Molecular Orbital Considerations on Interaction of 2-Aminopyridine with Formic Acid in the Ground State

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In order to ascertain the formation processes of the tautomer and proton-transferred complexes in the 2-aminopyridine–acetic acid system in the ground state, a molecular orbital calculation was carried out for the 2-aminopyridine–formic acid system by the ab initio STO-3G method with full-geometry optimization of the complex. The following conclusions were drawn from the present calculation: (1) The amino–imino tautomerization in the 2-aminopyridine–formic acid system proceeds through a double proton transfer process between 2-aminopyridine and formic acid. (2) The formation of a proton-transferred complex in the 2-aminopyridine–formic acid system is difficult in the ground state. This conclusion may be applicable to the 2-aminopyridine–acetic acid system. (3) In the case of the ab initio STO-3G calculation a full-geometry optimization of the complex plays an important role in elucidating the stabilization energies and geometries of the tautomer and proton-transferred complexes. (4) A full-geometry optimization of the complex model is not so important for evaluating the hydrogen bond energy of the stable hydrogen-bonded complex, but is necessary for elucidating the effect of hydrogen bond formation on the molecular geometry of the complex. (5) The bisectal angle of the NH_2 group, calculated by the ab initio STO-3G method, becomes much larger than the experimental value. Further, the energy difference between the planar and pyramidal 2-aminopyridine with respect to the NH_2 group is much larger than the experimental value.

In a previos paper[1] the UV absorption spectrum of 2-aminopyridine was measured in isooctane (2,2,4-trimethylpentane) containing various amounts of acetic acid at room temperature; the temperature dependence (20—−80 °C) of the spectra was also determined, while the concentration of acetic acid was maintained constant. An additional weak shoulder and appeared at around 335 nm in the spectra obtained when the acetic acid concentration was higer than 1×10^{-2} mol dm^{-3}. The 335 nm band was assigned to the π–π^* transition of the (*E*)-2(1*H*)-pyridinimine moiety in the 2-aminopyridine-acetic acid complex from theoretical results involving a molecular orbital calculation as well as spectroscopic experimental results.[1] The previous assignment was ascertained by a measurement of the UV spectrum of 1-methyl-2(1*H*)-pyridinimine as a model compound of 2(1*H*)-pyridinimine.[2] However, the previous calculated results suggested that a proton-transfer from acetic acid to 2-aminopyridine in the complex may be difficult energetically in the ground state. In a previous paper,[1] molecular models of 2-aminopyridine and its related compounds optimized by the MINDO/3 method and a formate model by the ab initio 4-31G method,[3] as well as the formic acid model of experimental geometry[4] were used. The complex formation energies for those models were calculated by the ab initio STO-3G method within the limited number of optimization.

In this paper, in order to clarify the formation processes of the tautomer and proton-transferred complexes in the 2-aminopyridine–acetic acid system an ab initio STO-3G calculation was carried out for the 2-aminopyridine–formic acid system using the full-geometry optimization of the composite parts of the complex models.

Methods of Calculation and Molecular Models

The molecular models of 2-aminopyridine, (*E*)-2(1*H*)-pyridinimine, and 2-aminopyridinium with the planar and pyramidal NH and NH_2 groups were optimized by the ab initio STO-3G method under the assumption that the ring frame works of the models are planar.

Molecular models of formic acid and formate were obtained by the same MO method. Figure 1 shows three kinds of complex models used for the present calculation. Model **1** corresponds to the 2-aminopyridine–formic acid complex (hydrogen-bonded model), Model **2** to the (*E*)-2(1*H*)-pyridinimine–formic acid complex (tautomer model), and Model **3** to the 2-aminopyridinium–formate complex (proton-transferred model), respectively. An ab initio STO-3G calculation was carried out using the Gaussian 80 source program[5] on a FACOM VP-100E computer.

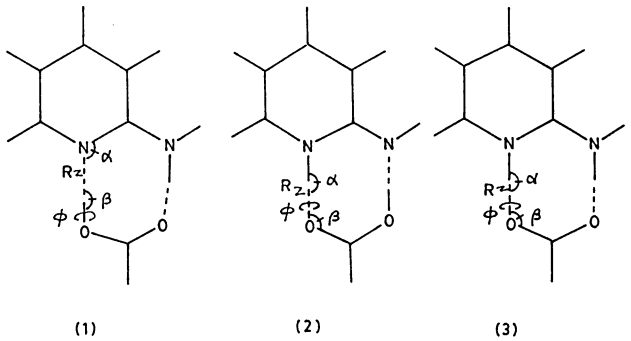

Fig. 1. Molecular models of three complexes used in the present calculation.
Figure (1) corresponds to Model **1**, Figure (2) to Model **2**, and Figure (3) to Model **3**, respectively.

