Band Assignment of Anomalously Strong Absorption Band of 2,6-Diaminopyridine by Interaction with Acetic Acid

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(Received February 1, 1992)

Upon the addition of acetic acid to 2,6-diaminopyridine in isooctane, a new anomalously strong band appears near 340 nm over 2×10^{-3} mol dm^{-3}. The corresponding band was, on the basis of the results of a molecular orbital calculation and spectroscopic experiment, assigned to the π–π^* absorption band of (*E*)-6-amino-2(1*H*)-pyridinimine (tautomer) formed through the hydrogen-bond formation of 2,6-diaminopyridine with two acetic acid molecules.

The UV absorption spectrum of 2,6-diaminopyridine was measured in an ethanol and isooctane (2,2,4-trimethylpentane) mixed solvent, while increasing the ethanol concentration at room temperature and changing the temperature from 20 to −100 °C at a constant concentration of ethanol. A clear weak, broad-shoulder band near 345 nm was observed as the concentration of ethanol was increased to over 5×10^{-1} mol dm^{-3} at room temperature, and as the temperature decreased from 20 to −100 °C in 1×10^{-1} mol dm^{-3} of ethanol in the isooctane solution.

The corresponding band was assigned to the π–π^* absorption band of the (*E*)-6-amino-2(1*H*)-pyridinimine formed through the hydrogen-bond formation of 2,6-diaminopyridine with two ethanol molecules.[1] Such an assignment was experimentally ascertained by measuring the absorption spectrum of 1-methyl-2(1*H*)-pyridinimine as a model compound of (*E*)-6-amino-2(1*H*)-pyridinimine.[2]

In this paper, concerning the addition of acetic acid to 2,6-diaminopyridine in isooctane, a new clear band appears near the wavelength at which the tautomer band was observed upon the addition of ethanol. Its band intensity greatly increases as the concentration of acetic acid increases to over 2×10^{-3} mol dm^{-3}, and the temperature decreases from 40 to 15 °C. The intensity of the new band near 340 nm becomes comparable to that of the main band of 2,6-diaminopyridine hydrogen-bonded with acetic acid in 6.0×10^{-3} mol dm^{-3} of acetic acid at 15 °C. The enhancement of the band intensity near 340 nm seems to be anomalously strong compared with the tautomer band intensities of the 2,6-diaminopyridine–ethanol and 2-aminopyridine–acetic acid systems.[1,3]

Experimental

The purifications of 2,6-diaminopyridine, 2-amino-6-(dimethylamino)pyridine, acetic acid, and isooctane were described in previous papers.[1,3] The UV absorption measurement apparatus was used as described elsewhere.[3]

Methods of Calculation and Molecular Models

The molecular models of 2,6-diaminopyridine, (*E*)-6-amino-2(1*H*)-pyridinimine, and 2,6-diaminopyridinium with planar and pyramidal NH_2 groups were optimized by the ab initio STO-3G method based on the assumption that the ring frameworks of the models are planar. For the sake of simplicity, the formic acid model was used for the acetic acid model in the present calculation. The formic acid and formate models were obtained by the same method. Figure 1 shows the four kinds of complex models used for the present calculation. Model **1** corresponds to the 2,6-diaminopyridine-acetic

