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Electronic Spectra and Structures of Organic π-Systems

II. SCFMO Calculations of Five- and Six-Membered Heterocyclic Systems, Quinones, Tropone, Tropolone and Sulphur-Containing Systems with the Variable Integrals Methods*

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The variable integrals method II presented in the preceding paper, which needs no guess work in choosing a set of parameters to calculate the electronic spectra of molecules and contains no arbitrary adjusting parameters, is applied to various kinds of nitrogen- or oxygen-containing heteroatomic molecules in order to check the applicability of this method. At the same time the variable integrals method I, a simplified method of the variable integrals method II, is also applied to the same systems and some sulphur-containing molecules. The both methods give similar results and the agreement between theory and experiment is satisfactory.

Die in der vorangehenden Arbeit dargestellte „II. Methode variabler Integrale" benötigt zur Auswahl eines Parametersatzes zur Berechnung von Molekülspektren keine Abschätzungen oder willkürliche Parameteradjustierungen. Sie wird in der vorliegenden Arbeit auf eine Reihe von Stickstoff oder Sauerstoff enthaltenden Heterocyclen angewendet, um ihre Leistungsfähigkeit zu untersuchen. Die Ergebnisse sind mit denjenigen, die mit der ähnlichen „I. Methode variabler Integrale" gewonnen wurden, vergleichbar. Zusätzlich werden mit der letzteren Methode einige Schwefel enthaltene Heterozyklen behandelt. Die Übereinstimmung von Theorie und Experiment ist zufriedenstellend.

Introduction

In the preceding paper [1] we have proposed a new type of semiempirical PPP-type SCF method, the variable integrals method II, which needs no guess work in choosing a set of parameters to calculate the electronic spectra of molecules and contains no arbitrary adjusting parameters in itself. This method has been applied to several molecules with great success.

In this paper we will further apply this variable integrals method II and the variable integrals method I which is a simplified method of the variable integrals method II to various kinds of five- and six-membered heterocyclic systems, quinones, tropone and tropolone to check the applicability of these methods. The variable integrals method I is applied also to some sulphur-containing systems.

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Method of Calculation

The methods used in this study are the variable integrals methods I (VI/1) and II (VI/2/only NNβ). The details of these methods have been described in the preceding paper [1], therefore only a brief summary of the methods is given here.

The Variable Integrals Method I (VI/1)

a) The so called zero-differential overlaps approximation is used and all the overlap integrals between two different atomic orbitals are neglected.

b) 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. The W_p-value for sulphur atom is -22.91 eV consulting Ref. [2].

c) One-centre Coulomb repulsion integrals, $\gamma_{pp} \equiv \langle pp|pp\rangle$'s, are reevaluated according to the next formula in the first five iteration steps of SCF procedures:

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

where α is constant and evaluated using an appropriate electron transfer reaction. The α_p-value for sulphur atom is 2.1761 eV consulting Ref. [2].

d) The two-centre Coulomb repulsion integral, $\gamma_{pq} \equiv \langle pp|qq\rangle$, is reevaluated by the next formula when the interatomic distance is shorter than 4 Å:

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

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

When R is longer than 4 Å, γ_{pq} is evaluated by the point charge approximation.

e) Core resonance integral, β_{pq}, is reevaluated by the next formula:

$$\beta_{pq} = 0{,}86767\, S_{pq}(W'_p + W'_q)/2 \tag{3}$$

where

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

All the non-nearest neighbour β_{pq}'s are neglected.

f) For the sake of simplicity the penetration integrals are thoroughly neglected in the evaluation of the Hartree-Fock diagonal matrix elements.

