I+A}{2}$ $\left\{ \begin{array}{l} s \\ p \end{array} \right.$	—	5,57	—	5,57	—	5,60	—	—

* Approximation of γ_{AB} according to the formula from [15].

TABLE 5. Energies of the Excited States of Ethylene and Formaldehyde, eV

State	Ethylene		State	Formaldehyde	
	S-CNDO	[22, 20]		S-CNDO	[20]
$^3B_{3u}(\pi\pi^*)$	4,44	4,6	$^1A_2(\pi\pi^*)$	3,58	3,5
$^1B_{3g}(\sigma\pi^*)$	6,95	6,4	$^3A_1(\pi\pi^*)$	5,84	—
$^1B_{3u}(\pi\pi^*)$	7,24	7,6	$^1A_1(\pi\pi^*)$	10,4	—

The $^1A_{1g} \rightarrow ^1B_{3g}$ transition is forbidden.

The system of parameters obtained by us differed little from that used in [8] to obtain electronic absorption spectra. We therefore carried out subsequent calculations using the parameters from [8] while retaining the two-center approximations for γ_{AB} . We will call this system of parameters the spectroscopic system (S-CNDO). As can be seen from Table 1, calculation of benzene by the S-CNDO method gives the correct sequence of single-electron energies and is in good agreement with photoionization results [11].* We regard this fact as being most important for validating the reliability of the results of excited-state calculations.

A different approach was used in [2], where the parameters were selected so as to adjust the energy of the $^1A_{1g} \rightarrow ^3B_{1u}$ transition and the ionization potential of the benzene molecule to their experimental values. It can be seen from Tables 1 and 3 that the parameters used in [2] lead to almost degenerate π and σ molecular orbitals in benzene and ethylene; in addition, the sequence of levels in benzene is incorrect. This reduces the value of the results of [2] in relation to the excited states. The necessity of introducing different values of $\beta^0(\pi)$ and $\beta^0(\sigma)$ is also evident in the case of the parameters adopted in [13, 18] (see Tables 1 and 3). Sischel and Whitehead [13] obtained good results for the heats of atomization and MO energies of a wide class of nonplanar molecules, but for systems in which a clear division into π and σ electrons can be made, much worse results are obtained. Theoretical bases for separating π and σ parameters are given in [9]. Thus, we can say that the best agreement both with accurate calculations and with experimental data is obtained when spectroscopic parametrization is used (see Tables 1 and 3).

EXCITED STATES

The results of calculating a series of planar molecules are given in [6]. On the basis of these, the configuration interaction (CI) was calculated taking into account only single excitations. We will discuss the results for the example of the benzene molecule (see Table 1). The majority of authors [3-5] have not given data on the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ transitions in benzene. We have considered all transitions lying below the ionization potential and have calculated their intensities. Since the $\sigma\sigma^*$ and $\pi\pi^*$ configurations

* The Kumpens theorem was shown in [9] to be valid for the first two ionization potentials of the benzene molecule.

do not interact with the $\pi\sigma^*$ and $\sigma\pi^*$ configurations, the CI matrix breaks down into blocks. In the calculation for the $\pi\pi^*$ states in benzene, only the $e_{1g} \rightarrow e_{1u}$ configurations were taken into account. No $\sigma\sigma^*$ excitations were included in the calculation. The moment of the $\sigma \rightarrow \pi^*$ ($\pi \rightarrow \sigma^*$) transition was estimated from the formula

$$q_{\sigma \rightarrow \pi^*} = 3a_0 \sqrt{2} \sum_A c_{2s,\sigma}^A c_{2p,\pi^*}^A Z_A^{-1},$$

$$q_{\pi \rightarrow \sigma^*} = 3a_0 \sqrt{2} \sum_A c_{2p,\pi}^A c_{2s,\sigma^*}^A Z_A^{-1},$$

where $a_0 = 0.529 \text{ \AA}$, Z_A is the effective nuclear charge of atom A, and $c_{2s,\sigma}^A$ is the coefficient of the 2s orbital of atom A in molecular orbital σ . The overall moment of the transition from the ground state (${}^1A_{1g}$) to an excited state X ($\sigma\pi^*$ - or $\pi\sigma^*$ -type), taking into account the different configurations, is written in the form

$$Q_{A_{1g} \rightarrow X} = \sum_{\sigma \rightarrow \pi^*} K_{\sigma \rightarrow \pi^*, X} q_{\sigma \rightarrow \pi^*} + \sum_{\pi \rightarrow \sigma^*} K_{\pi \rightarrow \sigma^*, X} q_{\pi \rightarrow \sigma^*},$$

where K are the expansion coefficients of the eigenvectors of the CI matrix. The transitions determined in this way are polarized perpendicular to the plane of the molecule. Only the allowed $\pi\sigma^*$ ($\sigma\pi^*$) states are given in Table 2.

