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Electronic Structures of Pyridinols and of Their Anions and Cations

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Electronic structures of the lactim and lactam forms of 2-, 3-, and 4-pyridinols, and of their anions and protonated cations were calculated by a modified CNDO-CI (mCNDO-CI), CNDO/S-CI, and a modified π-SCF-MO-CI methods. The theoretical results agree well with the observed spectra of both the neutral and ionic species, and predict satisfactorily the shorter wavelength shift of lower excited π-π^* and n-π^* bands of the lactim form compared to the corresponding bands of the lactam form. The π-π^* assignment to the lowest triplet states of 2- and 4-pyridones, and of 2- and 3-pyridinols, together with the n-π^* assignment to the lowest singlet state of 4-pyridone was predicted by the mCNDO-CI method, in agreement with the suggestion based on emission properties. The orbital energies calculated by the mCNDO method were compared with the observed photoelectron spectra; the results show that the fourth highest occupied orbital is π-orbital in 2- and 3-pyridinols, and σ-orbital in 4-pyridinol and 4-pyridone.

N-heterocyclic compounds having hydroxy substituents show the lactim-lactam tautomerism. This is important in photochemical reaction and in molecular biology. The electronic structure of uracil has recently been studied theoretically in our previous paper.[1] For pyridinols which are the simplest hydroxy-substituted *N*-heterocyclic compounds, quantum mechanical studies have been devoted to the estimation of the relative stabilities of the tautomers and to the assignment of the electronic spectra using the semiempirical methods considering π-electrons[2-6] or all-valence electrons,[6-9] as well as the nonempirical SCF-LCAO-MO method.[8,10] However, as far as we are aware, the neutral and ionic forms of pyridinols have not been studied systematically by any all-valence electron (AVE) SCF-MO-CI methods. The aim of the present paper is to apply both the AVE-SCF-MO-CI and π-SCF-MO-CI methods to understand the electronic structures and spectra of different forms of pyridinols and of their ions. Ultraviolet photoelectron spectra (UPS) of neutral forms of the molecules are also discussed in comparison with the calculated orbital energies.

Theoretical

The details of a modified CNDO-CI (mCNDO-CI) method and a modified π-SCF-MO-CI (mPPP) method, as well as the semiempirical parametrization in these methods are described in previous papers.[1,11,12] In the mPPP method a polarizable σ-core is introduced in the evaluation of the π-electron Hartree-Fock matrix elements.[1]

The molecular structures of the lactim and lactam forms of isomeric pyridinols were the same as in a previous paper[10] and they are shown in Fig. 1, together with the coordinate system. The molecular structures of the anions were assumed to be the same as those of the corresponding neutral forms except that the proton of either N–H (in the lactam forms) or O–H (in the lactim forms) was removed. In the case of protonated cations the additional proton was located at either the nitrogen atom (in the lactim forms) or at the oxygen atom (in the lactam forms) with the assumed distance of the proton-protonated atom to be equal to 1.03 or 1.00 Å, respectively.

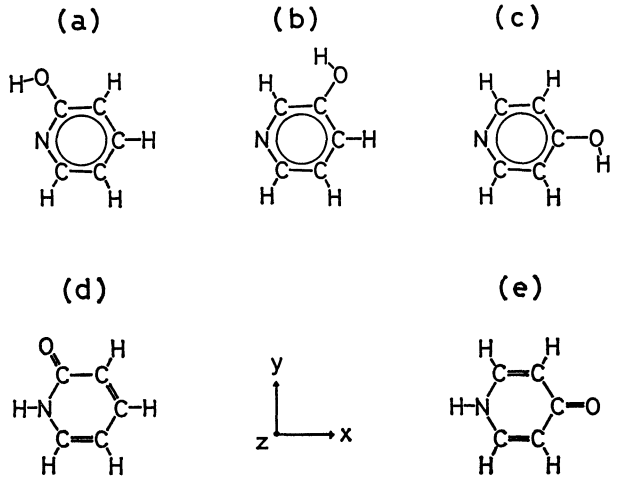

Fig. 1. Molecular structures of (a) 2-pyridinol, (b) 3-pyridinol, (c) 4-pyridinol, (d) 2-pyridone, and (e) 4-pyridone, and coordinate system.

