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Theoretical Considerations of the Dimer-formation Energy and Electronic Structures of the Monomer and Dimer of the 2-Pyridone by the Molecular Orbital Method

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When the dimer-formation energy of 2-pyridone was measured by means of ^{1}H-NMR spectroscopy, the value of 65.3 kJ mol^{-1} was obtained. It is much larger than the hydrogen-bond energies which are generally observed for the C=O···H–N system. The dimer-formation energy of 2-pyridone was calculated by means of the CNDO/2 method; its formation energy ($-\Delta H$) was estimated to be 68.2 kJ mol^{-1}. The electronic structures of the monomer and dimer of 2-pyridone were calculated by means of the CNDO method with configuration interaction (CNDO/CI) in order to clarify the previous band assignment of the UV spectrum of 2-pyridone. According to the calculated results, the absorption bands at 305 and 228 nm in isooctane (2,2,4-trimethylpentane) were assigned to the monomer, while those at 297.5 and 230.5 nm were assigned to the dimer.

In the previous paper[1] the longest-wavelength UV absorption of 2-pyridone in isooctane (2,2,4-trimethylpentane) was ascribed to π-π^* electronic transitions of the monomer and dimer. The dimer-absorption band appears at a wavenumber higher than that of the monomer by *ca.* 830 cm^{-1}. The dimer band corresponds to the π-π^* transition from the ground ^1A_g state to the excited ^1B_u state. No π-π^* transition absorption from the ground ^1A_g state to the excited ^1A_g state could be observed.

In this paper, the previous experimental considerations of the UV spectrum of 2-pyridone[1] were examined and further clarified by means of the CNDO method with CI. In addition, the formation energy of 2-pyridone dimer was evaluated by the CNDO/2 method; also, the dimer-formation energy was measured by the method of ^{1}H-NMR spectroscopy. The calculated energy was compared with the observed value.

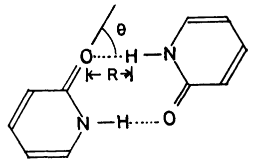
Experimental

2-Pyridone was purified in the way described previously.[1] Tetrahydrofuran (THF) was refluxed with solid potassium hydroxide for at least 24 h, distilled from it, and again distilled from lithium aluminum hydride immediately before use. Benzene-d_6, Canada Merck (99.5% purity), was used as the solvent without further purification. The measurement of the ^{1}H-NMR spectrum was carried out with a JEOL FX-90Q NMR spectrometer at each of four temperatures, 8, 19, 32, and 42 °C. The concentration of the 2-pyridone solution was changed twelve times in the range of 10^{-3} to 10^{-1} mol dm^{-3}. The UV absorption spectrum was obtained at room temperature with a Hitachi Model 323 spectrophotometer.

Methods of Calculation and Molecular Models

The formation energy of the dimer, the π-bond orders, and the charge densities of 2-pyridone in the ground state were calculated by the CNDO/2 method[2,3] using the same parameter as in the previous paper.[1] The values of the bond distance and bond angle of 2-pyridone as measured by Penfold[4] were used. The data of 1-methyl-2-pyridone were the same as in the previous paper.[1]

For the dimer, the following planar model was used:



The present dimer model without the C_{2h} symmetry has the two parameters of R and θ, which correspond to the distance between the O atom of the C=O group and the H atom of the N–H group, and to the angle between the C=O axis and the direction of hydrogen bond of the O···H–N, respectively. The dimer-formation energy was calculated under an assumption that the ring framework of the 2-pyridone monomer and its N–H distance are invariant on the dimer formation. The enthalpy change ($-\Delta H$) for the dimerization of 2-pyridone was obtained by changing the R and the θ until the value of $-\Delta H$ reaches its maximum.

