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VESCF-MO-CI Calculation on the π-π^* Electronic Transitions of Pteridine and Its All Amino-derivatives

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A semiempirical VESC-FMO-CI calculation was performed with the purpose of making a systematic survey on the π–π^* electronic transitions of pteridine and its all possible amino-derivatives. The calculated data, particularly those for the singlet π–π^* transition energies, were in good agreement with the observed data on both of the mono- and poly-substituted derivatives. Also, the effects of amino-substitution upon the polarization directions and upon the changes of the electron densities in going from the ground state to the lowest $^1(\pi,\pi^*)$ state were discussed.

A few SCF-MO calculations have been reported concerning the π-electronic structures of the substituted pteridines which form fundamental framework of the complicated biopteridines.[2–4] Little information is available, however, regarding a systematic and sucessful explanation of the π-π^* electronic spectra of the hydroxy- or amino- derivatives. Needless to say, a main reason for this is that the usual semiempirical parametrizations for heteroatoms are prevented by the remarkable electron localization at the pteridine ring. As a part of the molecular orbital studies on the heteroaromatic compounds of biological interest,[5–8] this paper reports a semiempirical SCF-MO-CI calculation on the compounds in the title with the aid of the variable electronegativity (VE) approximation.

Experimental

Calculation Method——The calculation of the self-consistent matrix elements is done with the P–P–P approximation.[9,10] Adopting the VE approximation,[11] the valence-state ionization potential (I_r) and one-center Coulomb integral (γ_{rr}) are combined with the effective nuclear charge on the basis of the following quadratic equations:

For $=\mathrm{C}-$ and $-\overset{|}{\mathrm{N}}-$ (sxyz, V_4)

$$I_r = 3.390Z_r^2 - 7.899Z_r + 1.157, \quad \gamma_{rr} = -0.432Z_r^2 + 9.164Z_r - 14.527$$

For $=\mathrm{N}-$ (sx^{2}yz, V_3)

$$I_r = 3.455Z_r^2 - 10.594Z_r + 3.256, \quad \gamma_{rr} = -0.415Z_r^2 + 9.912Z_r - 19.435$$

The coefficients in the equations are settled using the atomic spectroscopic data by Pritchard and Skinner.[12] The two-center Coulomb integral (γ_{rs}) is obtained using the Pariser-Parr's approximation.[9] The core-

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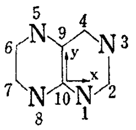

Fig. 1. The Coordinate Axes and Numbering of Pteridine

resonance integral (β_{rs}) is recalculated after each SCF iteration process by the equation of: $\beta_{rs} = -\frac{1}{2}S_{rs}(I_r + I_s)$, where s_{rs} is the overlap integral between the Slater-type atomic orbitals. In the configuration interaction procedure all singly excited configurations are allowed to interact. The molecular geometry of the pteridine ring is taken from the X-ray analysis data by Hamor and Robertson,[13] and the bond-length and -direction of the C–NH_2 bond is assumed as 1.34 Å and as bisecting the valence-angle of the substituted carbon atom, respectively. The intramolecular coordinate axes and numbering of the pteridine ring are shown in Fig. 1.

The present calculation was performed using the HITAC 5020-E computer at the computation center of the University of Tokyo.

Result and Discussion

A comparison of the calculated and observed data for the electronic spectra is shown in Table I. The calculated values of the transition energies and oscillator strengths of pteridine itself are in fairly good agreement with the maximum absorption energies and relative intensities of the observed bands, and are greatly improved as compared with the previous data obtained using a standard P-P-P type calculation.[4] Furthermore, the calculated results of polarization direction well fit an early Mason's suggestion that the polarization directions