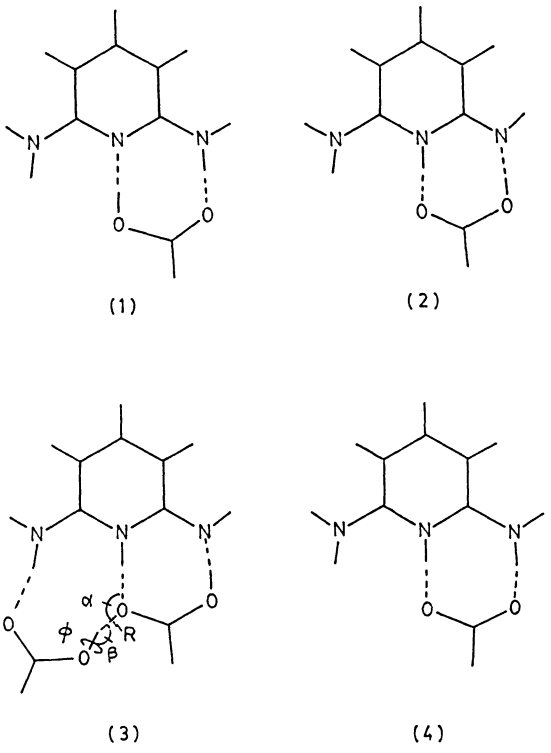

Fig. 1. Molecular models of four complexes used in the present calculation. Model **1** corresponds to the 2,6-diaminopyridine–acetic acid complex (hydrogen-bonded model), Model **2** to the (*E*)-6-amino -2(1*H*)-pyridinimine–acetic acid 1 : 1 complex (tautomer model A), Model **3** to the (*E*)-6-amino-2(1*H*)-pyridinimine–acetic acid 1 : 2 complex (tautomer model B), and Model **4** to the 2,6-diaminopyridinium–acetate complex (proton-transferred model), respectively.

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An ab initio STO-3G calculation was carried out using the Gaussian 80 source program[4] on a FACOM VP-100E computer.

Results and Discussion

Experimental. The addition of a small amount of acetic acid perturbs the absorption spectrum of 2,6-diaminopyridine in isooctane, as shown in Fig. 2. The large band shift to a longer wavelength, the enhancement of the band intensity, and the presence of an isosbestic point at 300 nm were attributed to the formation of a hydrogen-bonded 1 : 1 complex, as in Model **1** (Fig. 1). An additional band appears at around 340 nm in the spectrum of the 2,6-diaminopyridine-acetic acid system in isooctane when the concentration of acetic acid is higher than 10^{-3} mol dm^{-3} (Fig. 2); the isosbestic point then shifts to a longer wavelength. This experimental result indicates the appearance of another complex in the 2,6-diaminopyridine-acetic acid system. The intensity of the new band near 340 nm is much stronger than that of the 335 nm band of the 2-aminopyridine-acetic acid system which was assigned to the first π-π^* transition band of (*E*)-2(1*H*)-pyridinimine.[3] Figure 3 shows the temperature dependences of the absorption spectra of the 2,6-diaminopyridine-acetic acid system in isooctane, the concentration of acetic acid being kept at 10^{-3} mol dm^{-3}. The intensity of the additional 340 nm band increases with a decrease in the temperature. The concentration effect of acetic acid on the spectra of 2,6-diaminopyridine-acetic acid system was investigated at various temperatures within the range from 15 to 40 °C in order to ascertain the presence of the isosbestic point. However, no other isosbestic point was observed under high concentrations, except for the isosbestic point near 300 nm under low concentration, as shown in Fig. 2. Further, in order to elucidate the relation between the enhancement of the intensity of the 340 nm band with the two NH_2 groups, the UV absorption spectrum of the 2-amino-6-(dimethylamino)pyridine-acetic acid system was measured, as is shown in Fig. 4. The anomalously

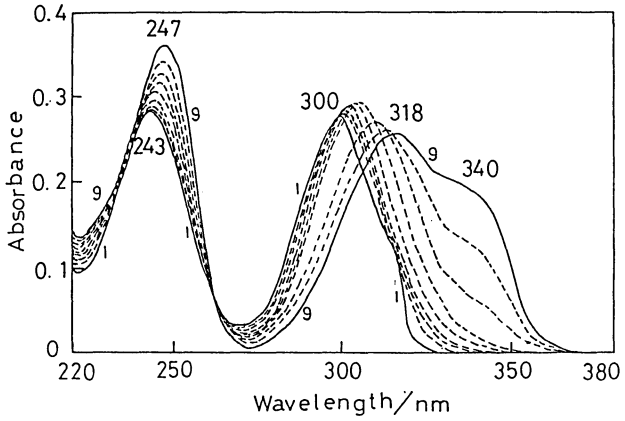

Fig. 2. UV absorption spectra of the 2,6-diaminopyridine-acetic acid system in isooctane at 20 °C. Concentration of 2,6-diaminopyridine: 4×10^{-5} mol dm^{-3}; concentrations of acetic acid (mol dm^{-3}): (1) 0, (2) 4×10^{-5}, (3) 1×10^{-4}, (4) 2×10^{-4}, (5) 4×10^{-4}, (6) 1×10^{-3}, (7) 2×10^{-3}, (8) 4×10^{-3}, (9) 6×10^{-3}.

