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Electronic Spectra of Amino-substituted Pteridines

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Several SCF-MO calculations have been reported for the π-electronic structure of pteridines, chiefly of the parent molecule,[1–6] but little is known about a systematic calculation for a series of substituted pteridines forming fundamental structures of complicated biopteridines. Here, the semiempirical VESCF-MO-CI[7–9] calculations on pteridines and all its monoamino derivatives and a few of its diamino derivatives have been performed in making a systematic survey of amino-substitution effects upon electronic spectra. The elements of the F matrix are usually evaluated by adopting the zero differential overlap approximation. On the basis of the atomic spectroscopic data reported by Pritchard and Skinner,[10] the equations representing

TABLE 1. COMPARISON BETWEEN CALCULATED AND OBSERVED SPECTRA

Compound	Calculated $\Delta E^{a)}$ $(f^{b)})$	$\alpha^{0\ c)}$	Observed $\Delta E^{a)}$ $(\varepsilon_{max}\times 10^{-3})$	Compound	Calculated $\Delta E^{a)}$ $(f^{b)})$	$\alpha^{0\ c)}$	Observed $\Delta E^{a)}$ $(\varepsilon_{max}\times 10^{-3})$
Pteridine	4.417 (0.253);	16	4.12 (7.5)[11]	7-Amino	3.655 (0.288);	14	3.71 (10.7)[13]
	4.937 (0.051);	70	5.27 (2.9)		4.489 (0.029);	−12	4.73 (6.3)
	5.897 (0.280);	−35	5.90 (11.0)		5.282 (0.040);	59	
	6.250 (0.039);	−40			5.779 (0.478);	32	5.44 (18.2)
	6.645 (0.562);	−49			5.918 (0.654);	33	
2-Amino	3.582 (0.304);	25	3.35 (6.6)[12]	2,4-Diamino	3.370 (0.296);	27	3.41 (6.3)[14]
	4.341 (0.106);	−22			4.064 (0.019);	−15	
	5.064 (0.018);	−72			4.966 (0.426);	−49	4.86 (17.8)
	5.535 (0.542);	−24	5.51 (24.0)		5.194 (0.422);	−13	
	6.032 (0.003);	60			5.503 (0.019);	−87	
4-Amino	3.818 (0.281);	48	3.70 (6.6)[12]	4,6-Diamino	3.404 (0.329);	32	3.31 (6.5)[15]
	4.353 (0.008);	−70			4.138 (0.084);	18	
	5.177 (0.379);	−36	5.08 (15.8)		4.754 (0.369);	−43	4.71 (15.1)
	5.376 (0.202);	21			5.159 (0.157);	−11	
	5.749 (0.048);	33			5.314 (0.122);	64	
6-Amino	3.509 (0.333);	22	3.42 (5.6)[13]	4,7-Diamino	3.532 (0.244);	5	3.66 (11.2)[15]
	4.482 (0.135);	−15	4.81 (10.2)		4.052 (0.091);	84	
	5.028 (0.004);	79			4.968 (0.184);	−17	
	5.730 (0.190);	−35	5.56 (19.9)		5.044 (0.420);	66	5.14 (24.0)
	6.145 (0.973);	−38			5.289 (0.121);	−15	

a) Singlet π-π^* transition energy in eV.
b) Oscillator strength.
c) Polarization direction measured counterclockwise to the x-axis.

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the parabolic dependence of the valence-state ionization potential (I_r) and one-center repulsion integral (γ_{rr}) upon the effective nuclear charge (Z_r) are taken to be as follows:

for =C– and –$\overset{|}{\text{N}}$– ($sxyz$, V_4)

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

for =N– (sx^2yz, V_3)

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

The two-center repulsion integrals (γ_{rs}) and the core-resonance integrals (β_{rs}) of all the atomic pairs were recalculated after each SCF iteration process according to the Pariser-Parr method[7] and the equation of $\beta_{rs} = -1/2S_{rs}(I_r + I_s)$, respectively. S_{rs} is the theoretically calculated overlap integral between the Slater-type atomic orbitals. The molecular orbitals became self-consistent to five-decimal places in fifteen interations, on the average. Full-configuration interaction is included between all singly-excited configurations. The molecular geometry of the pteridine ring is obtained from the X-ray analysis data by Hamor and Robertson,[16] and the bond-length of the C-NH_2 bond is assumed to be 1.34 Å and the direction of the bond is assumed to bisect the intra-ring angle around the substituted position. Actual numerical calculations were performed with the HITAC 5020-E computer at the University of Tokyo.

Table 1 shows that the two lowest transitions in the calculated spectrum of pteridine are polarized in agreement with the experimental data by Mason.[11] This fact suggests that the first and second π–π^* bands are polarized along the long-axis and the short-axis respectively. The calculated (observed) lowest π–π^* transition energy of the monoamino derivatives is in the increasing order of: $6 \leqq 2 < 7 < 4$ ($2 < 6 < 4 \leqq 7$). This indicates that the amino-group substituted parallel to the long-axis, especially to the 2- and/or 6-position, exerts a large bathochromic effect on this transition. The corresponding oscillator strength is in the increasing order of: $4 \leqq 7 < 2 < 6$, while the observed intensity is mostly enhanced by the 7-substitution. Furthermore, on all monoamino-substitutions except that to the 4-position, the polarization direction of the second π–π^* transition is also turned to the long-axis, and a weak theoretical transition appears between the two transitions correlated with the observed second and third π–π^* bands. The calculated spectra of the diamino derivatives are in fairly good agreement with those observed for the 2,4-, 4,6-, and 4,7-substituted derivatives. In this case also, it can be predicted that the substitution to the 7- and 4-positions causes the lowest π–π^* transition to be polarized quite close to the long-axis.

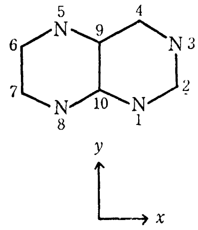

Fig. 1. The numbering of pteridine ring.

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