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Electronic Properties and π-π^* Absorption Spectrum of 2-Pyridone

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The IR and UV absorption spectra as well as the Raman spectra of monomer and dimer of 2-pyridone were studied. The molecular weight of 2-pyridone in benzene and dimethyl sulfoxide was determined in order to examine the association. 2-Pyridone in nonpolar solvents shows two types of carbonyl stretching vibration bands due to the coexistence of the monomer and dimer. The highest wavelength UV absorption of 2-pyridone in isooctane (2,2,4-trimethylpentane) is ascribed to π-π^* electronic transitions of the monomer and dimer. The dimer absorption band appears at a higher wavenumber 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 because of the g-g Laporte forbiddance in the transition under an assumption of the molecular C_{2h} symmetry.

Equilibrium between the monomer and dimer of 2-pyridone, investigated by ultrasonic[1] and dipole moment[2] measurements, is attained in certain solvents. As regards the solvent effect on the absorption and fluorescence spectra of 1-methyl-2-pyridone, the π-π^* absorption spectra were found to shift toward short-wavelengths on the hydrogen-bonding formation of 1-methyl-2-pyridone with ethanol, this being attributed to the decrease of dipole moment in the excited states.[3]

We have observed the C=O stretching vibration bands and π-π^* absorption bands of 2-pyridone, the band assignment for the monomer and dimer of 2-pyridone being made from the results for 1-methyl-2-pyridone.[3]

Experimental

2-Pyridone was recrystallized several times from ethanol and sublimed *in vacuo* at *ca.* 120 °C. 1-Methyl-2-pyridone was purified in the same way as described previously.[3] Purification of benzene, dioxane, isooctane (2,2,4-trimethylpentane), chloroform, and ethanol was carried out by conventional methods.[4] Dimethyl sulfoxide (DMSO) was dried over a calcium chloride-calcium hydride mixture and distilled in a stream of nitrogen. The distilled DMSO was further dehydrated with a mixture of calcium hydride and molecular sieves 3A. The dehydrated DMSO was distilled at 56—57 °C in a nitrogen atmosphere of 667 Pa.

Measurement of IR and UV absorption spectra were carried out with the spectrophotometers reported.[3] The molecular weight of 2-pyridone was measured in benzene and DMSO solvents with a modified Shibayama freezing point depression equipment (SS-50$_e$-KM). The measurement was carried out six times, the concentration of 2-pyridone being in the range 10^{-3}—10^{-2} mol dm^{-3}. The errors inherent to the measurement were ±0.1%.

Methods of Calculation and Molecular Models

The dipole moments, π-bond orders, and charge densities of 2-pyridone and 1-methyl-2-pyridone in the ground state were calculated by the CNDO/2 method using the parameter given by Pople, Santry, and Segal.[5,6] The values of the bond distance and bond angle of 2-pyridone measured by Penfold[7] were used. The data were also used for the ring framework of 1-methyl-2-pyridone. For the methyl group the following values were used:

C-N: 1.48 Å, C-H: 1.096 Å, ∠HCH: 109°28′.

The P-P-P SCF-MO-CI method[8,9] was employed for calculated molecular properties such as the π-π^* transition energies, π-π^* transition oscillator strengths, π-charge densities, and π-bond orders in the lower excited states, and π-dipole moments of the monomer of 2-pyridone in the lower excited and ground states. The following empirical parameters were used:

Atom, μ	I_μ/eV	A_μ/eV
C	11.42	0.58
-NH-	27.50	11.20
=O	17.30	2.60

The value −2.50 eV was taken for all the resonance integrals of 2-pyridone. The Mataga-Nishimoto approximation[10] was used for the calculation of two-center Coulomb integrals. All singly excited configuration interactions were taken into account for the monomer.

Results and Discussion

Electronic Properties in the Ground State. The charge densities and π-bond orders of the two compounds calculated by the CNDO/2 method are given in Fig. 1. There is little difference in the charge density distributions of 2-pyridone and 1-methyl-2-pyridone except for the charge density on each nitrogen atom. The π-bond orders of the two molecules are also similar to each other.