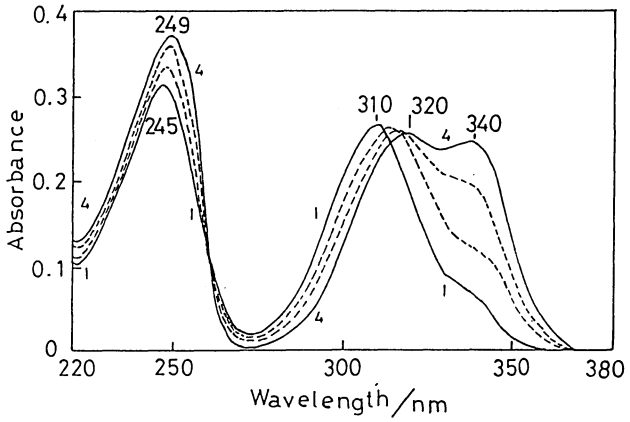

Fig. 3. Temperature dependences of the UV absorption spectra of the 2,6-diaminopyridine-acetic acid system in isooctane, the concentrations of 2,6-diaminopyridine and acetic acid being kept at 4×10^{-5} and 1×10^{-3} mol dm^{-3}, respectively; (1) 45°C, (2) 30°C, (3) 20°C, (4) 15°C.

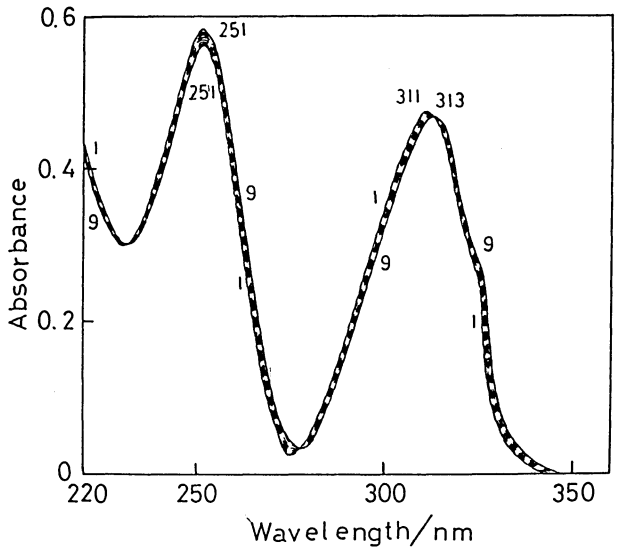

Fig. 4. UV absorption spectra of the 2-amino-6-(dimethylamino)pyridine-acetic acid system in isooctane at 20°C. Concentration of 2-amino-6-(dimethylamino)pyridine: 6×10^{-5} mol dm^{-3}; concentrations of acetic acid (mol dm^{-3}): (1) 0, (2) 4×10^{-5}, (3) 1×10^{-4}, (4) 2×10^{-4}, (5) 4×10^{-4}, (6) 1×10^{-3}, (7) 2×10^{-3}, (8) 4×10^{-3}, (9) 6×10^{-3}.

strong band observed in Fig .2 was not found for the 2-amino-6-(dimethylamino)pyridine–acetic acid system. This spectral behavior is similar to that of the 2-amino-6-(dimethylamino)pyridine–ethanol system. Accordingly, this result suggests that the intensity enhancement of the band near 340 nm may be associated with the two NH_2 groups at the 2- and 6-positions.

Theoretical. The calculated results of the optimized models of 2,6-diaminopyridine and its related compounds are shown in Table 1. The optimized total energies of formic acid and formate anion are −186.21788 and −185.45627 a.u., respectively. In Table 1 2,6-diaminopyridine, (*E*)-6-amino-2(1*H*)-pyridinimine, and 2,6-diaminopyridinium are more stable in the pyramidal form with respect to the NH_2 group than in the planar form.

