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Electronic Spectra and Structures of Organic π-Systems

I. SCFMO Calculations of Heterocyclic Systems with the Variable Integrals Method I

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Semiempirical SCFMO calculations have been carried out on heterocyclic π-systems such as benzoxazole, benzotriazole, γ-pyrone, pyridonimine, pyridonemethide, benzothiazole and so on. A new modification of the Wolfsberg-Helmholz formula has been introduced in the evaluation of the core resonance integrals. The calculated transition energies are in good agreement with the experimental data.

Introduction

Though there have been many Pariser-Parr-Pople (PPP) type SCF calculations of π-systems, it is rather difficult to find a single consistent set of parameters suitable to the prediction of electronic spectra of a large number of different types of molecules without consulting the results for other similar molecules or electronic spectra of the molecules in question.

In the course of studies to solve this problem, we have found that the following method gives satisfactory resulta for a wide range of compounds though it contains only one arbitrary molecular parameter.

Method of Calculation

The method used in this study is a semiempirical SCFMO CI method for π-systems.

a) The ZDO approximation is used.

b) The one-centre Coulomb integral, W_p, is put equal to $-I_p$ where I_p is the first or the second ionization potential of the p_π-atomic orbital.

c) The one-centre Coulomb repulsion integral, γ_{pp}, is reevaluated according to the next formula in the first five iteration steps of the SCF procedures as in the VESCF method [1].

$$\gamma_{pp} = z\alpha_p \tag{1}$$

where α_p is constant and evaluated using an appropriate electron transfer reaction.

d) The two-centre Coulomb repulsion integral, γ_{pq}, is reevaluated by the parabolic formula (2) when the interatomic distance R is shorter than $4A$.

$$\gamma_{pq} = 0.5\,(\gamma_{pp} + \gamma_{qq}) + AR^2 + BR \tag{2}$$

Table 1. W_p *and* α_p *values*

	W_p(eV)	α_p		W_p(eV)	α_p
C^+	−11.16	3.8379	S^{++}	−22.91	2.1761
N^+	−14.12	3.4761	O^+	−17.28	3.6357
N^{++}	−28.71	4.2949	O^{++}	−34.15	4.2945

where A and B are constant and evaluated using γ_{pq}'s calculated at distances $R=4A$ and $5A$ by the point charge approximation. When R is longer than $4A$, γ_{pq} is evaluated by the point charge approximation.

e) The core resonance integral, β_{pq}, is reevaluated in the first five iteration steps of the SCF procedure by the following modified Wolfsberg-Helmholz type of formula:

$$\beta_{pq} = kS_{pq}(W'_p + W'_q)/2 \tag{3}$$

where

$$W'_p = W_p + (P_{pp} - 1)\gamma_{pp} \tag{4}$$

and P_{pp} is the π-electron charge density of the atomic orbital p. This formula (3) can be easily derived with the help of the ZDO approximation. Here an arbitrary parameter k is adjusted to reproduce the longest wavelength observed transition energy of benzene and found to be 0.8676 [7]. All the non-nearest neighbour β_{pq}'s are neglected.

f) For the sake of simplicity the penetration integrals are neglected.

g) All the variable integrals are reevaluated only in the first five iteration steps of the SCF procedure.

h) All the singly excited configurations are taken into account in the configuration interaction.

For convenience, this set of approximation is designated as the variable integrals method I (VI/1).

In Table 1 the values of W_p and α_p used in this calculation are summarized. These were estimated from the atomic spectral data listed in Ref. [2] and [3].

The bond lengths and bond angles of the molecules treated in this study are estimated from the structural data of similar compounds collected in Ref. [4] and [5].

Results and Discussion

In order to examine the applicability of the VI/1 method, this method has been applied to various types of organic π-systems. We have consequently found that this method is extremely useful for all kinds of π-systems. As the example, the calculated transition energies of heterocyclic systems are shown in Table 2.

