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Electronic Structures of Uracil and Its Anions

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Electronic structures of uracil and its anions were theoretically investigated by a modified CNDO-CI method. Theoretical results were in good agreement with the observed spectra of uracil and of both the uracil-3-ide and uracil-1-ide anions, indicating that the second π-π^* band of uracil may tentatively be assigned to the 215 nm band observed in circular dichroism spectrum, and that the lowest singlet and triplet states of uracil are n-π^* and π-π^* states, respectively, in accord with the observed solvent dependence on emission properties. The first π-π^* band of uracil-1-ide anion was correctly predicted by the method at longer wavelengths than the corresponding band of uracil-3-ide anion. For the purpose of comparison, a modified INDO-CI, CNDO/S-CI, and a modified π-SCF-MO-CI methods were also applied to the molecules under consideration. The results were only partly successful in predicting the observed spectra.

Electronic structures and spectra of pyrimidinic nucleic acid bases and their model compounds have been studied extensively from experimental and theoretical points of view.[1,2] As for uracil and thymine, electronic spectra were predicted less satisfactorily by the semiempirical calculations[1–7] compared with the results for other pyrimidinic bases.[1,2,8] This is partly because the σ-core charge in atomic valence state usually taken to be an integral number in π-electron approximation changes significantly in the actual molecule by redistribution of σ-electrons over the whole molecule,[9] and is partly related to the unestablished band assignment concerning the 215 nm band observed in circular dichroism (CD) spectrum of uridine.[10]

The ordering of the lowest n-π^* and π-π^* states is important in understanding the photophysical properties of nucleic acid bases. Fluorescence and phosphorescence lifetimes and quantum yields of uracil and thymine were found to be largely affected by a variety of solvents.[11] The experimental results strongly suggested that in aprotic solvents the lowest singlet state is of highly forbidden character.[11] Theoretical investigation of the lowest excited state is necessary in order to interpret the photophysical properties of uracil.

Studies on the electronic structure of anionic species are few.[1,4,9,12] In aqueous alkaline solution, uracil exists as a mixture of two monoanionic species (*i.e.*, uracil-3-ide and uracil-1-ide anions) of comparable amounts.[1] The electronic spectra of these monoanions differ from each other, particularly in the nearest ultraviolet (UV) region.[13,14] The relative positions of the first π-π^* band of the anions could not be predicted correctly by the CNDO/S calculation.[9]

Under these circumstances, in order to interpret satisfactorily the experimental results, the electronic structures of uracil and of its anions have been investigated by a modified CNDO-CI method[15] by employing new semiempirical parameters for C, N, and O atoms. The calculated results have been compared with the observed results and also with the theoretical ones calculated by CNDO/S-CI method,[16] a modified INDO-CI method,[17] and a modified π-SCF-MO-CI method[9,18] which considers the effect of σ-core charge in the π-electron approximation.

Theoretical

Modified CNDO-CI Method. A modified CNDO-CI (mCNDO-CI) method[15] was applied by evaluating the two-center Coulomb repulsion integrals by Nishimoto-Mataga approximation.[19] To choose the best semiempirical parameters, various sets of the bonding parameters (β^0's) and one-center Coulomb repulsion integrals (γ_{AA}'s) which consider several atomic valence states of C, N, and O atoms were tested in the preliminary calculations of benzene, pyridine, pyrrole, aniline, formaldehyde, and phenol. Considering the agreement with the observed orbital sequences[21–25] and transition energies,[26–30] the semiempirical parameters listed in Table 1 were finally employed in the present paper. In the course of the preliminary calculations, it was found that the adoption of the Nishimoto-Mataga equation instead of the Klopman's equation[20] results in an SCF procedure that often converges very slowly and sometimes practically does not converge at all. Taking the one-center Coulomb repulsion integrals of σ-AO's to be equal to those of π-AO's, as in the case of CNDO/S method,[16] is in some cases necessary and in others effective in improving convergence of the SCF procedure. The parameters for N atom were mainly