The optimized bisectal angles (τ) of the NH_2 group of 2,6-diaminopyridine and (*E*)-6-amino-2(1*H*)-pyridinimine models are 52.5 and 52.6 degrees, respectively. However, the bisectal angle of 2,6-diaminopyridinium is much smaller than those of the former two models, and the energy difference between the planar and pyramidal forms is nearly zero, as is shown in Table 1. 2,6-Diaminopyridine and 2,6-diaminopyridinium are more stable at different sign bisectal angles of ±52.5 and ±16.1 degrees than in that of same sign of 52.5 and 16.1 degrees, as in *p*-phenylenediamine.[5] The calculated bisectal angles of 2,6-diaminopyridine and (*E*)-6-amino-2(1*H*)-pyridinimine are much larger than the corresponding observed values of 2-aminopyridine (31.6°)[6] and aniline (37° 29′),[7] respectively. The ab initio STO-3G method overestimated the bisectal angle of the amino group of 2-aminopyridine (52.8°)[8] in comparison with the observed value. However, the calculated dipole moment of 2,6-diaminopyridine is closer to the experimental value[9] in the pyramidal form than in the planar form. The present calculation shows that 2,6-diaminopyridine is more stable than (*E*)-6-amino-2(1*H*)-pyridinimine by 108.4 kJ mol^{-1} in the gound state. In Fig. 5 the optimized geometries of each model are