As is seen in Table 2, the agreement between theory and experiment is satisfactory on the whole, and especially quite excellent in case of benzofuran, benzoxazole, indoxazene, anthranil, indazole, dibenzofuran, quinoline, isoquinoline, γ-pyrone, thiazole, benzothiazole and 1,3-dithiolium ion. Of those

Table 2. *Calculated singlet-singlet transition energies, E(eV), and oscillator strengths, f*

	E(eV)	f(logε)	E(eV)	f(logε)	E(eV)	f(logε)	E(eV)	f(logε)	Ref.
Benzofuran									
calc.	4.613	0.003	5.144	0.173	6.166	0.439	6.755	0.150	
obs.	4.59	(3.3)	5.17	(4.2)	6.02	(4.4)			[9, 10]
Benzoxazole									
calc.	4.641	0.018	5.187	0.137	5.857	0.259	6.289	0.023	
obs.	4.5	(3.6)	5.4	(4.0)					[11]
Indoxazene									
calc.	4.452	0.058	4.940	0.234	6.039	0.286	6.325	0.147	
obs.	4.43		5.06						[12]
Anthranil									
calc.	3.896	0.323	4.645	0.064	5.204	0.001	5.987	0.078	
obs.	4.04	(3.6)							[13]
Indazole									
calc.	4.330	0.096	4.801	0.173	5.875	0.079	6.091	0.545	
obs.	4.3	(3.6)	4.96	(3.6)					[14]
1H-Benzotriazole									
calc.	4.246	0.144	4.566	0.205	5.577	0.096	5.689	0.253	
obs.	4.51^{sh}	(3.7)	4.77	(3.75)					[15]
Dibenzofuran									
calc.	4.481	0.004	4.812	0.042	4.949	0.192	5.714	0.026	
obs.	4.43	(4.2)	5.06	(4.0)	5.64	(4.3)			[9]
Quinoline									
calc.	4.113	0.066	4.390	0.188	5.621	0.026	5.778	0.293	
obs.	4.0	(3.6)	4.43	(3.5)					[16]
Isoquinoline									
calc.	4.016	0.074	4.535	0.104	5.634	0.063	5.992	0.107	
obs.	3.87	(3.4)	4.59	(3.5)	5.77	(4.7)			[17]
γ-Pyrone									
calc.	4.982	0.495	5.045	0.019	5.423	0.126	7.082	0.368	
obs.	4.96	(4.1)							[18]
1-Methyl-2-pyridonemethide									
calc.	3.225	0.118	4.809	0.512	6.134	0.220	6.410	0.229	
obs.	3.0	(3.2)	4.5	(3.3)					[19]
1-Methyl-2-pyridonimine									
calc.	3.619	0.158	4.693	0.407	5.927	0.095	6.487	0.278	
obs.	3.5	(3.5)							[19]
Thiazole									
calc.	5.284	0.215	5.705	0.082	7.394	0.565	7.496	0.698	
obs.	5.34		5.93						[20]
Benzothiazole									
calc.	4.608	0.015	5.097	0.164	5.880	0.305	5.959	0.184	
obs.	4.43	(3.27)	4.96	(3.70)	5.73	(4.20)	6.25	(4.36)	[20]
1,3-Dithiolium ion									
calc.	4.860	0.305	5.982	0.035	7.493	1.353	8.395	0.281	
obs.	4.86	(3.58)	5.8	(3.53)					[21]

no SCFMO treatments of benzoxazole, benzotriazole, γ-pyrone, pyridonimine, pyridonemethide and benzothiazole have been reported so far. And for indoxazene [6], anthranil [6], quinoline [7], isoquinoline [7] and thiazole [8], the calculated values by VI/1 method are far better than those by the other methods including PPP calculations.

VI/1 method has also been found to give quite satisfactory results for ethylene, formaldehyde, trans-butadiene, aniline, phenol, benzaldehyde, nitrosobenzene, benzoic acid, acetanilide, indole, quinolinium ion, isoquinolinium ion, quinolizium ion, tropone, tropolone, thiophenol, benzothiophene, dibenzothiophene and so on.

The arbitrary molecular parameter $k = 0.8676$ [7] which is evaluated based on the electronic spectrum of benzene might be used without changing its value throughout various types of bonds with satisfactory results.

The calculation has been carried out on a HITAC 5020 computer at the computation centre of the University of Tokyo.

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