The calculated dipole moments of 2-pyridone and 1-methyl-2-pyridone are 4.385 and 4.305 D, respectively. The observed dipole moments[2] of the latter molecule are 4.04 D in benzene and 4.07 D in dioxane. It seems that the dipole moment of 1-methyl-2-pyridone is independent of solvent. The calculated value (4.305 D) of 1-methyl-2-pyridone is in fairly good agreement with the observed values. The calculation shows that the dipole moment of 2-pyridone is close to that of 1-methyl-2-pyridone. However, the observed dipole moment of 2-pyridone is 1.73 D in benzene and 2.94 D in dioxane,[2] showing that the dipole moment of 2-pyridone changes with solvent. A large discrepancy between the values of the calculated and observed dipole moments and the dependence of the values

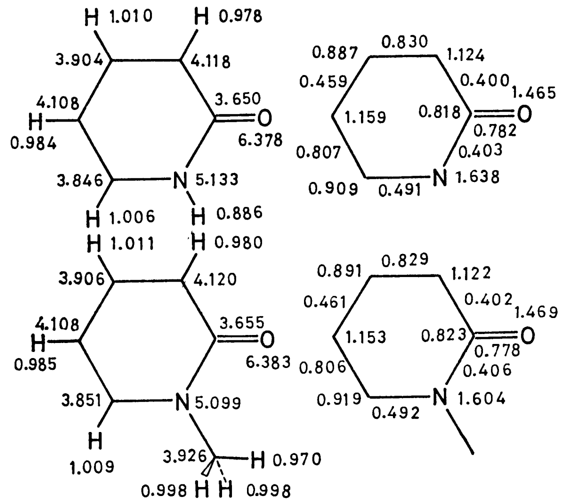

Fig. 1. Several molecular properties of 2-pyridone and 1-methyl-2-pyridone calculated by the CNDO/2 method; the total charge densities of valence electron, π-charge densities, and π-bond orders in the ground state.

of dipole moment on solvents are due to the coexistence of 2-pyridone dimer in such solutions.[1,2]

On the other hand, the IR absorption spectra of 2-pyridone and 1-methyl-2-pyridone were measured both in benzene and dioxane. The spectra in the range 1650—1700 cm^{-1} are shown in Fig. 2. 2-Pyridone shows two strong bands and 1-methyl-2-pyridone only one. The 1667 cm^{-1} IR band of 1-methyl-2-pyridone in carbon tetrachloride was assigned to the C=O stretching vibration on the basis of the band intensity and frequency-shift to the low frequency side taking place on addition of ethanol to carbon tetrachloride solution of 1-methyl-2-pyridone (Fig. 1, Ref. 3). The two bands of 2-pyridone are related to the C=O stretching vibrations of monomer and dimer as seen from their intensities and band positions. The higher-frequency band of 2-pyridone was assigned to the C=O stretching vibration of the monomer and the other to that of the dimer. The C=O stretching frequency of the monomer of 2-pyridone is thus higher than that of 1-methyl-2-pyridone. This is in line with the calculated π-bond orders of the carbonyl groups of 2-pyridone and 1-methyl-2-pyridone (Fig. 1). The IR band intensity of the monomer relative to that of the dimer increases with change of solvent from benzene to dioxane. On the assumption that the molar absorption coefficient of the C=O group of the dimer is approximately equal to that of the monomer, we conclude that the concentration of dimer is higher than that of monomer in benzene, and *vice versa* in dioxane. This is in line with the change of dipole moments observed in these solvents.[2] For the sake of comparison we have measured the bands of 2-pyridone in the range 1650—1700 cm^{-1} in isooctane and chloroform. The result in each case is similar to that of benzene (Figs. 2(1), (3), and (6)).