The CNDO method with CI (CNDO/CI) using the parameter given by Jaffé *et al.*[5,6] was employed for the calculation of the transition energies, transition oscillator strengths, charge densities, and π-bond orders in the lower-excited states. The Mataga-Nishimoto approximation[7] was used for the calculation of two-center Coulomb integrals. All the π molecular orbitals were built into the singly excited configuration interactions, while the two bonding σ-MO's of the highest and next-highest energies and one anti-bonding σ-MO of the lowest energy were taken into account for the CI of the 2-pyridone monomer. For the CI of the 2-pyridone dimer, all the π-MO's, the four bonding σ-MO's in the order of energy from the highest occupied σ-MO, and the two anti-bonding σ-MO's in the order of energy from the lowest energy were taken into account. The oscillator strength of the n-π^* transition was calculated according to Jaffé *et al.*[6]

Results and Discussion

Dimer-formation Energy of 2-Pyridone. *Experimental*: It was assumed that the following equilibrium between the monomer and the dimer of 2-pyridone exists:

$$2A \rightleftarrows A_2. \qquad (1)$$

The equilibrium constant for the above reaction was defined by the following equation:

$$K = [A_2]/[A]^2, \tag{2}$$

where $[A_2]$ is the equilibrium concentration of the dimer and [A] is that of the monomer. The chemical shift of the N–H group moves to a lower magnetic field side as the concentration of 2-pyridone increases. The chemical shift, δ^i, of 2-pyridone in benzene-d_6 was represented by the following equation:

$$\delta^i = (1 - x^i)\delta_M + x^i\delta_D \tag{3}$$

where x^i corresponds to the mole fraction of the dimer and where δ_M and δ_D stand for the chemical shift of the monomer and dimer of 2-pyridone. The superscript, i, represents the i-th concentration of 2-pyridone. To bring the value of δ^i close to the observed value, δ^i_{obsd}, the next equation was used:

$$S = \sum_i (\delta^i_{obsd} - \delta^i)^2 \quad (i = 1,2,\cdots,n) \tag{4}$$

The K and δ_M values were determined by the trial-and-error method using Eqs. 2, 3, and 4 and the assumed value of 14.20 ppm for δ_D. In the present calculation, the value of 11.61 ppm was obtained for the chemical shift of the monomer of 2-pyridone. In Fig. 1 the values of the chemical shift, calculated by means of Eq. 3 with the assumed values of δ_M and δ_D, are plotted with the observed values for the various concentrations and temperatures. The agreement between the calculated and observed δ values seems relatively good except for the results at 42 °C. The enthalpy change, $-\Delta H$, that is, the hydrogen-bond dimer-formation energy, was obtained by plotting $\ln K$ *versus* $1/T$, as is shown in Fig. 2. The value of $-\Delta H_{obsd}$, 65.3 kJ mol^{-1}, was evaluated from Fig. 2 using the least-squares method.

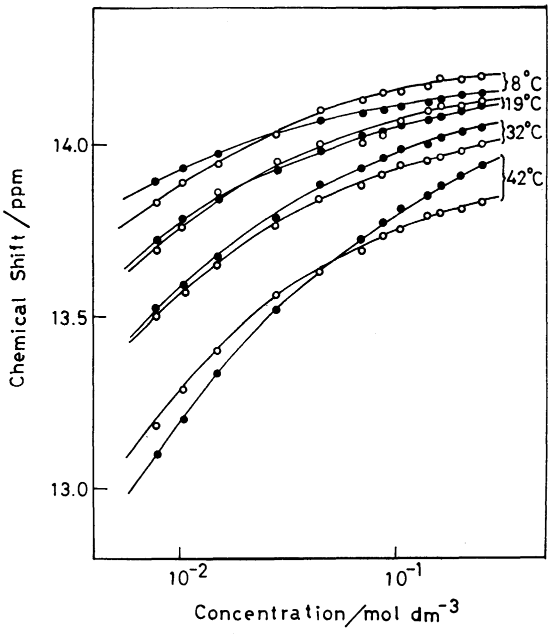


Fig. 1. The observed chemical shift (—○—) of NH proton of 2-pyridone *versus* total concentration of 2-pyridone and the calculated chemical shift (—●—) by Eq. 3. See Text.

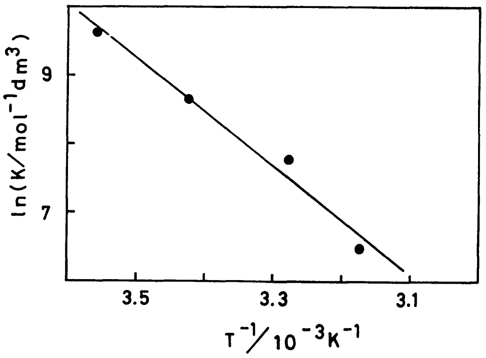


Fig. 2. Plots of ln K *vs.* $1/T$.