TABLE 1. ONE-CENTER COULOMB REPULSION INTEGRAL (γ_{AA}/eV) AND BONDING PARAMETER (β_A^0/eV)) FOR H, C, N, AND O ATOMS USED IN THE MODIFIED CNDO-CI METHOD

	H	C		N		O	
		σ-AO	π-AO	σ-AO	π-AO	σ-AO	π-AO
γ_{AA}	12.85	10.60	10.60	12.03	12.03	14.67	14.67
β_A^0	−12.0	−16.8	−12.1	−23.2	−16.4	−31.4	−20.4

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determined from the calculated result of pyridine. Somewhat different parameters for N atom are acceptable in pyrrole and aniline, but for simplicity of the following calculations the same set of the semi-empirical parameters were used for all the valence states of N atom.

The $(I+A)/2$ values needed for the evaluation of one-center core matrix elements,[15,31] $U_{\mu\mu}$, were taken to be the same as the original values[31] for C and N atoms, and for O atom to be 24.390 eV for the 2s AO and 8.111 eV for the $2p_x$, $2p_y$, and $2p_z$ AO's as in a previous paper.[15]

In the configuration interaction (CI) treatment, 40 singly excited π-π^* and σ-σ^* configurations, 23—25 singly excited π-σ^* configurations, and 20 singly excited n-π^* and σ-π^* configurations were taken into account.

Modified π-SCF-MO-CI (mPPP) Method. In order to avoid the problems which appear in the description of anionic forms of heterocyclic molecules within the original π-SCF-MO-CI (Pariser-Parr-Pople) method,[32,33] the modification in view of polarizable σ-core was introduced[9] in the evaluation of core integral, W_i, core potential, V_i, and resonance integrals, β_{ij}. The modified diagonal and off-diagonal elements[9,18,34] of the π-electron Hartree-Fock matrix are

$$F_{ii} = \left(1 + \kappa \frac{\delta Z_i}{Z_i}\right) [- I_i - (n_i - 1)\gamma_{ii}] + 1/2\, P_{ii}\gamma_{ii}$$

$$+ \sum_{j \neq i} \left[P_{jj} - \left(1 + \frac{\delta Z_j}{Z_j}\right) n_j\right] \gamma_{ji},$$

and

$$F_{ij} = \beta_{ij}\left[1 + 0.5\left(\frac{\delta Z_i}{Z_i} + \frac{\delta Z_j}{Z_j}\right)\right] - 1/2\, P_{ij}\gamma_{ij},$$

where Z_i is the formal core charge with integral number in the valence state of isolated atom, i, and δZ_i stands for the change of σ-charges introduced by redistribution of σ-electrons over the whole molecule. The symbol κ denotes the empirical "scaling" parameter which has been fixed[9] to be 0.85 in the present calculation.

A more precise expression for the diagonal element, F_{ii}, which includes penetration integrals shows that the expression for the one-center Coulomb integral for the difinite atom i (*i.e.*, from which a proton was removed) in the anionic species differs from that in the neutral species. The integral for atom i in the anion decreases mainly by the penetration integral between atom i and removed proton. For a series of hydroxypyridines,[34] the decrease of the integral for N atom was calculated to be of the order 2.7—3.1 eV. In the present calculation for the uracil anions, an average value of 3.0 eV was taken as the decrement of the integral for the N_3 or N_1 atom. This means that in the case of the anions, the ionization potential, I_i, for N_3 or N_1 atom was increased by 3.0 eV compared to the

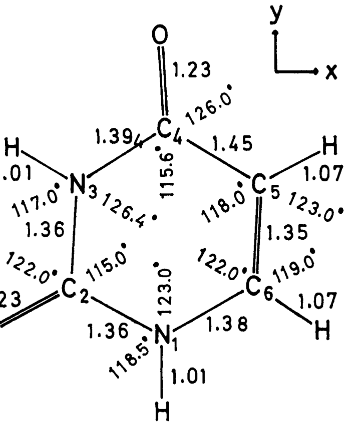

Fig. 1. Molecular structure of uracil, numbering of atoms, and coordinate system.