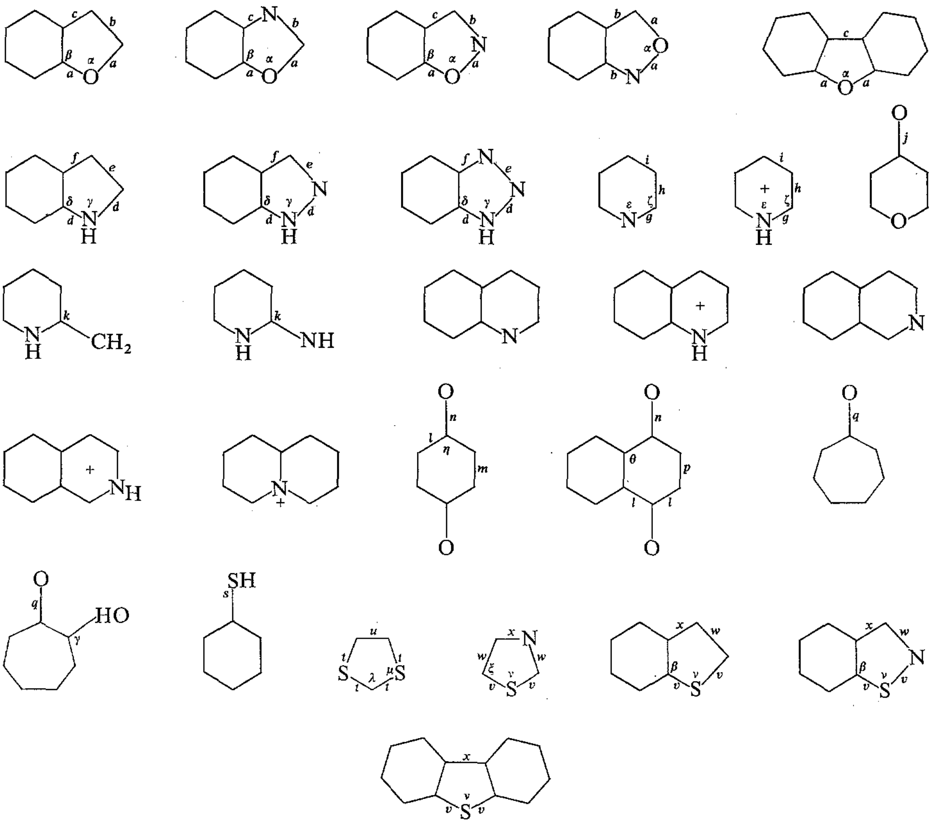
The Variable Integrals Method II (VI/2)

g) Core resonance integral, β, is reevaluated be the next formula in stead of the formula (3):

$$\begin{aligned}\beta_{pq} = \tfrac{1}{2}\{&SW'_p + SW'_q - S\langle\chi_p|U_q^{\text{core}}|\chi_p\rangle - S\langle\chi_q|U_p^{\text{core}}|\chi_q\rangle \\ &- \langle\chi_p|T|\chi_q\rangle - \langle\chi_q|T|\chi_p\rangle - S(P_{pp} + P_{qq} - 2)\gamma_{pq}\}\end{aligned} \tag{5}$$

where $\langle\chi_p|T|\chi_q\rangle$ and $\langle\chi_q|U_p^{\text{core}}|\chi_q\rangle$ are theoretically evaluated as described in the preceding paper [1].

In the other respects the VI/2 method is the same as the VI/1 method.



$a = 1.371$ Å
$b = 1.354$ Å
$c = 1.440$ Å
$d = 1.383$ Å
$e = 1.378$ Å
$f = 1.429$ Å

$g = 1.340$ Å
$h = 1.395$ Å
$i = 1.394$ Å
$j = 1.21$ Å
$k = 1.335$ Å
$l = 1.49$ Å

$m = 1.32$ Å
$n = 1.23$ Å
$p = 1.397$ Å
$q = 1.26$ Å
$r = 1.34$ Å
$s = 1.817$ Å

$t = 1.7$ Å
$u = 1.4$ Å
$v = 1.714$ Å
$w = 1.370$ Å
$x = 1.423$ Å

$\alpha = 106°$
$\beta = 111°$
$\gamma = 108.9°$
$\delta = 108°$
$\varepsilon = 116.8°$
$\zeta = 123.9°$

$\eta = 116°$
$\theta = 122°$
$\lambda = 120°$
$\mu = 91°$
$\nu = 92.2°$
$\xi = 111.5°$

Fig. 1. Assumed structures of molecules

For the sake of simplicity the variable integrals are reevaluated only in the first five iteration steps of SCF procedures. All the singly excited configurations are taken into account in the configuration interactions.

The bond lengths and bond angles of molecules are assumed as shown in Fig. 1 consulting Ref. [3] and [4]. The structures of the six-membered rings of pyridinium ion, 2-pyridonemethide and 2-pyridonimine are assumed as that of pyridine. All the other six-membered rings except for those in quinones are assumed to be regular hexagons ($R_{CC} = 1.397$ Å). The benzene ring of 1,4-naphthoquinone is also assumed as regular hexagon ($R_{CC} = 1.397$ Å). The heptagons of tropone and tropolone are assumed to be regular heptagons. The C–C bond lengths of tropone and tropolone are assumed to be 1.410 Å [5] and 1.39 Å [6] respectively.