When the dimer of 2-pyridone belongs to the point group of the C_{2h} symmetry, its 66 normal vibrations are grouped into the following four species.

$$\Gamma = 23A_g + 10B_g + 11A_u + 22B_u$$

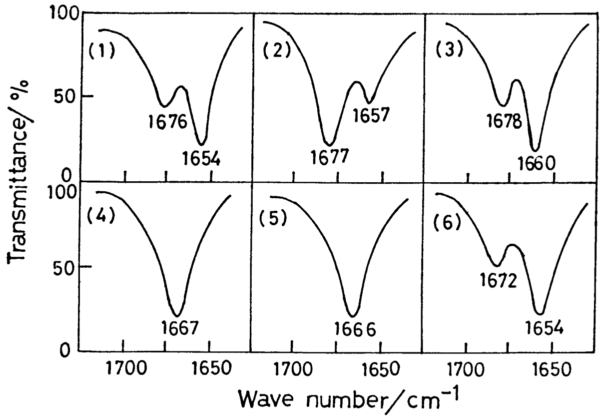

Fig. 2. The IR C=O absorption bands of 2-pyridone (1.2×10^{-2} mol dm^{-3}) and 1-methyl-2-pyridone (1.1×10^{-2} mol dm^{-3}) in various solvents:
(1) 2-Pyridone in benzene, (2) 2-pyridone in dioxane, (3) 2-pyridone in isooctane, (4) 1-methyl-2-pyridone in benzene, (5) 1-methyl-2-pyridone in dioxane, (6) 2-pyridone in chloroform. A cell of 0.5 mm path length was used.

Table 1. IR and Raman spectra of 2-pyridone

IR[a,b] (cm^{-1})	Raman[a,c] (cm^{-1})
1672 s	
1654 s	
	1625 w
1616 s	
1540 w	1539 m
1468 m	1462 m
1438 m	
1375 w	1374 m
	1256 s
1152 m	1153 w
1095 w	1096 w
	1008 w
990 m	988 w
903 w	
875 w	
840 w	841 s
	613 m
557 m	549 m
	460 w
	387 w

a) s, Strong; m, medium; w, weak. b) 4.6×10^{-2} mol dm^{-3} in chloroform, c) 1 mol dm^{-3} in chloroform.

The vibrations with species A_g and B_u belong to the in-plane vibration and the others to the out-of-plane vibration. The vibrations with species A_g and B_g are Raman-active, the others being infrared-active.

In order to ascertain whether the dimer belongs to the point group of C_{2h} or not, we measured the Raman spectrum of 2-pyridone† in chloroform. The results are given in Table 1. Both the IR band at 1654 cm^{-1} and the Raman band at 1625 cm^{-1} were assigned to the stretching vibration of the C=O groups of the dimer, the former being strong and the latter

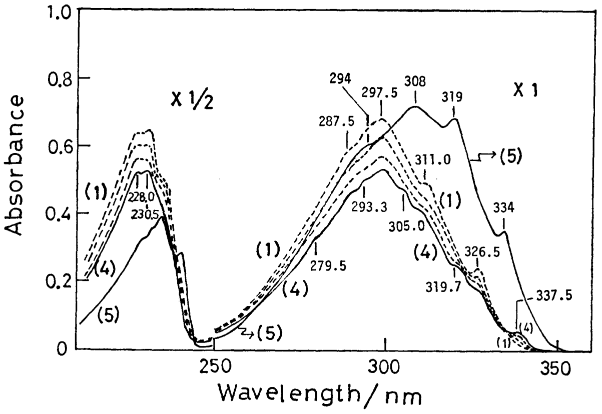

Fig. 3. The UV absorption spectra of 2-pyridone in isooctane solution with UV absorption spectrum of 1-methyl-2-pyridone in isooctane solution: (1) 1.68×10^{-3} mol dm^{-3} 2-pyridone, 1 mm cell, (2) 1.68×10^{-4} mol dm^{-3} 2-pyridone, 10 mm cell, (3) 3.36×10^{-5} mol dm^{-3} 2-pyridone, 50 mm cell, (4) 1.68×10^{-5} mol dm^{-3} 2-pyridone, 100 mm cell, (5) 1.0×10^{-4} mol dm^{-3} 1-methyl-2-pyridone, 10 mm cell.