Results and Discussion

Electronic Structures of Pyridinols. Electronic structures of the lactam and lactim forms of 2-, 3-, and 4-pyridinols have been calculated by the mCNDO-CI, the original CNDO/S-CI,[13] and the mPPP methods. The theoretical results calculated by the mCNDO-CI and mPPP methods are compared with the corresponding experimental data[2,9,14-16] in Tables 1—3. Electronic spectra of the lactam form (*i.e.*, 2- and 4-pyridones) are predicted well by all the three methods. In the case of 4-pyridone, the first π-π^* absorption band is predicted to be composed of two π-π^* bands. Both the AVE methods predict the weak first π-π^* band to appear on the longer wavelength side of the strong 2nd π-π^* band, whereas the mPPP method predicts the reverse order of the two π-π^* states.

Electronic structures of the lactim form of 2- and

Table 1. Singlet and triplet transition energies ($^1\Delta E$/eV and $^3\Delta E$/eV) and oscillator strengths (f) calculated and observed for 2-pyridone and 2-pyridinol

Assignment	mCNDO-CI			mPPP		Obsd[b]	
	$^1\Delta E$	$^3\Delta E$	f[a]	$^1\Delta E$	f	$^1\Delta E$	f
2-Pyridone							
n-π^*		2.73	0.001 (z)				
π-π^*	4.07	2.14	0.211 (y)	4.53	0.325	4.09—4.28	0.12
n-π^*		4.56	0.002 (z)				
π-π^*	5.40	3.10	0.308 ($x\bar{y}$)	5.48	0.148	5.40—5.60	0.14
σ-π^*		5.75	0.001 (z)				
π-σ^*		6.39	0.019 (z)				
σ-π^*		6.69	0.004 (z)				
n-π^*		6.89	0.000_3 (z)				
π-π^*	6.92	4.54	0.009 (xy)	6.58	0.301		
σ-π^*		7.00	0.001 (z)				
π-σ^*		7.07	0.015 (z)				
π-π^*	7.29	5.85	0.241 ($\bar{x}$Y)	6.92	0.156		
2-Pyridinol							
n-π^*		3.90	0.005 (z)				
n-π^*		5.07	0.000 (z)				
π-π^*	5.38	3.52	0.096 (y)	4.59	0.099	4.54—4.59	0.11
π-π^*	6.11	4.40	0.171 (X$\bar{y}$)	5.85	0.136	5.72—5.79	0.14
σ-π^*		6.39	0.001 (z)				
σ-π^*		6.97	0.000 (z)				
n-π^*		7.01	0.004 (z)				
π-π^*	7.09	4.80	0.480 (Xy)	6.84	1.014	6.77	(26000)[c]
π-π^*	7.35	5.99	0.682 ($\bar{x}$Y)	6.92	0.939		
π-σ^*		7.83	0.000_2 (z)				

a) Oscillator strength is calculated for the singlet manifold. The direction of transition moment is shown in parentheses, x-, y-, and z-axes being taken as is shown in Fig. 1. When the transition moment has both x- and y-components, the larger one is designated by capital letter. x-Component with negative sign is designated as $\bar{x}$, and y-component, as $\bar{y}$. b) Refs. 2, 6, 9, 14, and 15. c) Molar extinction coefficient at the band maximum is shown in parentheses.

Table 2. Singlet and triplet transition energies ($^1\Delta E$/eV and $^3\Delta E$/eV) and oscillator strengths (f) calculated and observed for 4-pyridone and 4-pyridinol