Results and Discussions

The two methods give similar γ_{pq}- and β_{pq}-values on the whole. The $\beta_{O_1C_2}$ and $\beta_{O_1C_9}$ of benzofuran, the β_{OC} of dibenzofuran, the $\beta_{N_1C_2}$ and $\beta_{N_1C_9}$ of indole evaluated in the VI/2 method are -1.829 eV, -1.828 eV, -1.816 eV, -2.041 eV and -2.042 eV respectively. These values are quite similar to those empirically adjusted by Billingsley and Bloor [39] to reproduce well the observed electronic transitions of these molecules ($\beta_{CO} = \beta_{CN} = -1.80$ eV). The β_{CS}-value of thiophenol given by the VI/1 method is -1.488 eV and similar to that empirically adjusted β_{CS}-value -1.66 eV by Nagakura and Kimura [28] in the molecules in molecules method.

The SCF eigenvalues and eigenvectors given by the two methods are similar to each other. The π-electron densities and bond orders given by the two methods are also similar to each other.

The calculated transition energies are summarized in Table 1 with the observed ones. In the cases of nitrogen- or oxygen-containing systems two methods give similar transition energies and the agreement between theory and experiment is satisfactory on the whole, and quite excellent in the cases of benzofuran, benzoxazole, indoxazene, anthranil, indazole, dibenzofuran, quinoline, isoquinoline and γ-pyrone. It seems that no SCFMO treatments of benzoxazole, benzotriazole, γ-pyrone, pyridonimine and pyridonemethide have been reported.

Indoxazene and anthranil were treated by Berthier and Del Re [40] by the Pariser-Parr-Pople method using empirical formula for core resonance integrals. The results given by the VI methods are by far better than theirs. Fischer-Hjalmars and Sundborn [41] have recently treated quinoline and isoquinoline with their modified PPP method. The results given by the VI methods are better than theirs. Peacock [42] treated quinolizium ion with the PPP method using empirical β-values, but the calculated transition energies are unsatisfactory. Recently Galasso [43] also has treated quinolizium ion with the PPP method using empirical β's. The VI/2 method gives by far better result than their calculations. Sidman [32] treated p-benzoquinone with the PP method using empirically chosen β-values as suggested by Pariser and Parr, but the calculated transition energies were too larger than the observed ones. Nishimoto and Forster [29] treated p-benzoquinone with their variable β method recently. The result given by the VI/2 method is better than theirs.

There have been some confusions concerning the assignment of the first band of the absorption spectrum of tropone around 300 mμ. Hosoya and coworkers [25, 26] consider that this band is composed of one $\pi-\pi^*$ ($^1A_1-{}^1B_2$) transition based on the molecules in molecules method [26] and the PPP calculation [25]. On the other hand Weltin *et al.* [24] established that the 300 mμ band is composed of two different $\pi-\pi^*$ electronic transitions ($^1A_1-{}^1B_2$ and $^1A_1-{}^1A_1$) by measuring the absorption spectrum under electric field. The PPP calculation by them agreed with their observation. Julg *et al.* [34] carried out a calculation by their MO method and suggested that the 300 mμ band is composed of two $\pi-\pi^*$ transitions. Inuzuka *et al.* [35] and Kuroda *et al.* [36] also obtained similar results by PPP type SCF calculations. Yamaguchi *et al.* [23] also carried out a PP type calculation and based on this calculation and the experiment of