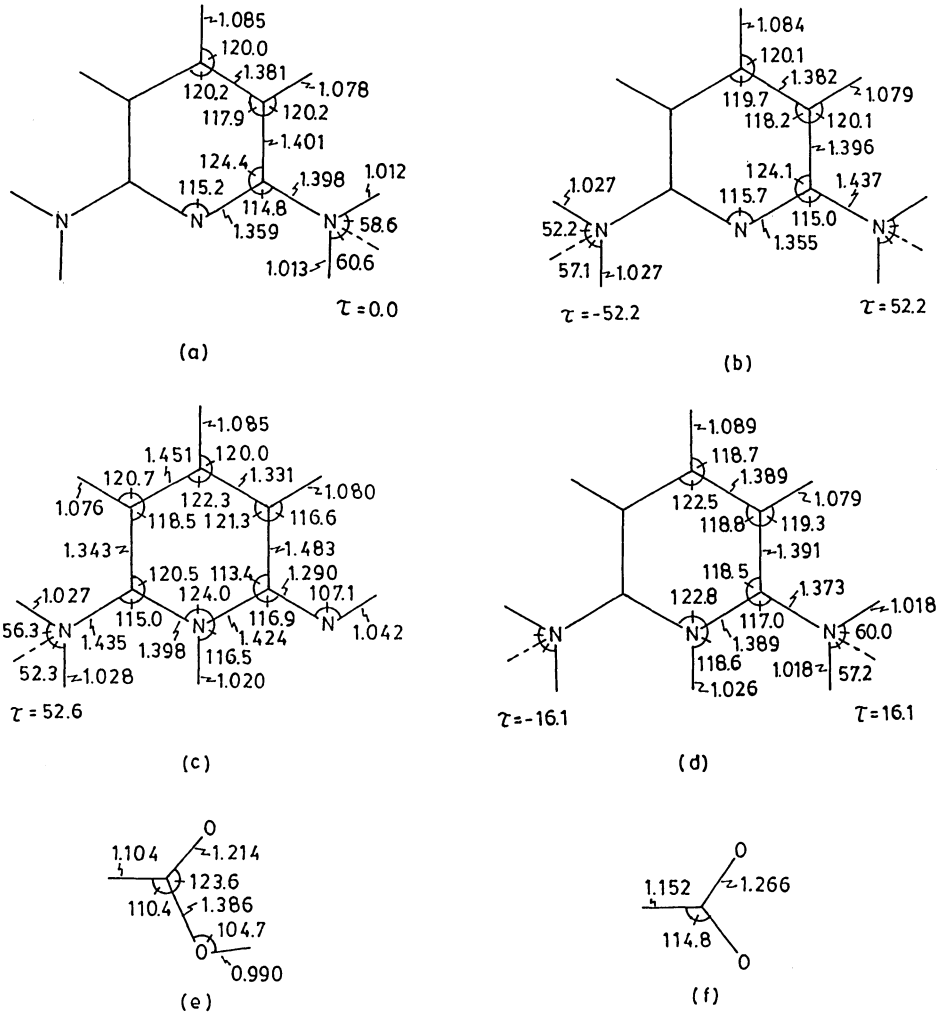

Fig. 5. Molecular geometries of optimized models by the ab initio STO-3G method; (a) planar 2,6-diaminopyridine, (b) pyramidal 2,6-diaminopyridine, (c) (*E*)-6-amino-2(1*H*)-pyridinimine, (d) 2,6-diaminopyridinium, (e) formic acid, and (f) formate anion.

Table 1. Total Energies (E_T), Energy Differences (ΔE_T), Dipole Moments (μ), and Bisectal Angles (τ) of Amino Group of Optimized Planar and Pyramidal Models of 2,6-Diaminopyridine and Its Related Compounds by the Ab Initio STO-3G Method

Model	E_T/a.u.	ΔE_T/kJ mol^{-1}	τ/deg	μ/D[b]	μ_{obsd}/D[b]
2,6-Diaminopyridine					
(1) Planar	−352.28242	0	0.0	0.264	
(2) Pyramidal	−352.29256	−26.6	±52.5	1.361	1.46[a]
(*E*)-6-Amino-2(1*H*)-pyridinimine					
(1) Planar	−352.24605	0	0.0	3.275	
(2) Pyramidal	−352.25124	−13.6	52.6	2.940	
2,6-Diaminopyridinium					
(1) Planar	−352.75300	0	0.0		
(2) Pyramidal	−352.75303	−0.02	±16.1		

a) Ref. 9. b) 1 D=3.3356×10^{-30} C m.

Table 2. Total Energies (E_T), Energy Differences (ΔE_T) between the Complex Models and Initial Levels, Equilibrium Distance (R_e) and Angles (α_e, β_e, and ϕ_e), Bisectal Angles (τ and τ') of Amino Group and Dipole Moments (μ) of the 2,6-Diaminopyridine–Acetic Acid Complex Models as Calculated by the Ab Initio STO-3G Method

Complex	E_T/a.u.	$\Delta E_T(1)$/kJ mol^{-1}	$\Delta E_T(2)$/kJ mol^{-1}	R_e/Å	α_e/deg	β_e/deg	ϕ_e/deg	τ/deg	τ'/deg	μ/D
Model **1**	−538.53226	−57.3	−83.9					−49.8	44.6	2.480
Model **2**	−538.50904	3.67	−22.9					49.1		2.954
Model **3**	−724.74585	−46.0	−72.6	1.591	128.8	175.9	36.8	49.1		1.800

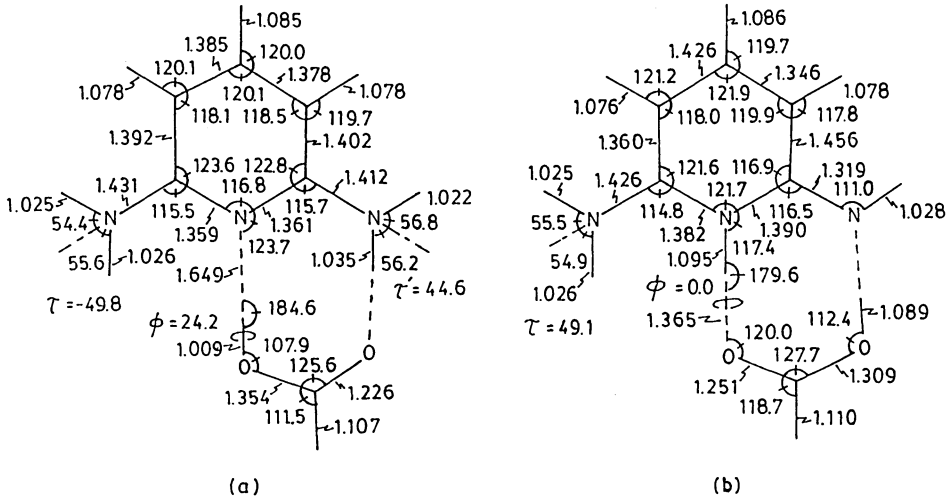

Fig. 6. Optimized geometries of complex models by the ab initio STO-3G method; (a) Model **1** and (b) Model **2**.

shown.