Assignment	mCNDO-CI			mPPP		Obsd[b]	
	$^1\Delta E$	$^3\Delta E$	f[a]	$^1\Delta E$	f	$^1\Delta E$	f
4-Pyridone							
n-π^*		2.06	0				
n-π^*		4.26	0.005 (z)				
π-π^*	4.65	2.08	0.029 (y)	4.85	0.557	4.77—4.86	0.21
π-π^*	4.84	3.08	0.559 (x)	4.99	0.050		
σ-π^*		5.50	0.001 (z)				
n-π^*		5.87	0				
π-π^*	6.42	4.13	0.128 (y)	5.93	0.143	>6.2	
π-σ^*		6.46	0.005 (z)				
σ-π^*		6.76	0				
π-π^*	7.09	5.26	0.064 (x)	7.30	0.575		
4-Pyridinol							
n-π^*		3.95	0.006 (z)				
n-π^*		5.10	0.000 (z)				
π-π^*	5.58	3.54	0.003 (y)	4.71	0.015	5.17—5.27[c]	
σ-π^*		5.81	0.000 (z)				
π-π^*	6.14	4.69	0.055 (x)	5.79	0.063	5.58	0.15
σ-π^*		6.22	0.000 (z)				
π-π^*	6.86	4.80	0.598 (y)	6.63	0.908		
π-π^*	6.89	5.42	0.724 (x)	6.69	1.148		
n-π^*		7.36	0.007 (z)				
σ-π^*		7.95	0.001 (z)				

a) See footnote (a) in Table 1. b) Refs. 2, 14, and 15. c) Shoulder.

Table 3. Singlet and triplet transition energies ($^1\Delta E$/eV and $^3\Delta E$/eV) and oscillator strengths (f) calculated and observed for 3-pyridinol

Assignment	mCNDO-CI			mPPP		Obsd[b]	
	$^1\Delta E$	$^3\Delta E$	f[a]	$^1\Delta E$	f	$^1\Delta E$	f
σ-π^*		3.68	0.005 (z)				
σ-π^*		4.94	0.000 (z)				
π-π^*	5.34	3.45	0.090 ($\bar{x}$Y)	4.56	0.091	4.44—4.51	0.07
π-π^*	5.98	4.32	0.130 (xy)	5.76	0.125	5.64—5.77	0.13
σ-π^*		6.29	0.002 (z)				
σ-π^*		6.67	0.001 (z)				
π-π^*	6.93	4.74	0.518 (x)	6.76	0.989		
σ-π^*		7.07	0.004 (z)				
π-π^*	7.19	5.82	0.647 (y)	6.85	0.931		
π-σ^*		7.71	0.000 (z)				
π-π^*	8.16	6.54	0.038 (xY)				

a) See footnote (a) in Table 1. b) Refs. 2, 9, and 14.

3-pyridinols are predicted satisfactorily by the mPPP and CNDO/S-CI methods. The mCNDO-CI method predicts the first π-π^* band to be 0.4—0.8 eV higher than the observed values. This is due to overestimation ($\approx$0.8 eV) in transition energy of the first π-π^* band of the reference molecules (*i.e.*, of benzene, phenol, and pyridine)[17] by the use of the semiempirical parameters adopted in the present calculation. Electronic structure of 4-pyridinol is predicted less satisfactorily by all the three methods compared with the ones of 2- and 3-pyridinols. Absorption bands of lower excited π-π^* (and n-π^*) states of the lactim form shift to shorter wavelengths than the corresponding bands of the lactam form. This is well reproduced by the three methods as is listed in Tables 1 and 2.

The assignment of the lowest excited state is important to understand the photophysical properties of substituted pyridines. In mCNDO-CI method, calculated transition energy for n-π^* state corresponds to that of the triplet manifold.[11] Considering the underestimation ($\approx$0.7 eV) of transition energy of the ^{3}n-π^* state,[1] calculated results by mCNDO-CI method listed in Tables 1—3 clearly predict the lowest triplet state is π-π^* state for 2-pyridone, 2-pyridinol, 3-pyridinol, and 4-pyridone in agreement with the suggestion based on phosphorescence quantum yield and lifetime.[22] In mCNDO-CI method, transition energy of the first ^{1}n-π^* state may be estimated to be $\approx$1.7 eV (or less) higher than the calculated value for the triplet manifold when we consider the singlet-triplet separation energy[1] of $\approx$1 eV (or less) and underestimation of ^{3}n-π^* transition energy ($\approx$0.7 eV).[1] In 2-pyridone, 2-pyridinol, and 3-pyridinol, energy separation between the first $^1\pi$-π^* and the first ^{3}n-π^* states is calculated to be 1.3—1.7 eV. Therefore, the calculation shows that the first $^1\pi$-π^* state locates near to the first ^{1}n-π^* state. However, owing to the approximations employed, it is difficult to decide which is the lowest excited singlet state. In 4-pyridone, the lowest excited singlet state is safely assigned to n-π^* state in agreement with the suggestion based on fluorescence properties.[22]