Theoretical: The dimer-formation energy, the π-bond order of the C=O group, the equilibrium distance, R_e, and angle, and the dipole moment of the dimer, which were obtained after the optimization of the parameters, R and θ, are given in Table 1. The optimized dimer model suggests that the 2-pyridone dimer belongs to the point group of the C_{2h} symmetry. The charge densities and π-bond orders of the 2-pyridone dimer are shown in Fig. 3. The dimer-formation energy $-\Delta H$, was 147.7 kJ mol^{-1}; the equilibrium distance, 1.35 Å, and the angle, 58.75°. The CNDO/2 method tends to overestimate the value of $-\Delta H$ and to underestimate Re.

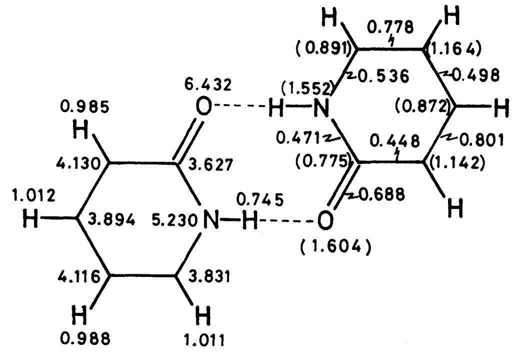


Fig. 3. Several molecular properties of 2-pyridone dimer calculated by the CNDO/2 method; the total charge densities of valence electron, π-charge densities, and π-bond orders. The values of π-charge densities are shown in parentheses.

TABLE 1. THE CALCULATED HYDROGEN-BOND ENERGY ($-\Delta H$), CORRECTED HYDROGEN-BOND ENERGY ($-\Delta H_c$), EQUILIBRIUM DISTANCE (R_e), AND ANGLE (θ), π-BOND ORDER OF THE CARBONYL GROUP ($p_{C=O}$), AND DIPOLE MOMENT (μ) OF THE 2-PYRIDONE DIMER WITH OBSERVED HYDROGEN-BOND ENERGY

Dimer	Sym.	R_e/Å	θ/°	$p_{C=O}$	μ/D	$\frac{-\Delta H}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H_c}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H_{obsd}}{\text{kJ mol}^{-1}}$
2-Pyridone	C_{2h}	1.35	58.75	0.688	0	147.7	68.2	65.3

The π-bond order of the C=O group of the dimer (0.688) is smaller than that of the monomer (0.782).[1] The IR band at 1654 cm^{-1} was assigned to the stretching vibration of the C=O group of the dimer, and the band at 1676 cm^{-1}, to that of the monomer in carbon tetrachloride.[1] This is in line with the calculated π-bond orders of the carbonyl groups of the dimer and monomer of 2-pyridone.

The charge density of the H atom of the N–H group of the dimer is smaller than that of the monomer (0.886).[1] This implies that the ^{1}H-NMR spectrum of the N–H group of the dimer may appear at a lower magnetic field than that of the monomer. The chemical shifts of the N–H group are 11.61 and 14.20 ppm for the monomer and dimer of 2-pyridone, respectively. This experimental result is in line with the theoretical result.

The present calculated value of the hydrogen-bond dimer-formation energy seems very large, although the hydrogen-bond energy calculated by the CNDO/2 method generally gives rise to values larger than the observed values.[9,10] In order to assess the reliability to be expected from the hydrogen-bond energy calculation by means of the CNDO/2 method and in order to obtain a correction factor by which to evaluate a desirable dimer-formation energy for 2-pyridone, the hydrogen-bond energies of several organic compounds were obtained theoretically by means of the CNDO/2 method and experimentally by means of the UV spectroscopic method. In the experiment, ethanol was used, but in the case of calculation, methanol was employed for the sake of simplicity.