Results and Discussion

The calculated results of the optimized models of 2-aminopyridine and its related compounds are shown in Table 1. The optimized total energies of formic acid and formate are −186.21788 and −185.45627 a.u., respectively. In Table 1 2-aminopyridine is more stable in the pyramidal form (1) with respect to the NH_2 group than in the planar form (2). The optimized bisectal angle (τ) of the NH_2 group of 2-aminopyridine, 52.8 degrees, is much larger than the corresponding observed value, 31.6 degrees.[6] The energy difference between the planar and pyramidal forms of 2-aminopyridine is 13.4 kJ mol^{-1}. This value seems to be much larger than the experimental value 2.99 kJ mol^{-1}.[7] The calculated dipole moments of 2-aminopyridines (1) and (2) are shown with the experimental value[8] in Table 1.

On the other hand, (*E*)-2(1*H*)-pyridinimine and 2-aminopyridinium are more stable in the planar form with respect to the NH and NH_2 groups than in the pyramidal form. The energy difference between (*E*)-2(1*H*)-pyridinimine and pyramidal 2-aminopyridine is 101 kJ mol^{-1} and it is larger than the corresponding one between (*E*)-2(1*H*)-pyridinimine and planar 2-aminopyridine. Those calculated values suggest the difficulty of direct amino-imino tautomerization of 2-aminopyridine.[1] In Fig. 2 the optimized geometry of each model is shown.

The total energy, E_T, of each model was obtained after optimization of geometries of the composite parts and that of the equilibrium distance R and angles α, β, and ϕ which are shown in Fig. 1, until the E_T value reached a minimum. Each of the total energies of the complex models was compared with the energies of the two kinds of initial levels, that is, (1) the sum of the total energies of pyramidal 2-aminopyridine and formic acid; E_1, and (2) the corresponding one of planar 2-aminopyridine and formic acid; E_2. The calculated results are shown in Table 2. In Fig. 3 the optimized geometries of

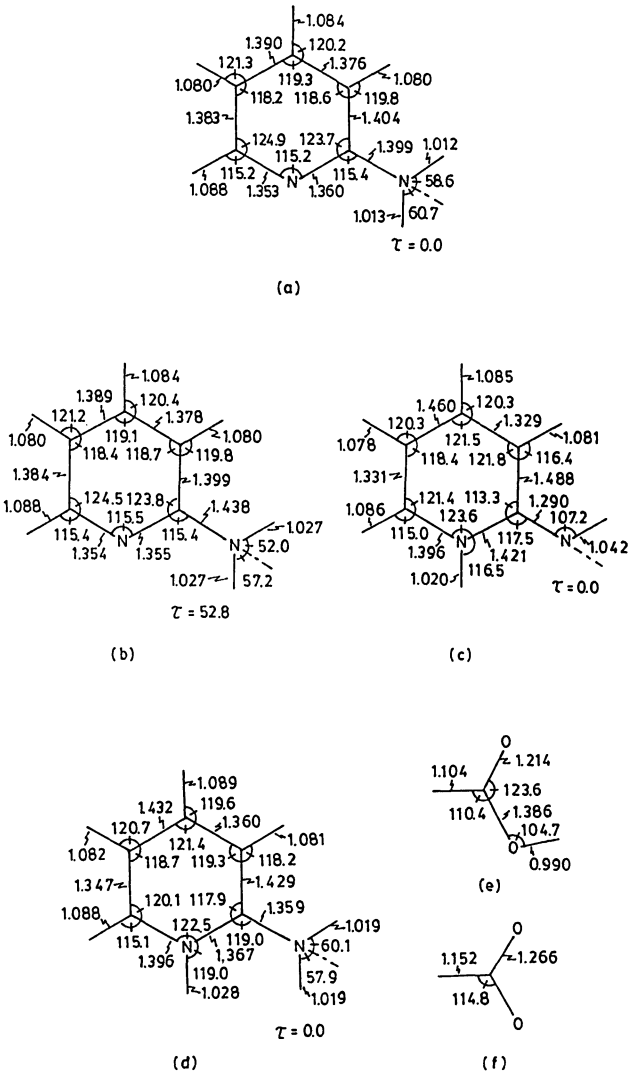

Fig. 2. Optimized geometries of molecular models by the ab initio STO-3G method; (a) planar 2-aminopyridine, (b) pyramidal 2-aminopyridine, (c) (*E*)-2(1*H*)-pyridinimine, (d) 2-aminopyridinium, (e) formic acid, and (f) formate anion.