Electronic Structures of the Anions and Cations of Pyridinols. Two different molecular structures based on the neutral parent molecules of either the lactam or lactim forms were assumed for each ionic species. Difference in calculated results between the two structures is due to the changes in geometrical structure and in mesomeric structure. As is shown in Tables 4 and 5, the difference in calculated π-π^* transition energies is more significant for the mPPP method (0.1—0.5 eV) than for the AVE method (0—0.2 eV). This is due to the fact that the electronic structures calculated by π-SCF-MO-CI method are much more sensitive to the assumed mesomeric structure of a system, *i.e.*, to the assumed numbers of π-electrons on each atom. However, in mPPP method, the mesomeric effect is reduced in some extent compared to the original PPP method, because consideration of σ-polarizable core in mPPP method partly cancels the effect of change in mesomeric structures.

In Table 4, the calculated results by the mCNDO-CI and mPPP methods are tabulated for the anions which are derived from the lactim forms of pyridinols. Compared with the results of the neutral molecules listed in Tables 1—3, the first n-π^* states of 2-, 3-, and 4-pyridinolate anions in Table 4 are shifted toward longer wavelengths (by $\approx$0.8 eV by mCNDO-CI method) by deprotonation. n-Orbitals pertinent to the first n-π^* states of the anions are localized on O atom, while those of pyridinols on N atom, thus the character of the first n-π^* state being changed. The third n-π^* states in 2-, 3-, and 4-pyridinolate anions have essentially n(N)-π^* character (calculated at 4.89, 4.37, and 4.21 eV, respectively, by mCNDO-CI method). Therefore, by deprotonation, n(N)-π^* state shifts toward shorter wavelength (by 0.3—1.0 eV by mCNDO-CI method). In the case of 4-pyridone and its anion, the first n-π^* states correspond to n(O)-π^* state. As in the case of n(N)-π^* state, n(O)-π^* state also shifts toward shorter wavelength (by 0.8 eV by mCNDO-CI method) by deprotonation. The first two π-π^* bands of the lactim forms were observed to shift toward longer wavelengths (by 0.3—0.5 eV) by deprotonation.[14-16] This is correctly predicted by the present calculations.

Table 4. Singlet and triplet transition energies ($^1\Delta E$/eV and $^3\Delta E$/eV) and oscillator strengths (f) calculated and observed for 2-, 3-, and 4-pyridinolate anions[a)]

Assignment	mCNDO-CI			mPPP		Obsd[c)]	
	$^1\Delta E$	$^3\Delta E$	f[b)]	$^1\Delta E$	f	$^1\Delta E$	ε[d)]
2-Pyridinolate anion[a)]							
n-π^*		3.11 (2.73)	0.000_4 (z)				
n-π^*		3.50	0.000_1 (z)				
π-π^*	3.97	2.88	0.093 (xy)	4.28 (4.10)	0.140 (0.152)	4.26	5070
n-π^*		4.89	0.013 (z)				
π-π^*	4.93	3.04	0.422 ($\bar{x}$Y)	5.40 (5.18)	0.383 (0.407)	5.39	9000
n-π^*		5.38	0.000 (z)				
σ-π^*		5.93	0.006 (z)				
σ-π^*		6.24	0.001 (z)				
π-σ^*		6.57	0.000_1 (z)				
π-π^*	6.68	4.25	0.008 (y)	6.40 (6.48)	0.148 (0.482)		
π-π^*	6.80	5.12	0.022 ($\bar{x}$Y)				
3-Pyridinolate anion							
n-π^*		2.91	0.000_2 (z)				
n-π^*		3.33	0.000_1 (z)				
π-π^*	3.84	2.63	0.103 ($\bar{x}$y)	4.16	0.126	4.16	4960
n(σ)-π^*		4.37	0.014 (z)				
π-π^*	4.70	2.91	0.361 (xY)	5.19	0.352	5.25	11000
n(σ)-π^*		5.56	0.001 (z)				
σ-π^*		6.15	0.000_1 (z)				
π-σ^*		6.39	0.008 (z)				
π-π^*	6.54	4.24	0.009 (y)	6.17	0.299		
σ-π^*		6.58	0.003 (z)				
π-π^*	6.74	5.09	0.112 (Xy)				
π-π^*	6.88	5.70	0.056 (y)				
4-Pyridinolate anion[a)]							
n-π^*		3.18 (2.84)	0				
n-π^*		4.02	0.001 (z)				
n-π^*		4.21	0.012 (z)				
π-π^*	4.26	2.92	0.071 (y)	4.59 (4.40)	0.014 (0.064)	4.77	2200
n-π^*		4.75	0				
π-π^*	4.92	3.32	0.421 (x)	5.23 (4.84)	0.360 (0.612)	5.19	14150
n-π^*		6.45	0				
σ-π^*		6.47	0.000 (z)				
π-π^*	6.57	4.22	0.113 (y)	6.06 (6.53)	0.514 (0.103)		
π-σ^*		6.64	0.017 (z)				
π-π^*	6.71	5.38	0.198 (x)				
π-π^*	6.94	5.38	0.258 (x)				