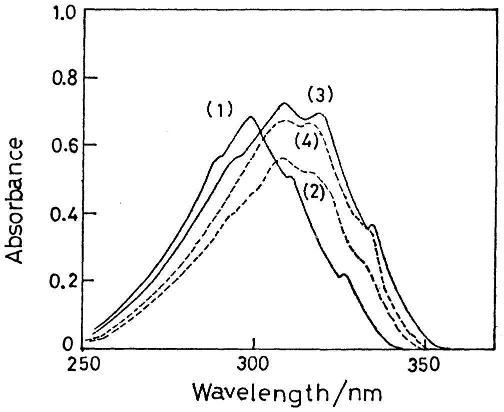

Fig. 4. The UV absorption spectra of 2-pyridone (1.6×10^{-3} mol dm^{-3}) and 1-methyl-2-pyridone (1.0×10^{-3} mol dm^{-3}): (1) 2-pyridone in isooctane, (2) 2-pyridone in DMSO, (3) 1-methyl-2-pyridone in isooctane, (4) 1-methyl-2-pyridone in DMSO. A cell of 1 mm path length was used.

weak. If the 2-pyridone dimer has the C_{2h} symmetry, the former should be assigned to the B_u species and the latter to the A_g species. No band was found in the Raman spectrum near 1672 cm^{-1} at which the carbonyl stretching band of the monomer was observed in the IR spectrum. The C=O band of the monomer might be too weak to be observed in the Raman spectrum, since the concentration of monomer is smaller than that of the dimer in chloroform. The 2-pyridone dimer seems to belong to the point group of C_{2h}. The fact that the dipole moment of 2-pyridone decreases with the change of solvent from dioxane to benzene also seems to support the interpretation that the 2-pyridone dimer belongs to the point group of C_{2h}.

π-π^* Absorption Spectrum of 2-Pyridone. The UV spectrum of 2-pyridone in isooctane in the concentration range 10^{-5}—10^{-3} mol dm^{-3} is shown in Fig. 3. In spectrum (1), the first π-π^* absorption system of 2-pyridone in the range 355—250 nm consists mainly of four vibrational bands. The first one appears at 326.5 nm, the second at 311.0 nm, the third at 297.5 nm corresponding to the band maximum, and the fourth at near 288 nm. Let us call these vibrational bands band system A. The concentration of 2-pyridone in spectrum (4) is 10^{-2} times lower than that of 2-pyridone in spectrum (1). In spectrum (4) band system A appears clearly, the other vibrational bands being observed at 337.5, 319.7, 305.0, 293.3, and 279.5 nm. Let us call these new vibrational bands band system B.

On the other hand, the first π-π^* absorption system of 1-methyl-2-pyridone shows the vibrational bands at 334, 319, 308, and 294 nm (Fig. 3(5)). The vibrational band at 308 nm is the band maximum of this system. The four bands seem to be related with the respective vibrational bands of 2-pyridone in isooctane, *i.e.*, the bands at 337.5, 319.7, 305.0, and 293.3 nm. The absorption spectra of 2-pyridone and 1-methyl-2-pyridone may be expected to be similar in their spectral features, since the π-charge densities and π-bond orders of 2-pyridone and 1-methyl-2-pyridone calculated by the CNDO/2 method are approximately equal to each other (Fig. 1). Good correspondence is seen between band system B of 2-pyridone and the vibrational bands of the first π-π^* absorption of 1-methyl-2-pyridone (Fig. 3).

In order to confirm which of the two molecular species of 2-pyridone is responsible for the appearance of band system B, we measured the absorption spectra of 2-pyridone and 1-methyl-2-pyridone in DMSO (Fig. 4). Each vibrational band position/intensity of 1-methyl-2-pyridone in isooctane solution is close to that in DMSO solution. The vibrational band features of 2-pyridone in DMSO are close to those of band system B (spectrum (4), Fig. 3). For the sake of comparison the molecular weight of 2-pyridone was determined by means of freezing point depression, benzene and DMSO being used as solvent. The observed values in benzene and DMSO are 217.1 and 96.3, respectively. The former is 2.28 times greater than the calculated molecular weight 95.1 and the latter almost equal to it, suggesting that 2-pyridone exists mainly as a dimer in the benzene soild solution although some associated complexes larger than a dimer may be formed, while 2-pyridone exists mainly as a monomer in the DMSO solid solution. The UV spectrum of 2-pyridone in DMSO is related to the monomer species of 2-pyridone. Band system B may be due to the monomer species, since its vibrational band position is close to that of 2-pyridone in DMSO (spectrum (4), Fig. 3). Band system A may thus be ascribed to the dimer species (Fig. 3). The band at 305.0 nm seems to be the maximum of the monomer band (Fig. 4). The energy difference of the maxima of the monomer and dimer