As can be seen from the calculation data, between the $\pi\pi^*$ states ${}^1B_{2u}$ and ${}^1B_{1u}$ (see Table 2), there is a $\sigma\pi^*$ ($\pi\sigma^*$) state in which transition is weakly allowed. We consider that, to the extent that semi-empirical calculations are suitable for the interpretation of spectra at all, this result is well founded, since the ratios between the π and σ molecular orbitals participating in these transitions are completely reliable.

In the CNDO method, it is usual to disregard the exchange integrals between the atomic orbitals on one center, which leads to the degeneration of singlet and triplet states of the type $\sigma\pi^*$ ($\pi\sigma^*$). Estimates of the exchange integrals for several $\sigma \rightarrow \pi^*$ transitions according to the method of [21] show that the error involved in determining the energy of the singlet $\sigma\pi^*$ states does not exceed 0.3 eV. The presence of weak $\sigma \rightarrow \pi^*$ transitions located near the first $\pi \rightarrow \pi^*$ absorption band is also characteristic of the other molecules that we have calculated (see Tables 2, 3, and 5). The first long-wavelength $\sigma \rightarrow \pi^*$ transition is always of low intensity compared with the other $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions. This is connected with the fact that the σ orbital in planar hydrocarbon molecules has a small contribution of 2s atomic orbitals (the percentage content of 2s atomic orbitals in the $3e_{2g}$ MO in benzene is 0.3%; in the $7a_g$ MO in trans-butadiene it is 1.8%; and in the $3a_g$ MO in ethylene it is 0.7%). In the benzene molecule, transitions from the ground state to the ${}^1B_{2u}$ and ${}^1B_{1u}$ states are forbidden, but they are allowed on account of e_{2g} vibrations of the benzene ring [20]. The transition to the ${}^1A_{2u}$ state (see Table 2) is weakly allowed and does not have additional effective intensity sources due to vibrations.

In the absorption spectrum of benzene, besides the well studied system of bands at 2600 Å corresponding to the ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition (O-O band with an energy of 4.72 eV), there is intense absorption in the 2000 Å region (maximum at 6.2 eV) [20]. This is usually ascribed to a transition to the ${}^1B_{1u}$ state. According to our calculation, it can be supposed that the weak $\sigma \rightarrow \pi^*$ band (A_{2u}) is overlapped by this absorption.

The presence in olefins of $\sigma \rightarrow \pi^*$ bands related to the $n - \pi^*$ bands of the isoelectronic ketones was first noted by Berry, who assumed that the weak absorption of ethylene in the 6 eV region was connected with a $\sigma \rightarrow \pi^*$ transition [22]. Calculation of the excited states of the ethylene and formaldehyde molecules (see Tables 3 and 5) for the equilibrium configurations by the S-CNDO/2 CI method confirms Berry's hypothesis. We obtained the following sequence of singlet states for the trans-butadiene molecule: 1B_u ($\pi\pi$) 5.82 eV; 1A_u ($\sigma\pi^*$) 6.73 eV; and 1A_g ($\pi\pi^*$) 7.81 eV, the dipolar transition to the 1A_u state being forbidden. A nonempirical calculation [16] taking into account only the singly excited configurations gives the same sequence of levels. Taking multiple excitation into account lowers the energy of the 1A_g state but does not alter the qualitative conclusion that the energy of the $\sigma \rightarrow \pi^*$ transition is very low [16].

Thus, from a calculation of the ethylene, formaldehyde, butadiene, and benzene molecules, we can assume that the $\sigma\pi^*$ states must have considerably lower energy than has been supposed previously [20]. Careful experimental investigations into the polarization of the absorption bands will be necessary to check this assumption.

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