The calculated and experimental results are listed in Table 2. When the calculated energy values are plotted against the experimental energy values, there is a good linear relationship between the calculated and experimental values. The line was determined by the least-squares method. The dimer-formation energy of 2-pyridone was obtained from the line using the calculated value of 147.7 kJ mol^{-1}. The present value of $-\Delta H_c$ was evaluated as 68.2 kJ mol^{-1}. The value of 68.2 kJ mol^{-1} is very close to the observed value. This value is larger than the dimer-formation energy of acetic acid (44.8 kJ mol^{-1}).[14] However, Hammes and Park,[15] by means of the ultrasonic absorption method, obtained 25 kJ mol^{-1} for the dimer-formation energy of 2-pyridone in chloroform. The values of 68.2 and 65.3 kJ mol^{-1} are much larger than Hammes and Park's value.[15] Chloroform is known to form a hydrogen bond. As 2-pyridone in chloroform is stabilized by a hydrogen-bond formation with the solvent, the dimer-formation energy of 2-pyridone may be smaller than it is in benzene. Another reason may be a difference in the experimental means for the measurement of the dimer-formation energy. The values of 68.2 and 65.3 kJ mol^{-1} are larger than the hydrogen-bond energy between the C=O and N–H groups which is generally observed.

TABLE 2. THE HYDROGEN-BONDING ENERGIES OBTAINED THEORETICALLY BY MEANS OF THE CNDO/2 METHOD AND EXPERIMENTALLY BY MEANS OF THE UV SPECTROSCOPIC METHOD FOR SEVERAL HYDROGEN-BONDING COMPLEXES

No.	H-Bonded complex	$-\Delta H_{\mathrm{calcd}}$ / kJ mol^{-1}	$-\Delta H_{\mathrm{obsd}}$ / kJ mol^{-1}
1	Aniline–Methanol	17.11[a]	8.8[a]
2	Crotonaldehyde –Methanol	29.37[b]	14.2[b]
3	Benzaldehyde –Methanol	29.87[b]	14.2[b]
4	Cinnamaldehyde –Methanol	29.41[b]	13.0[b]
5	Pyridine–Methanol	34.69[a]	17.6[a]
6	1-Methyl-2-pyridone –Methanol	40.71[b]	18.0[c]
7	2-Aminopyridine –Acetic acid	74.48[b]	34.7[b]
8	Acetic acid dimer	96.19[b]	44.8[d]

a) Ref. 11. b) Ref. 12. c) Ref. 13. d) Ref. 14.

The charge density of the O atom of the C=O group of the 2-pyridone monomer[1] is larger than that of the [1]benzopyrano[3,4-*c*]pyridine derivatives[9] and aldehydes.[10] The large charge density of the O atom of 2-pyridone may result in the large Coulombic interaction between the C=O and N–H groups of the 2-pyridone dimer.

TABLE 3. CALCULATED TRANSITION ENERGIES (E), WAVELENGTHS (λ), AND OSCILLATOR STRENGTHS (f) OF THE 2-PYRIDONE MONOMER

State	Sym.	E/eV	λ/nm	f	λ_{obsd}/nm
1	A''	3.595	345	0.000	
2	A'	4.330	286	0.248	305
3	A''	5.475	226	0.000	
4	A'	5.553	223	0.377	228

Electronic Structures of 2-Pyridone. In order to clarify the n,π^* state of 2-pyridone, the calculation of the transition energies and oscillator strengths of the 2-pyridone monomer was carried out by means of the CNDO/CI method. The calculated results are given in Table 3, along with the experimental values.[1] It is noteworthy that the lowest excited singlet state is of an n,π^* character and that the n-π^* transition band is expected near 350 nm for 2-pyridone. However, we could not observe any band in this region. It may be difficult to observe the corresponding band near 350 nm for the following reasons: (1) a low intensity as suggested by the calculated f value, and (2) the band position near 350 nm is too close to the strong π-π^* band in the vicinity of 300 nm, and so the n-π^* band may overlap with the first π-π^* band.

As is shown in Fig. 4, the addition of THF to the 2-pyridone in isooctane separated the monomer bands from the dimer bands. As the addition of THF results in the red-shift of the absorption band of the 2-pyridone monomer, the peak at 228 nm in isooctane may be assigned to the band maximum of the second π-π^* system of the monomer, which corresponds to the peak at 230 nm in the THF-isooctane solvent.