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† The measurement, made at the laboratory of Prof. M. Ito, Tohoku University, was carried out in chloroform since the solubility of 2-pyridone in carbon tetrachloride is low.

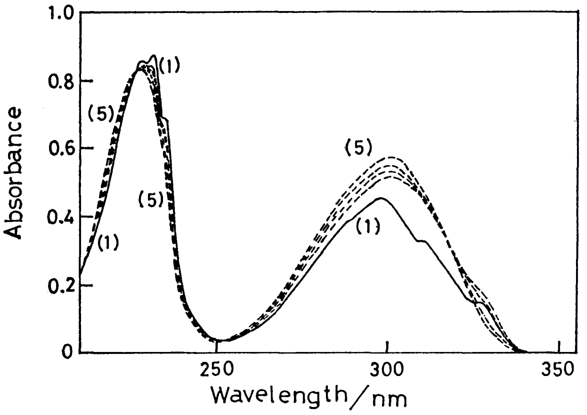

Fig. 5. The UV absorption spectra of 2-pyridone in isooctane-ethanol mixed solvents at room temperature.
Concentration of 2-pyridone: 2.19×10^{-4} mol dm^{-3}. Concentrations of ethanol (mol dm^{-3}): (1) 0, (2) 7.0×10^{-2}, (3) 1.5×10^{-1}, (4) 5.0×10^{-1}, (5) 2.0.

absorptions is *ca.* 830 cm^{-1}.

The second π-π* absorption system of 2-pyridone appears near 230 nm (Fig. 3). The concentration effect on the system is not so clear as the first one. As shown in spectrum (4) of Fig. 3, the band maximum of the second system apparently splits into two (228.0 and 230.5 nm), although a similar splitting is also observed in spectrum (1). The splitting energy is *ca.* 480 cm^{-1}.

The UV spectrum of 2-pyridone changes with a change in the concentration of ethanol (Fig. 5). The band maximum of the first π-π* absorption system shifts toward longer-wavelengths with increase in the amount of ethanol, the second π-π* absorption system, *e.g.*, the peak at 228.0 nm, shifting toward shorter-wavelengths accompanied by intensity decrease. When ethanol is added to an isooctane solution of 2-pyridone, the shift direction of the first band is opposite that of the first band of 1-methyl-2-pyridone.[3]

The π-π* transition of the monomer is related to the excited state of A′ symmetry under the point group of the symmetry C_s, and that of dimer to the excited states of the A_g and B_u symmetries under the point group of the C_{2h} symmetry. Transition from the ground to the excited A_g state of the dimer is symmetry-forbidden, whereas transition to the excited B_u state is allowed by the dipole selection rule. Dimer formation gives rise to the paired excited states essentially based on the monomer electronic state. One of the states is lower in energy than the original monomer state and the other is higher if there is no remarkable difference between the solvent effects on the two molecular species. We have tentatively assigned the vibrational band at 337.5 nm to the 0-0 band of the first π-π* absorption band of the 2-pyridone monomer, since the vibrational band at 337.5 nm is a member of system B which appears in DMSO solution. 2-Pyridone exists in DMSO almost as a monomer. The observed band maximum of the 2-pyridone dimer at 297.5 nm seems to correspond to the second π-π* absorption band of the dimer with the B_u symmetry which is produced by the splitting of the monomer states on the formation of the dimer. The first π-π* absorption band of the dimer would thus correspond to the electronic transition to the ^1A_g state. However, it might be difficult to observe the first π-π* absorption band of the dimer due to the symmetry-forbidden band by a dipole selection rule. It is hard to decide which of the peaks at 230.5 and 228.0 nm in the second absorption band belongs to the vibrational band of the dimer; one belongs to the peak of the monomer band and the other to that of the dimer as judged by the experimental results.