TABLE I. Comparison between the calculated and observed Spectra

	Calculated			Observed*1
	ΔE_s[a]	(f)[b]	$\alpha°$[c]	ΔE_s ($\varepsilon_{max} \times 10^{-3}$)
Pteridine	4.42	(0.25) ;	16	4.12 (7.5)[d]
	4.94	(0.05) ;	70	5.27 (2.9)
	5.90	(0.28) ;	−35	5.90 (11.0)
	6.25	(0.04) ;	−40	
	6.64	(0.56) ;	−49	
2-Amino	3.58	(0.30) ;	25	3.35 (6.6)[e]
	4.34	(0.11) ;	−22	
	5.06	(0.02) ;	−72	
	5.53	(0.54) ;	−24	5.52 (24.0)
	6.03	(0.00_3);	60	
4-Amino	3.82	(0.28) ;	48	3.70 (6.6)[e]
	4.35	(0.01) ;	−70	
	5.18	(0.38) ;	−36	5.08 (15.8)
	5.38	(0.20) ;	21	
	5.75	(0.05) ;	33	
6-Amino	3.51	(0.33) ;	22	3.42 (5.6)[f]
	4.48	(0.13) ;	−15	4.81 (10.2)
	5.03	(0.00_4);	79	
	5.73	(0.19) ;	−35	5.56 (19.9)
	6.14	(0.97) ;	−38	
7-Amino	3.65	(0.29) ;	14	3.71 (10.7)
	4.49	(0.03) ;	−12	4.73 (6.3)
	5.28	(0.04) ;	59	
	5.78	(0.48) ;	32	5.44 (18.2)
	5.92	(0.65) ;	33	
2,4-Diamino	3.37	(0.30) ;	27	3.41 (6.3)[g]
	4.06	(0.02) ;	−15	
	4.97	(0.43) ;	−49	4.86 (17.8)
	5.19	(0.42) ;	−13	
	5.50	(0.02) ;	−87	
	5.87	(0.12) ;	−4	5.53 (10.7)

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13) T.A. Hamor and J.M. Robertson, *J. Chem. Soc.*, **1956**, 3586.

	Calculated ΔE_s[a)]	(f)[b)]	a°[c)]	Observed*[1] ΔE_s ($\varepsilon_{max} \times 10^{-3}$)
2,6-Diamino	3.13	(0.36) ;	27	
	4.12	(0.24) ;	-27	
	4.53	(0.02) ;	12	
	5.17	(0.24) ;	-17	
	5.32	(0.00_1);	18	
2,7-Diamino	3.45	(0.38) ;	3	
	4.12	(0.00_2);	-39	
	4.58	(0.19) ;	-69	
	5.20	(0.48) ;	-4	
	5.41	(0.60) ;	16	
4,6-Diamino	3.40	(0.33) ;	32	3.31 (6.5)[h)]
	4.14	(0.08) ;	18	
	4.75	(0.37) ;	-43	4.71 (15.1)
	5.16	(0.16) ;	-11	
	5.31	(0.12) ;	64	
4,7-Diamino	3.53	(0.24) ;	5	3.66 (11.2)[h)]
	4.05	(0.09) ;	84	
	4.97	(0.18) ;	-17	
	5.04	(0.42) ;	66	5.14 (24.0)
	5.29	(0.12) ;	-15	
6,7-Diamino	3.59	(0.50) ;	4	
	4.08	(0.03) ;	87	
	4.90	(0.01) ;	77	
	5.34	(0.30) ;	-76	
	5.43	(0.01) ;	-18	
2,4,6-Triamino	3.04	(0.34) ;	29	
	3.92	(0.15) ;	-21	
	4.59	(0.19) ;	-52	
	4.93	(0.44) ;	-14	
	5.08	(0.08) ;	83	
2,4,7-Triamino	3.32	(0.36) ;	8	3.54 (14.8)[h)]
	3.91	(0.01) ;	71	
	4.65	(0.21) ;	-53	4.82 (13.5)
	4.97	(0.32) ;	62	
	5.20	(0.05) ;	61	
	5.39	(1.15) ;	-11	5.46 (34.7)
2,6,7-Triamino	3.27	(0.51) ;	12	
	3.88	(0.08) ;	-62	
	4.55	(0.04) ;	-46	
	4.98	(0.42) ;	-19	
	5.12	(0.24) ;	-55	
4,6,7-Triamino	3.42	(0.43) ;	7	3.59 (12.9)[h)]
	3.94	(0.01) ;	-81	
	4.80	(0.28) ;	-79	4.36 (4.3)
	4.87	(0.15) ;	41	4.84 (14.8)
	5.08	(0.23) ;	-42	
	5.57	(0.23) ;	9	5.46 (21.4)
2,4,6,7-Tetramino	3.14	(0.46) ;	13	
	3.76	(0.06) ;	-67	
	4.65	(0.15) ;	-45	
	4.75	(0.19) ;	59	
	4.84	(0.35) ;	-33	