In order to interprete the spectral behavior of the 2,6-diaminopyridine–acetic acid system, as is shown in Figs. 2 and 3, an ab initio STO-3G calculation was carried out for each model shown in Fig. 1 with a full-geometry optimization, except for Model **3**. In Fig. 6 the optimized geometries of Model **1** and Model **2** are shown.

In Table 2 their total energies are compared with the energies of the two kinds of initial levels, that is: (1) the sum of the total energies of pyramidal 2,6-diaminopyridine and formic acid (E_1) and (2) the corresponding sum of the total energies of the planar 2,6-diaminopyridine and formic acid (E_2). The hydrogen-bond energies of Model **1** correspond to $\Delta E_T(1)$ and $\Delta E_T(2)$ for the two initial levels, E_1 and E_2. The values of $\Delta E_T(1)$ and $\Delta E_T(2)$ of Model **1** are −57.3 and −83.9 kJ mol^{-1}, respectively. These calculated values are larger than the corresponding ones of the 2-aminopyridine-formic acid system calculated using the same approach, −51.5 and −65.0 kJ mol^{-1}.[8] These calculated values suggest that the hydrogen-bonding strength is greater in 2,6-diaminopyridine than in 2-aminopyridine for the proton donor. The bisectal angle (τ') of the NH_2 group at the 2-position which participates in hydrogen-bond formation with formic acid varies from 52.5 to 44.6 degrees, and the corre-

sponding angle (τ) of the free NH_2 group at the 6-position varies from −52.5 to −49.8 degrees. The total energy of Model **2** with the bisectal angles of different sign, 44.6 and −49.8 degrees, is more stable than the corresponding one with the bisectal angles of same sign, 44.6 and 49.8 degrees, by 1.36 kJ mol^{-1}. Hydrogen-bond formation leads to a flattening of the pyramidal NH_2 group through the σ-bond system. These results suggest a large band shift of the π–π^* transition to the longer wavelength side upon the hydrogen-bond formation of the amino-substituted pyridine with acetic acid in Fig. 2 and ethanol (as shown in Fig. 2).[1)]

The stabilization energy of Model **2** depends on the initial levels, E_1 and E_2. In the case of E_1 the stabilization energy of Model **2** is 3.67 kJ mol^{-1}, and its formation is difficult; in the case of E_2, however, the corresponding energy of Model **2** is −22.9 kJ mol^{-1} and the tautomer model A is more stable regarding energy than the initial level. However, its stabilization energy of tautomer model A, −22.9 kJ mol^{-1}, is much smaller than the hydrogen bond energy of Model **1**, −83.9 kJ mol^{-1}. It may therefore be difficult to interpret the strong new band near 340 nm in Fig. 2 by the tautomer model A.