a) Molecular structures based on the corresponding lactim forms were employed in the calculations. For the purpose of comparison, calculated results for the ions, molecular structures of which are based on the lactam forms were listed in part in parentheses. b) See footnote (a) in Table 1. c) Refs. 2 and 16. d) Molar extinction coefficient at the band maximum.

As is shown in Table 5, theoretical calculations for the protonated cations predict satisfactorily the shorter wavelength shift of the first n(σ)-π^* state by protonation. The first two π-π^* bands of the lactam forms are correctly predicted to shift to shorter wavelengths by protonation in agreement with observations.[16)]

Orbital Assignment in UPS of Pyridinols. Ionization potentials (IP's) of the lactam and lactim forms of pyridinols were evaluated by the mCNDO method according to Koopmans' theorem.[23)] The results are shown in Fig. 2, compared with the observed values in ultraviolet photoelectron spectra (UPS).[24)] In the

TABLE 5. SINGLET AND TRIPLET TRANSITION ENERGIES ($^1\Delta E$/eV AND $^3\Delta E$/eV) AND OSCILLATOR STRENGTHS (f) CALCULATED AND OBSERVED FOR THE PROTONATED CATIONS OF 2-, 3-, AND 4-PYRIDINOLS[a)]

Assignment	mCNDO-CI			mPPP		Obsd[c)]	
	$^1\Delta E$	$^3\Delta E$	f[b)]	$^1\Delta E$	f	$^1\Delta E$	ε[d)]
Cation of 2-pyridinol[a)]							
π-π*	4.94 (4.87)	3.57 (3.42)	0.245 (y) (0.281)	4.37 (4.55)	0.280 (0.424)	4.48	6950
σ-π*	5.29		0.001 (z)				
σ-π*	6.06		0.000_3 (z)				
π-π*	6.12 (6.04)	3.84 (3.82)	0.117 (x) (0.154)	5.83 (5.71)	0.110 (0.112)	5.93	3600
σ-π*	6.41		0.001 (z)				
σ-π*	7.14		0.000_4 (z)				
π-π*	7.24	4.97	0.694 (x)	6.71	0.913		
π-σ*	7.36		0.001 (z)				
π-π*	7.79	6.00	0.311 (y)				
σ-π*	7.88		0.002 (z)				
Cation of 3-pyridinol							
π-π*	4.84	3.25	0.211 (y)	4.37	0.248	4.38	5840
σ-π*	4.97		0.001 (z)				
σ-π*	5.75		0.000 (z)				
π-π*	5.91	3.77	0.057 (xy)	5.67	0.048	5.58	3730
σ-π*	6.13		0.000 (z)				
π-π*	6.80	4.61	0.704 (Xy)	6.63	0.908		
σ-π*	7.00		0.000_2 (z)				
π-σ*	7.20		0.001 (z)				
π-π*	7.55	5.78	0.450 (y)				
π-σ*	7.90		0.001 (z)				
Cation of 4-pyridinol[a)]							
σ-π*	5.07		0.000 (z)				
π-π*	5.44 (5.56)	4.00 (3.96)	0.141 (y) (0.101)	4.64 (4.81)	0.142 (0.446)	5.30	9800
π-π*	5.91 (5.68)	4.02 (4.12)	0.188 (x) (0.317)	5.60 (5.34)	0.095 (0.018)		
σ-π*	5.94		0.000_2 (z)				
σ-π*	6.24		0.000_2 (z)				
π-π*	6.88	4.40	0.392 (y)	6.59	1.081		
σ-π*	6.92		0.000_3 (z)				
π-π*	6.99	5.39	0.766 (x)				
σ-π*	7.79		0.000_2 (z)				
π-σ*	7.83		0.000 (z)				