TABLE 2. SINGLET AND TRIPLET TRANSITION ENERGIES ($^1\Delta E$/eV AND $^3\Delta E$/eV) AND OSCILLATOR STRENGTHS (f) CALCULATED AND OBSERVED FOR URACIL

Assignment	mCNDO-CI				CNDO/S-CI		INDO-CI			mPPP		Obsd	
	$^1\Delta E$		$^3\Delta E$	f[a]	$^1\Delta E$	f	$^1\Delta E$	$^3\Delta E$	f	$^1\Delta E$	f	$^1\Delta E$	(f)
n-π^*		2.74		0.001 (z)	3.42		3.65	3.20	0.000_4				
n-π^*		3.62		0.000 (z)	4.09		4.37		0.000				
π-π^*	5.28		2.80	0.359 (y)	5.42	0.214	5.13	3.21	0.371	5.00	0.288	5.08[b] 4.79	(0.16)[c]
n-π^*		5.34		0.000_4(z)	6.19		6.52		0.000_4				
n-π^*		5.81		0.000_1(z)	6.81								
π-π^*	5.95		3.66	0.095 (xY)	6.34	0.048	5.88	4.25	0.199	5.78	0.221	5.77[d]	
π-π^*	6.17		4.01	0.176 (X$\bar{y}$)	6.54	0.108	6.29		0.379	5.92	0.385	6.05[b] 6.14	(0.26)[c]
π-π^*	6.59		5.72	0.283 (xY)	7.26	0.264	6.57		0.496	6.49	0.518	6.63[b] 6.85[c]	
n-π^*		6.67		0.004 (z)									
π-σ^*		6.67		0.010 (z)	7.49								
σ-π^*		7.09		0.004 (z)									
π-σ^*		7.31		0.061 (z)									
π-π^*	7.38		6.64	0.007 (x)	7.49	0.057							
π-σ^*		7.60		0.013 (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) Observed value in the vapor phase; Ref. 39. c) Observed value in aqueous solution at pH=7; L. B. Clark and I. Tinoco, Jr., *J. Am. Chem. Soc.*, **87**, 11 (1965). d) Observed value in the CD spectrum of uridine; Ref. 10.

value of I_i for the neutral molecule. The two-center Coulomb repulsion integrals were evaluated by the Nishimoto-Mataga equation. The other semiempirical parameters adopted in the present mPPP method are the same as used previously.[35,36] In the CI treatment, all the singly excited configurations were taken into account.

Molecular Structure. Considering the results of X-ray crystal analysis[37] and of theoretical calculation,[38] molecular structure of uracil was assumed as is shown in Fig. 1. The molecular structures of uracil-3-ide and uracil-1-ide anions were assumed to be the same as the one of the neutral molecule, except that one proton bonded to N_3 and N_1 atoms, respectively, was removed.

Results and Discussion

The electronic structures of uracil calculated by mCNDO-CI, CNDO/S-CI, INDO-CI, and mPPP methods are presented in Table 2. Comparison of the result calculated by mCNDO-CI method with the observed spectrum in the vapor phase[39] and with the CD spectrum[10] strongly suggests that the first, third, and fourth π-π* states predicted at 5.28, 6.17, and 6.59 eV, respectively, can be assigned to the 244 nm (5.08 eV), 205 nm (6.05 eV), and 187 nm (6.63 eV) bands in the vapor phase,[39] respectively. The weak second π-π* band predicted at 5.95 eV may correspond to the 215 nm (5.77 eV) band in the CD spectrum.[10]

As tabulated in Table 2, INDO-CI and mPPP methods predict that the transition energies for π-π* states agree semiquantitatively well with the result by mCNDO-CI method, but the transition intensity to the second π-π* state is not weak. CNDO/S-CI method, on the other hand, predicts the second π-π* band being weak, although the calculated transition energies for π-π* states are high. The theoretical result presented by only one of the above three methods is not conclusive to support any assignments of the spectrum (see Ref. 1 for more detailed discussion of the excited states of uracil), bu they altogether suggest that the assignment based on mCNDO-CI method mentioned above is a plausible one for uracil.