Since Model **3** is too large in size for a full-geometry optimization, a partial geometry optimization was applied to evaluate its total energy. In Model **3**, only the four parameters which are shown as R, α, β, and ϕ in Fig. 1 were optimized. Therefore, Model **3** was comprised the optimized Model **2** shown in Fig. 6(b) and formic acid shown in Fig. 5(e). In Table 2 the calculated results of Model **3** are shown. The stabilization energies of Model **3** are −46.0 and −72.6 kJ mol^{-1} for $\Delta E_T(1)$ and $\Delta E_T(2)$, respectively. However, the stabilization energy of Model **3** may become larger in a full-geometry optimization than the present calculated values in a partial geometry optimization. Therefore, the magnitude of the stabilization energies of Model **3** may become comparable to those of the hydrogen-bond energies of Model **1**, −57.3 and −83.9 kJ mol^{-1}. The band maximum at 340 nm may be assigned to the π–π^* transition of the (*E*)-6-amino-2(1*H*)-pyridinimine moiety in the 2,6-diaminopyridine–acetic acid complex from the experimental and calculated results of the 2,6-diaminopyridine-ethanol and 2-aminopyridine–acetic acid systems,[1,3)] and from the observed spectrum of 1-methyl-2(1*H*)-pyridinimine.[2)] The observed bands near 340 nm corresponding to the imino-form of the above-mentioned systems are very weak, since their stabilization energies are much smaller than the hydrogen-bonding energies of the amino-form.[1,3)] However, the intensity of the (*E*)-6-amino-2(1*H*)-pyridinimine moiety of the present system may be enhanced by a large stabilization of the imino-form through cooperation with the second acetic acid and the NH_2 group at the 6-position, since its stabilization energy is comparable to the hydrogen-bonding energy of the amino-form. In addition to the above discussion,

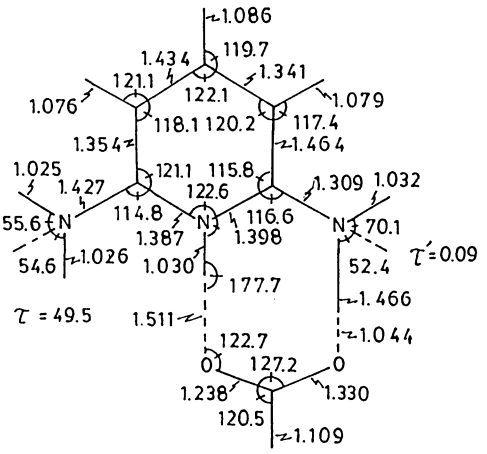

Fig. 7. Optimized geometry of Model **4** by the ab initio STO-3G method, keeping the bond length of the ring N–H group 1.030 Å.

complex formation with acetic acid results in a geometry change of the composite parts. In tautomer model B the geometry change of the (*E*)-6-amino-2(1*H*)-pyridinimine moiety may induce an enhancement of the transition moments which contribute to the anomalously strong band near 340 nm. Therefore, the anomalously strong band near 340 nm may be assigned to the π–π^* absorption band of the (*E*)-6-amino-2(1*H*)-pyridinimine moiety formed through the hydrogen-bond formation of 2,6-diaminopyridine with two acetic acid molecules, like the tautomer model B.

On the other hand, in order to clarify the formation process of the proton-transferred complex in the ground state, the total energy of Model **4** was optimized for each bond length of the ring N–H group of Model **4** in the range from 1.03 to 1.20 Å. The total energy curve of Model **4** against the bond length of the ring N–H group has a flat region from 1.08 to 1.10 Å; this region corresponds to the formation of a tautomer, such as Model **2**. In Fig. 7 the optimized geometry of Model **4** with a bond length of 1.030 Å for the ring N–H group is shown. Its geometry corresponds to that of tautomer complex model A; it is more unstable in energy than the optimized Model **2** shown in Fig. 6(b) by 4.80 kJ mol^{-1}. This calculated result suggests that the proton transfer from acetic acid to 2,6-diaminopyridine may be difficult in the ground state, as in the case of the 2-aminopyridine-acetic acid system.[3,8)]

Through the present calculation, the following points may be noted: (1) The amino group at the 6-position of 2,6-diaminopyridine plays an important role in the appearance of an anomalously strong band near 340 nm, at which the tautomer band was observed for the 2,6-diaminopyridine-ethanol system.[1)] (2) The ab initio STO-3G method overestimates the bisectal angle of the NH_2 group. This overestimation makes the stabilization energy of the tautomer 1 : 1 model unreasonable. A reasonable initial level may be between the present

calculated two levels, E_1 and E_2.

This work was supported by grants from the Research and Development Center of Engineering of Tokyo Denki University. One of the authors (K.I.) also acknowledges his gratitude for the financial assistance of Daicel Chemical Industries, Ltd. and for the staffs of the T.D.U. Computer Center.

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