Table 1. *Calculated $^1\pi - {}^1\pi^*$ electronic transitions in eV*

	VI/1		VI/2		Obs.		
	E	*f*	*E*	*f*	*E*	log ε	Ref.
Benzofuran							
	4.613	0.003	4.593	0.003	4.59	3.3	[7]
	5.144	0.173	5.153	0.149	5.17	4.2	
	6.166	0.439	6.188	0.471	6.02	4.4	[38]
	6.755	0.150	6.778	0.191			
Indole							
	4.524	0.009	4.514	0.008	4.28	3.6	[7]
	4.986	0.135	5.009	0.133	4.71	3.8	
	6.106	0.449	6.092	0.464	5.79	4.4	
	6.513	0.280	6.456	0.283	6.45		[37]
Benzoxazole							
	4.641	0.018	4.604	0.017	4.5	3.6	[8][b]
	5.187	0.137	5.146	0.146	5.4	4.0	
	5.857	0.259	5.848	0.233			
	6.289	0.023	6.358	0.043			
	6.656	0.230	6.634	0.258			
Indoxazene							
	4.452	0.058	4.445	0.049	4.43		[9]
	4.940	0.234	4.989	0.183	5.06		
	6.039	0.286	6.060	0.352			
	6.325	0.147	6.305	0.095			
	6.758	0.538	6.729	0.586			
Anthranil							
	3.896	0.323	3.851	0.321	4.04	3.6	[10]
	4.645	0.064	4.655	0.053			
	5.204	0.001	5.253	0.002			
	5.987	0.078	5.933	0.075			
	6.496	0.898	6.495	0.778			
Indazole							
	4.330	0.096	4.317	0.081	4.3	3.6	[11]
	4.801	0.173	4.847	0.149	4.96	3.6	
	5.875	0.079	5.795	0.054			
	6.091	0.545	6.038	0.577			
	6.654	0.396	6.645	0.478			
1H-Benzotriazole							
	4.246	0.144	4.125	0.143	4.51^{sh}	3.7	[12]
	4.566	0.205	4.503	0.208	4.77	3.75	
	5.577	0.096	5.399	0.139			
	5.689	0.253	5.630	0.147			
	6.151	0.064	6.036	0.058			
Dibenzofuran							
	$^1A_1$ 4.481	0.004	$^1A_1$ 4.474	0.003	4.43	4.2	[7]
	$^1B_2$ 4.812	0.042	$^1B_2$ 4.796	0.029	5.06	4.0	
	$^1B_2$ 4.949	0.192	$^1B_2$ 4.947	0.226			
	$^1A_1$ 5.714	0.026	$^1A_1$ 5.734	0.024	5.64	4.3	

Table 1 (continued)

VI/1		VI/2		Obs.		
E	f	E	f	E	log ε	Ref.
Pyridine						
$^1B_2$ 4.820	0.070	$^1B_2$ 4.818	0.065	4.79	(0.04)[a]	[13]
$^1A_1$ 5.739	0.009	$^1A_1$ 5.744	0.000	6.10	(0.10)[a]	
$^1B_2$ 7.340	0.999	$^1B_2$ 7.365	1.040	7.04	(1.30)[a]	
$^1A_1$ 7.458	1.264	$^1A_1$ 7.383	1.239			
$^1A_1$ 8.384	0.002	$^1B_2$ 8.528	0.011			
Pyridinium ion						
$^1B_2$ 5.218	0.164	$^1B_2$ 4.772	0.169	4.83		[14]
$^1A_1$ 6.065	0.0002	$^1A_1$ 5.637	0.008	5.50		
$^1A_1$ 7.743	1.167	$^1A_1$ 7.384	1.120			
$^1B_2$ 7.852	0.856	$^1B_2$ 7.445	0.739			
$^1B_2$ 9.393	0.034	$^1B_2$ 8.838	0.042			
Quinoline						
4.113	0.066	4.027	0.061	4.0	3.6	[15]
4.390	0.188	4.358	0.167	4.43	3.5	
5.621	0.026	5.593	0.023			
5.778	0.293	5.675	0.293			
6.192	0.108	6.125	0.049			
Quinolinium ion						
3.777	0.109	3.521	0.104	4.01	3.9	[16]
4.226	0.112	3.965	0.167			
5.663	0.638	5.423	0.455	5.28	4.5	
5.968	0.017	5.618	0.062			
6.118	0.207	5.909	0.142			
Isoquinoline						
4.016	0.074	3.956	0.068	3.87	3.4	[17]
4.535	0.104	4.473	0.101	4.59	3.5	
5.634	0.063	5.540	0.050	5.77	4.7	
5.992	0.107	5.900	0.049			
6.275	1.294	6.172	1.253			
Isoquinolinium ion						
3.565	0.174	3.265	0.173	3.7	3.7	[16]
4.278	0.009	4.081	0.006	4.59	3.3	
5.565	0.047	5.163	0.032	5.2	4.6	
5.909	0.364	5.643	0.367			
6.299	1.033	6.097	0.693			
Quinolizium ion						
$^1B_2$ 3.934	0.224	$^1B_2$ 3.550	0.236	3.85	4.23	[18]
$^1A_1$ 4.524	0.085	$^1A_1$ 4.314	0.039	4.35	3.47	
$^1B_2$ 5.838	0.002	$^1B_2$ 5.636	0.009	5.51	4.25	
$^1A_1$ 6.084	0.481	$^1A_1$ 5.708	0.511			
$^1B_2$ 6.534	1.323	$^1B_2$ 6.346	0.846			