Table 3. Occupied molecular orbital energies/eV calculated and observed for uracil

Assignment	Obsd[a)]	Calcd[b)] mCNDO	CNDO/S[c)]	INDO[d)]
π_1	9.55	9.56	9.5$_7$	11.4$_6$
n_1	10.15	9.82	10.5$_7$	12.0$_0$
π_2	10.65	10.29	11.0$_1$	12.4$_0$
n_2	11.12	10.37	11.5$_1$	12.8$_7$
π_3	12.63	13.24	13.4$_0$	18.7$_7$

a) Vertical ionization potential (I_V) taken from HeI photoelectron spectrum; Ref. 41. b) Minus sign of the occupied orbital energy (ε) is omitted. From Koopmans' theorem, $I_V = -\varepsilon$ holds. c) Ref. 42. d) Ref. 41.

The ordering of the lowest π-π* and n-π* states is important to understand the photophysical properties of pyrimidine bases.[11] In mCNDO-CI method, calculated transition energies for n-π*, σ-π*, and π-σ* states correspond to those of the triplet manifold.[15] Preliminary calculation of formaldehyde by mCNDO-CI method has shown that the calculated transition energy (2.31 eV) of the lowest n-π* triplet state is ≈0.7 eV lower than the observed value (3.0 eV).[40] Considering this underestimation of transition energy of the n-π* triplet state, nearly degenerate n-π* and π-π* triplet states of uracil predicted at ≈2.8 eV by mCNDO-CI method can be ordered as the π-π* state being the lowest triplet in agreement with the suggestion by Becker *et al.*[11] The singlet-triplet separation of n-π* state is expected to be ≈1 eV or less. In the singlet manifold, the n-π* state is predicted to be lower than the first π-π* state. This agrees with the prediction based on fluorescence lifetime measurement.[11]

In Table 3, the orbital energies calculated by mCNDO method are compared with the observed and theoretical values reported previously.[41,42] The predicted order of the occupied molecular orbitals, π>n>π>n>π, is in

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

<table>
<tr><th rowspan="2">Assignment</th><th colspan="3">mCNDO-CI</th><th colspan="2">CNDO/S-CI</th><th colspan="3">INDO-CI</th><th colspan="2">mPPP</th><th colspan="2">Obsd[b)]</th></tr>
<tr><th>$^1\Delta E$</th><th>$^3\Delta E$</th><th>f[a)]</th><th>$^1\Delta E$</th><th>f</th><th>$^1\Delta E$</th><th>$^3\Delta E$</th><th>f</th><th>$^1\Delta E$</th><th>f</th><th>$^1\Delta E$</th><th>f</th></tr>
<tr><td>n-π*</td><td colspan="2">2.39</td><td>0.000 (z)</td><td>3.24</td><td></td><td>3.28</td><td>3.14</td><td>0.000$_3$</td><td></td><td></td><td></td><td></td></tr>
<tr><td>n-π*</td><td colspan="2">3.64</td><td>0.002 (z)</td><td>4.31</td><td></td><td>4.34</td><td></td><td>0.000</td><td></td><td></td><td></td><td></td></tr>
<tr><td>n-π*</td><td colspan="2">3.82</td><td>0.000 (z)</td><td>4.45</td><td></td><td>4.79</td><td></td><td>0.000</td><td></td><td></td><td></td><td></td></tr>
<tr><td>π-π*</td><td>4.57</td><td>3.31</td><td>0.111 (xy)</td><td>4.19</td><td>0.032</td><td>4.30</td><td>3.18</td><td>0.102</td><td>4.72</td><td>0.025</td><td>4.68</td><td>0.15</td></tr>
<tr><td>n-π*</td><td colspan="2">4.80</td><td>0.001 (z)</td><td>5.41</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>π-π*</td><td>5.14</td><td>3.73</td><td>0.023 ($\bar{x}$Y)</td><td>5.24</td><td>0.013</td><td>4.82</td><td>3.79</td><td>0.020</td><td>5.33</td><td>0.395</td><td>≈5.4[c)]</td><td></td></tr>
<tr><td>n-π*</td><td colspan="2">5.54</td><td>0.012 (z)</td><td>5.94</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>π-π*</td><td>5.80</td><td>2.84</td><td>0.728 (y)</td><td>6.06</td><td>0.637</td><td>6.05</td><td></td><td>1.218</td><td>5.38</td><td>0.454</td><td>>5.8</td><td></td></tr>
<tr><td>n-π*</td><td colspan="2">6.29</td><td>0.004 (z)</td><td>6.40</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>π-π*</td><td>6.36</td><td>5.13</td><td>0.136 (Xy)</td><td>7.04</td><td>0.093</td><td>6.82</td><td></td><td>0.209</td><td>5.82</td><td>0.664</td><td></td><td></td></tr>
<tr><td>π-σ*</td><td colspan="2">6.69</td><td>0.013 (z)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>σ-π*</td><td colspan="2">6.81</td><td>0.000$_2$(z)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>π-π*</td><td>6.94</td><td>6.25</td><td>0.025 (x$\bar{y}$)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>σ-σ*</td><td>7.06</td><td>6.91</td><td>0.016 (y)</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