Table 1. The Total Energies (E_T), Energy Difference (ΔE_T), Dipole Moments (μ), and Bisectal Angles (τ) of Amino Group of Optimized Models of 2-Aminopyridine 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-Aminopyridine (1)	−297.96511	0	52.8	2.266	2.04[a]
2-Aminopyridine (2)	−297.95998	13.4	0	1.715	
(*E*)-2(1*H*)-Pyridinimine	−297.92674	101	0	2.375	
2-Aminopyridinium	−298.42098		0		

a) Ref. 8. b) 1 D=3.3356×10^{-30} C m.

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

Complex	E_T/a.u.	R_e/Å	α_e/deg.	β_e/deg.	ϕ_e/deg.	τ/deg.	$\Delta E_T(1)$/kJ mol^{-1}	$\Delta E_T(2)$/kJ mol^{-1}	μ/D
Model **1**	−484.20493	1.662	125.0	182.9	23.6	44.6	−57.6		2.722
Model **2**	−484.18232	1.381	178.5	121.0	0.0	0.0	1.76	−11.7	2.628

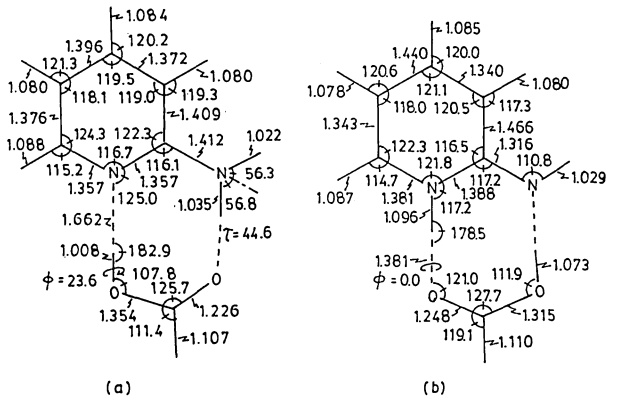

Fig. 3. Optimized geometries of complex models by the ab initio STO-3G method; (a) Model **1** and (b) Model **2**.

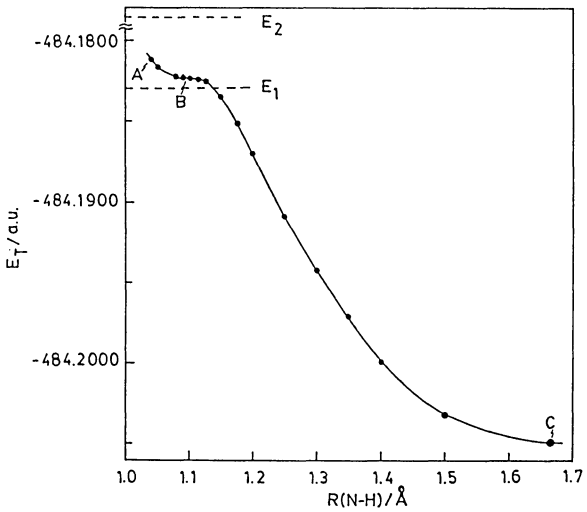

Fig. 4. Total energy of Model **3** optimized by the ab initio STO-3G method plotted against the bond length of the ring N–H group. E_1 and E_2 represent the two kinds of the initial levels. A corresponds to Model **3** shown in Fig. 5, B to Model **2** shown in Fig. 3(b), and C to Model **1** shown in Fig. 3(a).

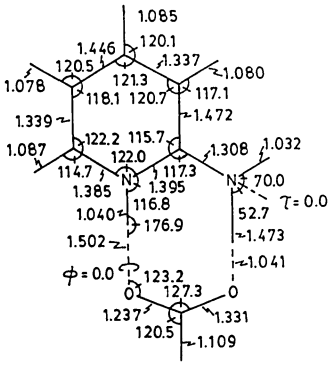

Fig. 5. Optimized geometry of Model **3** by the ab initio STO-3G method while keeping the bond length of the ring N–H group at 1.040 Å.