Table 1 (continued)

VI/1		VI/2		Obs.		
E	f	E	f	E	log ε	Ref.
γ-Pyrone						
$^1A_1$ 4.982	0.495	$^1B_2$ 5.104	0.030	4.96	4.1	[19]
$^1B_2$ 5.045	0.019	$^1A_1$ 5.134	0.425			
$^1B_2$ 5.423	0.126	$^1B_2$ 5.513	0.095			
$^1A_1$ 7.082	0.368	$^1A_1$ 7.314	0.964			
$^1A_1$ 7.746	1.037	$^1A_1$ 7.688	0.483			
1-Methyl-2-pyridonemethide						
3.225	0.118	3.409	0.154	3.0	3.2	[20]
4.809	0.512	5.057	0.369	4.5	3.3	
6.134	0.220	6.279	0.216			
6.410	0.229	6.483	0.422			
7.134	0.531	7.197	0.568			
1-Methyl-2-pyridonimine						
3.619	0.158	3.838	0.216	3.5	3.5	[20]
4.693	0.407	4.975	0.323			
5.927	0.095	6.124	0.115			
6.487	0.278	6.517	0.494			
7.386	0.191	7.430	0.383			
p-Benzoquinone						
$^1B_{3g}$ 4.082	0.0	$^1B_{3g}$ 4.589	0.0	4.41	2.60	[21]
$^1B_{1u}$ 4.971	1.110	$^1B_{1u}$ 5.305	0.988	5.12	4.39	
^1A_g 6.769	0.0	$^1B_{3g}$ 7.086	0.0			
$^1B_{3g}$ 6.854	0.0	^1A_g 7.127	0.0			
^1A_g 7.415	0.0	^1A_g 7.379	0.0			
1,4-Naphthoquinone						
$^1B_2$ 3.936	0.003	$^1B_2$ 4.262	0.002	3.76	3.4	[22]
$^1A_1$ 4.214	0.114	$^1A_1$ 4.320	0.079			
$^1B_2$ 4.831	0.781	$^1B_2$ 5.033	0.619	5.06	4.4	
$^1A_1$ 5.626	0.289	$^1A_1$ 5.631	0.302			
$^1B_2$ 6.022	0.071	$^1B_2$ 5.994	0.132			
$^1A_1$ 6.721	0.061	$^1A_1$ 6.747	0.096			
Tropone						
$^1B_2$ 3.193	0.069	$^1B_2$ 3.308	0.092	3.5	(0.13)[a]	[24]
$^1A_1$ 3.982	0.229	$^1A_1$ 3.963	0.172	4.0		
$^1B_2$ 5.708	0.0001	$^1B_2$ 5.722	0.003	5.5	(0.37)[a]	[24]
$^1A_1$ 5.966	0.713	$^1A_1$ 6.162	1.173			
$^1B_2$ 7.101	1.025	$^1B_2$ 6.928	0.800	6.9	(0.1)[a]	[25]
Tropolone						
3.279	0.079	3.387	0.107	3.4		[26,27]
3.880	0.240	3.938	0.193	3.9		
5.594	0.009	5.716	0.028	5.3		
5.889	0.568	6.203	1.086			
6.904	1.018	6.875	0.587			

Table 1 (continued)