a) See footnote (a) in Table 4. b) See footnote (a) in Table 1. c) Refs. 2, 14, and 16. d) Molar extinction coefficient at the band maximum.

figure, the calculated and observed values for pyridine[25)] are also shown for the purpose of comparison. A good correlation between observed and calculated values for pyridinols (Fig. 2a) and pyridones (Fig. 2b) clearly indicates that the order of the first three highest occupied molecular orbitals is π>n>π for 2- and 3-pyridinols, and 2- and 4-pyridones in agreement with the assignment by Cook, *et al.*[24)] Assignments to the fourth and fifth bands in UPS have not yet been established for pyridinols and pyridones. In pyridine, the fifth IP (which is from π-orbital)[25)] was calculated to be $\approx$2.5 eV higher by the present calculation. When we adjust the relative shift of the calculated fourth and fifth IP's, a good correlation can be obtained in Fig. 2a between the observed and calculated IP's for pyridinols, indicating that the fourth and fifth bands in UPS are π- and σ-orbitals, respectively, for both 2- and 3-pyridinols, and that the fourth band of 4-pyridinol is σ-orbital. From the correlation diagram in Fig. 2b, the fourth band of 4-pyridone can safely be assigned to σ-orbital, and the one of 2-pyridone, plausibly to σ-orbital, too.

From the orbital energy calculations by the CNDO/S method, a correlation diagram which is qualitatively similar to the one in Fig. 2 was obtained. Although the sequence in the calculated molecular orbitals by the CNDO/S method is partly incorrect, the argument mentioned to Fig. 2 also holds in the results by the CNDO/S method, and the same conclusion as to the orbital assignment in UPS could be drawn.

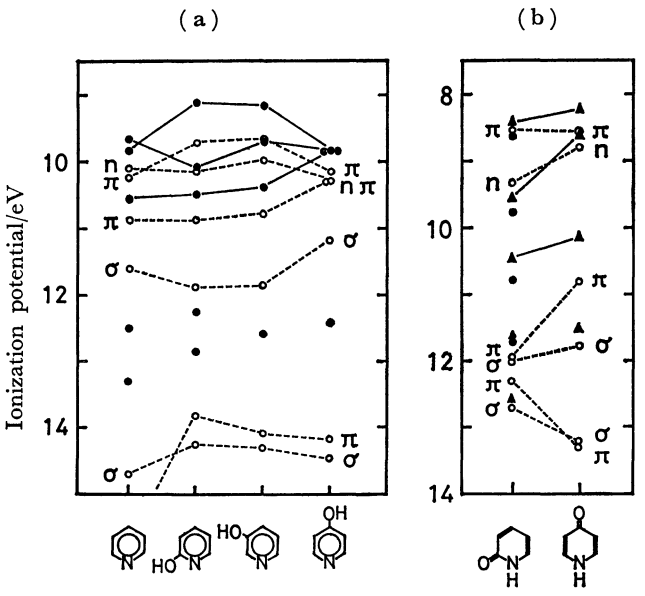

Fig. 2. Ionization potentials (IP's/eV) observed in UPS (●) and calculated by mCNDO method (○) for (a) pyridine, and 2-, 3-, and 4-pyridinols, and (b) 2- and 4-pyridones. ▲; IP's observed for 1-methyl-2(or 4)-pyridone.

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