In order to clarify the previous assertions that the band with the maximum at 297.5 nm belongs to the dimer and that the band maximum at 305 nm corre-

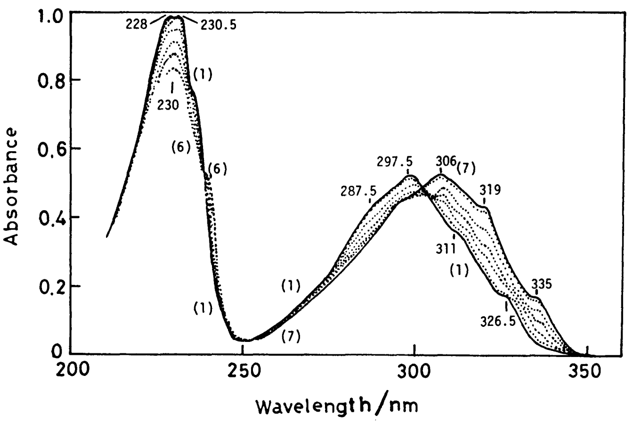


Fig. 4. The UV absorption spectrum of 2-pyridone in isooctane–THF mixed solvents at room temperature. Concentration of 2-pyridone: 1.22×10^{-4} mol dm^{-3}, concentrations of THF (mol dm^{-3}): (1) 0, (2) 4.89×10^{-2}, (3) 1.96×10^{-1}, (4) 4.98×10^{-1}, (5) 9.78×10^{-1}, (6) 4.89, (7) 7.33.

sponds to the monomer in isooctane,[1] and in order to clarify the assignment of the second band near 230 nm, the transition energy and oscillator strength of the dimer were calculated by the CNDO/CI method. The CI of 96th-orders was taken into account, including all π-MO's and six σ orbitals. The optimized equilibrium distance of 1.35 Å seems to be so short that it gives too large a hydrogen-bond energy. The equilibrium distance corresponding to the value of $-\Delta H_{\text{obsd}}$, 65.3 kJ mol^{-1}, should be longer than 1.35 Å. In the present calculation, the distances of 1.80 and 1.90 Å, which give rise to 76.27 and 61.34 kJ mol^{-1} for the values of $-\Delta H$ calculated by the CNDO/2 method, were used. The distance of the dimer with the formation energy of 65.3 kJ mol^{-1} lies between 1.80 and 1.90 Å.

The calculated transition energies and oscillator strengths for the dimer model (1.80 Å) are both listed in Table 4, because there is no essential difference between the two models with respect to the results of the CNDO/CI calculation. All the π,π^* excited states of the dimer are split into the two states of the A_g and B_u symmetries, while the n,π^* excited states are split into the two states of the B_g and A_u symmetries. A comparison of Table 3 with Table 4 shows that the 1st π-π^* transition energy of the dimer is higher than that of the monomer, but the 2nd π-π^* transition energy of the former is lower than that of the latter.

Table 4. Calculated transition energies (E), wavelengths(λ), and oscillator strengths (f) of the 2-pyridone dimer

State	Model (1.80 Å)				λ_{obsd}/nm
	Sym.	E/eV	λ/nm	f	
1	B_g	3.769	328	0	
2	A_u	3.771	328	0.000	
3	A_g	4.284	289	0	
4	B_u	4.412	281	0.469	297.5
5	B_g	5.252	236	0	
6	A_u	5.252	236	0.000	
7	B_u	5.515	224	0.893	230.5
8	A_g	5.567	222	0	
9	B_u	5.687	218	0.000	
10	A_g	5.688	218	0	

The present results, calculated by means of the CNDO/CI method and obtained by the use of the UV spectrum of 2-pyridone in the THF–isooctane system, agree with the previous band assignment of the 2-pyridone monomer and dimer.[1] Further, the calculation has clarified that the peak at 228 nm is to be assigned to the second π-π^* transition of the A′ symmetry of the monomer, and the peak at 230.5 nm, to that of the B_u symmetry of the dimer, although the assignments of those bands were unclear in the previous paper.[1]

Table 5. Energy difference between the $^1A'$ state of the monomer and the ^1B_u state of the dimer in the first and second π-π^* regions

	Energy difference between $^1A'$ and ^1B_u states in 1st- and 2nd-regions/cm^{-1}	
	(1st)	(2nd)
Dimer model (1.80 Å)	660	−310
Obsd	830	−480

In Table 5 the energy differences between the first $^1A'$ state of the monomer and the first ^1B_u state of the dimer and between the second $^1A'$ and ^1B_u states are given. The calculated energy differences between $^1A'$ and ^1B_u states for the monomer and dimer are in good agreement with the observed values.

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