a) singlet π–π^* transition energy in eV

b) oscillator strength

c) polarization direction in degree measured counterclockwise to the x-axis

d) S.F. Manson, *J. Chem. Soc.*, **1955**, 2336

e) A. Albert, *et al.*, *J. Chem. Soc.*, **1951**, 474

f) A. Albert, *et al.*, *J. Chem. Soc.*, **1954**, 3832

g) M.F. Mallete, *et al.*, *J. Amer. Chem. Soc.*, **69**, 1814 (1947)

h) A. Albert, *et al.*, *J. Chem. Soc.*, **1956**, 4621

1* The observed data quoted here are taken only from the spectrum measured in neutral solution.

of the first and second π-π^* transitions of pteridine should be close to the x- and y-axis, respectively.[14]

As for the monoamino-derivatives, the calculated values of the lowest two transition energies are also in good correlation with the observed values. On all the monoamino-substitutions but for the 4-substitution, the present calculation gives a weak transition which is polarized fairly close to the short molecular axis and is located in the vicinity between two transitions assigned to the second and third transitions of the observed spectra. Also, the polarization direction of the first transition is turned toward the short molecular axis by the 4-substitution, while that of the second transition is turned toward the long molecular axis by the 2,6, or 7-substitution.

In the case of the polyamino-derivatives also, good correlation is found between the calculated and observed values of transition energies. On the basis of the present calculation, the mean values of the decrements of the calculated transition energies which go along with the amino-substitution indicate that the bathochromic shift of the first transition proceeds in the increasing order of $4 \leqq 7 < 6 < 2$ by the second substitutions, and in the increasing order of $7 < 4 < 6 < 2$ by the third substitutions. This appears to deny the existence of large electronic interactions between the polysubstituted amino-groups. On the 7-substitution, the polarization direction of the first transition is always turned fairly close to the long molecular axis.

TABLE II. The π-Electron Distributions of Pteridine and Its Monoamino-derivatives at the Ground and Lowest $^1(\pi,\pi^*)$ States

Compound		1	2	3	4	5	6	7	8	9	10	11
Pteridine	G	1.147	0.882	1.142	0.886	1.104	0.941	0.924	1.104	0.961	0.909	—
	E	1.102	0.817	1.142	0.940	1.235	0.893	0.959	1.203	0.867	0.841	—
2-Amino	G	1.325	0.932	1.213	0.884	1.110	0.972	0.937	1.120	0.984	0.896	1.626
	E	1.069	0.929	1.256	1.008	1.326	0.963	1.015	1.245	0.907	0.891	1.390
4-Amino	G	1.203	0.879	1.301	0.931	1.129	0.964	0.937	1.108	0.989	0.901	1.658
	E	1.036	0.900	1.123	0.979	1.370	1.018	1.013	1.294	0.963	0.913	1.390
6-Amino	G	1.151	0.909	1.153	0.900	1.277	0.965	0.992	1.102	0.953	0.948	1.650
	E	1.207	0.879	1.195	0.979	1.217	0.980	1.083	1.296	0.920	0.832	1.412
7-Amino	G	1.155	0.894	1.166	0.896	1.106	1.010	0.956	1.269	0.993	0.899	1.657
	E	1.191	0.943	1.143	1.013	1.313	1.064	0.980	1.207	0.875	0.899	1.372

Table II shows the changes of the electron densities in going from the ground state to the lowest $^1(\pi,\pi^*)$ state. On this excitation, a remarkable increase of the electron densities of the 5- and 8-nitrogens is found at the pteridine ring. The present data on the monoamino-derivatives indicate, in a manner quite different from the previous P-P-P calculation,[4] that the lowest $^1(\pi,\pi^*)$ excitation induces nearly the same degree and the remarkable amount of electron transfer in a direction from amino-group to the ring. In this sense the first transitions of the monoamino-derivatives can be considered as having a considerable amount of charge-transfer contribution.

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[14] S.F. Mason, *J. Chem. Soc.*, **1955**, 2336.