VI/1		VI/2		Obs.		
E	*f*	*E*	*f*	*E*	log ε	Ref.
Thiophenol						
$^1B_2$ 4.751	0.006			4.58	(0.013)[a]	[28]
$^1A_1$ 5.487	0.038			5.30	(0.347)[a]	
$^1A_1$ 6.844	1.022			6.22	(0.398)[a]	
$^1B_2$ 7.020	0.937			6.79	(0.587)[a]	
$^1A_1$ 7.782	0.267			(7.30)	(0.438)[a]	
$^1B_2$ 8.008	0.256					
$^1A_1$ 8.574	0.002					
Benzothiophene						
4.530	0.014			4.30	3.2	[7]
5.025	0.171			4.82	3.8	
6.008	0.594			5.46	4.4	
6.365	0.405					
6.843	0.152					
Dibenzothiophene						
$^1B_2$ 4.373	0.018			3.90	3.3	[7]
$^1A_1$ 4.809	0.061			4.43	3.8	
$^1A_1$ 4.918	0.085			4.86	4.1	
$^1A_1$ 5.655	0.001			5.30	4.7	
$^1B_2$ 5.980	2.092					
$^1A_1$ 6.451	0.813					
Thiazole						
5.284	0.215			5.34		[30]
5.705	0.082			5.93		
7.394	0.565					
7.496	0.698					
Benzothiazole						
4.608	0.015			4.43	3.27	[30]
5.097	0.164			4.96	3.70	
5.880	0.305			5.73	4.20	
5.959	0.184			6.25	4.36	
6.701	0.331					
6.933	1.038					
1,3-Dithiolium ion						
$^1A_1$ 4.860	0.305			4.86	3.58	[31]
$^1B_2$ 5.982	0.035			5.8	3.53	
$^1B_2$ 7.493	1.353					
$^1A_1$ 8.395	0.281					

[a] Oscillator strength, *f*.

[b] 2-Methylbenzoxazole.

the solvent effect and the oxime effect concluded that the 300 mμ band is composed of two $\pi - \pi^*$ transitions. The VI/2 and the VI/1 calculations in this study are also consistent with Weltin and coworkers' observation.

In the case of tropolone the calculated transition energies are in adequate agreement with experiment. Hosoya *et al.* [26] interpreted the 320 mμ band of tropolone as the intramolecular charge-transfer band associated with the electron transfer from the hydroxyl group to the tropolone system. However from the CI coefficients the second longest wavelength transition of tropolone is mainly associated with the local transition in the tropone group. This is suggested also by Kuroda and coworker [36] based on the variable β method.

The calculated transition energies for sulphur-containing systems by the VI/1 method are in adequate agreement with experiment, especially excellent in the cases of thiazole, benzothiazole and 1,3-dithiolium ion. Bouscasse, Vincent and Metzger [44] treated thiazole with the PPP method evaluating core resonance integrals with Kon's formula. The results given by the VI method seem to be by far improved than theirs. It seems there have been no SCFMO treatments of benzothiazole.

The π-electron ionization potentials given in Table 2 have been calculated from the expressions [1].

$$\text{VI/1}: \ I.P. = -\varepsilon_{\text{H.O.}} - 1.141\,, \tag{6}$$

$$\text{VI/2}: \ I.P. = -\varepsilon_{\text{H.O.}} - 1.109 \tag{7}$$

Table 2. *Calculated π-ionization potentials in eV*

	Calc.		Obs.	
	VI/1	VI/2	Electron-impact [45]	Photo-ionization [29]
Benzofuran	8.707	8.782		
Indole	8.328	8.440		
Benzoxazole	8.972	8.996		
Indoxazene	9.237	9.323		
Anthranil	8.323	8.334		
Indazole	8.703	8.816		
1H-Benzotriazole	8.976	9.077		
Dibenzofuran	8.613	8.647		
Pyridine	9.715	9.648	9.70	9.40
Pyridinium ion	16.704	16.582		
Quinoline	8.687	8.693		8.30
Quinolinium ion	14.242	14.267		
Isoquinoline	8.531	8.504		
Isoquinolinium ion	13.780	13.790		
Quinolizium ion	14.205	14.111		
γ-Pyrone	9.278	9.479		
2-Pyridonemethide	7.231	7.446		
2-Pyridonimine	8.147	8.368		
p-Benzoquinone	10.501	9.757		9.68
1,4-Naphthoquinone	10.021	10.126		
Tropone	8.528	8.611		
Tropolone	8.364	8.439		
Thiophenol	8.747			
Benzothiophene	8.277			
Dibenzothiophene	8.360			
Thiazole	8.868			
Benzothiazole	8.594			
1,3-Dithiolium ion	15.080			

where $\varepsilon_{H.O.}$ refers to the highest occupied molecular orbital energy. The correction factors in Eq. (6) and (7) are evaluated using the ionization potential of benzene by electron impact method. Electron impact method gives larger ionization potentials than those given by photoionization method by about 0.3 eV in general. Only few experimental data are available for comparison.

In conclusion the variable integrals method II is applicable also to these nitrogen- or oxygen-containing systems without any guess work, and the variable integrals method I reproduces well the results given by the VI/2 method.

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

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