a) See footnote (a) in Table 2. b) Observed value for 1-methyluracil-3-ide anion; Ref. 13. c) Shoulder.

TABLE 5. SINGLET AND TRIPLET TRANSITION ENERGIES ($^1\Delta E$/eV AND $^3\Delta E$/eV) AND OSCILLATOR STRENGTHS (f) CALCULATED AND OBSERVED FOR URACIL-1-IDE ANION

Assignment	mCNDO-CI			CNDO/S-CI		INDO-CI			mPPP		Obsd[b)]	
	$^1\Delta E$	$^3\Delta E$	f[a)]	$^1\Delta E$	f	$^1\Delta E$	$^3\Delta E$	f	$^1\Delta E$	f	$^1\Delta E$	f
n-π*	3.11		0.001 (z)	3.85		3.67	3.40	0.001				
n-π*	3.48		0.000_4(z)	4.13		4.85		0.001				
n-π*	4.00		0.003 (z)	4.44		5.45		0.001				
π-π*	4.38	2.89	0.347 (xY)	4.31	0.220	4.50	2.88	0.431	4.41	0.366	4.39	0.17
π-π*	5.59	3.52	0.246 (x)	5.74	0.172	5.62	3.88	0.352	5.52	0.278	5.69	0.17
n-π*	5.68		0.003 (z)	6.39								
n-π*	5.80		0.000 (z)	6.66								
π-π*	6.15	5.21	0.044 (y)	6.75	0.002	6.28		0.220	5.93	0.175		
n-π*	6.28		0.012 (z)	6.98								
π-σ*	6.50		0.016 (z)									
π-π*	6.65	4.39	0.030 (xy)	6.93	0.034	6.62		0.130	6.44	0.635		
n-π*	6.81		0.001 (z)									
π-π*	6.87	6.31	0.115 (xy)									
n-π*	7.33		0.001 (z)									

a) See footnote (a) in Table 2. b) Observed value for 3-methyluracil-1-ide anion; Ref. 13.

good agreement with the result by photoelectron spectroscopy.[41,42)]

The dipole moment of the ground state calculated by mCNDO method is 4.60 Debye,** in agreement with the observed value (4.16 Debye in dioxane).[43)]

Tables 4 and 5 present the calculated results for uracil-3-ide and uracil-1-ide anions, respectively. As can be seen from the tables, the agreement between the observed[13,14)] and predicted values for uracil-1-ide anion is satisfactory by all the methods presented here, but the spectrum of uracil-3-ide anion[13,14)] can be predicted satisfactorily only by mCNDO-CI method. It is worth noting that the first π-π* band of uracil-1-ide anion is correctly predicted at longer wavelengths than the corresponding band of uracil-3-ide anion only by mCNDO-CI and mPPP methods. CNDO/S-CI method as well as INDO-CI method failed to predict the first π-π* band position of uracil-3-ide anion. Very recent calculation using CNDO/S-CI method[4)] has predicted correctly the absorption band positions of both monoanions of uracil; however the authors have not described the details of the parametrization of the method.

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** 1 Debye=3.333×10^{-30} C m.

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