Table 2. Calculated transition energies (E), oscillator strength (f), and π-dipole moments (μ) of the singlet π,π* excited states of 2-pyridone monomer with π-dipole moment in the ground state

State	E/eV	λ/nm	f	μ/D	λ_{obsd}/nm
G	0	0	0	4.680	
1	4.022	308	0.257	2.502	305.0
2	5.356	231	0.334	2.492	
3	6.590	188	0.194	2.966	
4	6.703	185	0.664	4.905	

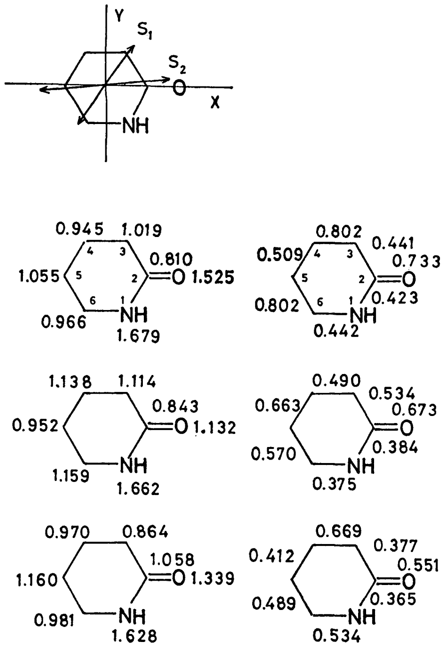

Fig. 6. The calculated π-charge densities and π-bond orders of 2-pyridone in S_0, S_1, and S_2. These calculations are based on the P-P-P SCF-MO-CI method. The uppermost drawing of this figure denotes the direction and the magnitude of the predicted dipole moments.

The transition energies, oscillator strengths and π-dipole moments in the excited states calculated by the P-P-P SCF-MO-CI method for the monomer of 2-pyridone are given in Table 2. The π-dipole moment of the monomer is larger in the ground state than in the excited states except for the fourth-excited state. The calculated results suggest that the first and second π-π^* absorption bands of the 2-pyridone monomer might move toward the shorter-wavelength side on the hydrogen-bonding formation with ethanol. This might be reasonable from the solvent effect on the absorption and fluorescence spectra of 1-methyl-2-pyridone.3) However, the first absorption band maximum of the 2-pyridone–ethanol system shifts to the longer-wavelength side (Fig. 5). This is opposite the shift of the first absorption band of the 1-methyl-2-pyridone–ethanol system, the band maximum of the 2-pyridone–ethanol complex being located at a longer-wavelength than that of the 2-pyridone dimer, and the former at a shorter-wavelength side than the band maximum of the monomer. Addition of ethanol to the isooctane solution of 2-pyridone disturbs the equilibrium between the monomer and dimer of 2-pyridone. The hydrogen-bonded monomer of 2-pyridone with ethanol may increase and the dimer may decrease in concentration with an increase of ethanol. Thus, the band maximum of 2-pyridone moves to the longer-wavelength side, but the shift of the band maximum depends on the concentration of the dimer, monomer, and monomer–ethanol complex.

The directions of transition moment for the first and second excited states, π-charge densities, and π-bond orders calculated by the P-P-P. SCF-MO-CI method for the ground and excited states of the 2-pyridone monomer are shown in Fig. 6. There is a large difference in the π-bond order and π-charge density of the ground and first excited states. The calculated π-bond orders suggest that there is a large change in bond length between the ground and first-excited states, which is similar to the result for polyenals. A large deformation of the ring framework between the ground and first excited states may give rise to the band broadening of 2-pyridone (Fig. 3) as shown in polyenal11) and fulvene spectra.12)

The photochemical dimerization property13) of 2-pyridone in the first-excited state can be attributed to an increase in π-charge density at the C_3 and C_6 atoms and in π-bond order between the C_4 and C_5 atoms.

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