Model **1** and Model **2** are shown. Model **1** was obtained after the geometry optimization of the initial model which was composed of the pyramidal 2-aminopyridine and formic acid molecules as is shown in Fig. 1. The ΔE_T of Model **1** corresponds to the hydrogen-bond energy of the 2-aminopyridine–formic acid system. The calculated hydrogen-bond energy, -57.6 kJ mol^{-1}, may be in relatively good agreement with the experimental value, -47.3 kJ mol^{-1}, of the 2-aminopyridine-acetic acid system.[9] The values of the bond length and bond angle of the composite parts are effected by complex formation, in comparison with the corresponding ones shown in Fig. 2. The variation of the ring C–H bond lengths is relatively small compared with that of the other bond lengths on the formation of hydrogen bond. The bisectal angle (τ) of the NH_2 group which participates in the hydrogen-bond formation with the formic acid varies from 52.8 to 44.6 degrees in Model **1**. The hydrogen-bond formation leads to a flattening of the pyramidal NH_2 group through the σ-bond system, and the π-conjugation increases between the ring system and the NH_2 group. This result suggests the large band shift of the π–π^* transition to the longer wavelength side on the hydrogen-bond formation of the amino-substituted pyridine with acetic acid and ethanol.[1,10] The stabilization energy of Model **2** depends on the energies of the initial levels: E_1 and E_2. In the case of E_1 the formation of Model **2** is difficult, while in the case of E_2 the stabilization energy of Model **2** becomes -11.7 kJ mol^{-1} and the tautomer complex is more stable than the initial level. From the experimental result of tautomer formation the initial level of E_1 seems to be large in energy. Referring to the experimental fact that 2-aminopyridine is pyramidal with respect to the NH_2 group, the initial level of E_2 may be unreasonable.

On the other hand, the stable proton-transferred complex was not obtained after the geometry optimization of the initial Model **3** shown in Fig. 1. This means that the proton-transferred complex, like the initial Model **3**, is unstable in energy and it can not exist in the ground state.

In order to make clear the formation process of the proton-transferred complex in the ground state the total energy of Model **3** was optimized for each bond length of the ring N–H group of Model **3**. In Fig. 4 the total energy of Model **3** was plotted against the bond length of the ring N–H group in the range from 1.04 to 1.50 Å. It is noteworthy that this energy curve has a flat region from 1.08 to 1.10 Å. The optimized ring N–H bond length 1.096 Å of Model **2** in Fig. 3(b), lies in this region as is denoted by B in Fig. 4. The optimized geometry of the complex model which corresponds to a ring N–H bond length of 1.040 Å is shown in Fig. 5. Figure 5 is of interest since one of the N–H bonds of the NH_2 group elongates from 1.019 Å of the original N–H bond length of the NH_2 group of 2-aminopyridinium (in Fig. 2(d)) to

1.473 Å toward the O atom of the formate anion. The atomic distance between the H and O atoms is 1.041 Å, as is shown in Fig. 5. This means that the N–H bond of NH_2 group is dissociated, for instance, upon contact of 2-aminopyridinium with the formate anion, newly an O–H bond is formed in the complex. The geometry of the complex model shown in Fig. 5 corresponds to that of the tautomer model. Figure 4 shows that the two H atoms of the ring N–H and NH_2 groups may move energetically according to the potential curve, as shown in Fig. 4; the H atom of the ring N–H group can not move independently between the ring N atom and the O atom of formate without a migration of the H atom from the NH_2 group toward the another O atom of formate in the ground state. The energy curve in Fig. 4 suggests that the formation of proton-transferred complex is energetically difficult in the ground state, but that of the tautomer complex may be possible. In Fig. 4, A corresponds to the complex model shown in Fig. 5, and C to Model **1**, respectively. Since the complex at A is energetically unstable, it may be converted easily to the complex at B, which corresponds to the tautomer complex. Although the tautomer at B seems to be metastable, equilibrium may exist between the tautomer complex and the stable hydrogen-bonded complex, such as Molel **1** at C.

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References

1) K. Inuzuka and A. Fujimoto, *Bull. Chem. Soc. Jpn.*, **63**, 971 (1990).
2) A. Fujimoto and K. Inuzuka, *Bull. Chem. Soc. Jpn.*, **64**, 3758 (1991).
3) L. Radom, *Aust. J. Chem.*, **29**, 1635 (1976).
4) R. G. Lerner, B. P. Dailey, and J. P. Friend, *J. Chem. Phys.*, **26**, 680 (1957).
5) GAUSSIAN 80, QCPE#525, University of Indiana, Bloomington, Indiana 47401, U.S.A.
6) R. A. Kydd and I. M. Mills, *J. Mol. Spectrosc.*, **42**, 320 (1972).
7) D. Christem, D. Norbury, D. G. Lister, and P. Palmieri, *J. Chem. Soc., Faraday Trans. 2*, **71**, 438 (1975).
8) M. T. Rogers, *J. Phys. Chem.*, **60**, 125 (1956).
9) K. Inuzuka and A. Fujimoto, *Spectrochim. Acta, Part A*, **42**, 929 (1986).
10) K. Inuzuka and A. Fujimoto, *Bull. Chem. Soc. Jpn.*, **63**, 216 (1990).