Theoret. chim. Acta (Berl.) 6, 320—332 (1966)

Electronic Structures and Spectra of Adenine and Thymine

MASASHI TANAKA*, and SABURO NAGAKURA

The Institute for Solid State Physics, the University of Tokyo, Tokyo, Japan

Received August 2, 1966

The near and vacuum ultraviolet spectra of adenine and thymine were measured with the evaporated film method and in solution. The absorption spectrum of the adenine anion in basic solution was also measured. The assignment of the absorption bands was made by comparing the observed transition energies and intensities with the theoretical results obtained by the LCAO-SCF-CI-method. The results indicated that the longest wavelength band of adenine at 269 mμ is a $\pi \rightarrow \pi^*$ transition band. This was supported by the fact that a new band due to the $n \rightarrow \pi^*$ transition was found at 278 mμ for the adenine anion. Furthermore, it was shown that the thymine molecule may interact strongly with the solvent molecules and that the electronic structure of thymine in solution may be different from that of the free molecule.

Die UV-Spektren von Adenin und Thymin in Lösung bzw. als dünne Filme wurden bis 160 mμ herunter gemessen, außerdem das Spektrum vom Adenin-Anion in basischer Lösung. Auf Grund der Ergebnisse einer LCAO-SCF-CI-Rechnung wurde eine Zuordnung der Banden vorgenommen. Danach ist die langwellige Bande bei 269 mμ ein $\pi \rightarrow \pi^*$-Übergang, die neue Bande des Adenin-Anions bei 278 mμ dagegen ein $n \rightarrow \pi^*$-Übergang. Die Elektronenstruktur von Thymin kann durch das Lösungsmittel stark beeinflußt werden.

Les spectres dans l'ultraviolet proche de l'adénine et de la thymine ont été mesurés avec la méthode du film évaporé et en solution. Le spectre d'absorption de l'anion adénine en solution basique a été aussi mesuré. L'identification des bandes d'absorption a été faite en comparant les énergies de transition et les intensités observées avec les résultats théoriques obtenus par la méthode LCAO-SCF-CI. Les résultats indiquent que la bande de plus grande longueur d'onde de l'adénine à 269 mμ, qui a été considérée comme une transition $n \rightarrow \pi^*$ par certains auteurs, est une bande de transition $\pi \rightarrow \pi^*$. Ceci est confirmé par le fait qu'une nouvelle bande, dûe à la transition $n \rightarrow \pi^*$, a été observée à 278 mμ pour l'anion adénine. De plus, on a montré que la molécule de thymine peut interagir fortement avec les molécules de solvant et que la structure électronique de la thymine en solution peut être différente de celle de la molécule libre.

Introduction

Investigations of the electronic structures of base components of nucleic acids are of importance in connection with the biological activities of desoxyribonucleic acid (DNA) and ribonucleic acid (RNA). The electronic absorption spectra of some purine and pyrimidine bases have been studied by several workers from both experimental and theoretical points of view.

MASON [*10*], VOET et al. [*28*], and CLARK and TINOCO [*1*a] measured the solution spectra of some of the bases and made the effort to systematize their absorption bands. NAKANISHI et al. [*13*] measured the absorption spectra of uracils at various pH's. STEWART and DAVIDSON [*25*] measured the polarized absorption spectra of single crystals of 9-methyl adenine, 1-methyl

---

* Present address: Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan.

thymine and the adenine (A) – thymine (T) dimer. Furthermore, Pullman et al. [*20*], and Ladik et al. [*6*] calculated the π-electronic structures of base components by means of the Hückel MO method. Semi-empirical SCF-MO calculations were also carried out by Veillard and Pullman [*27*], Nesbet [*14*], Nagata et al. [*12*], Ladik and Appel [*6*a], and Berthod et al. [*1*].

The aim of the present work is to obtain a more detailed knowledge about the π-electronic structures of adenine and thymine by extending the measurement of their spectra to the vacuum ultraviolet region (down to 160 mμ), and by comparing the observed absorption bands with the theoretical results obtained by the LCAO-SCF-CI calculation. In particular it has been undertaken to give a conclusion on the assignment of the 269 mμ band of adenine which was discussed from two different stand-points: from the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.

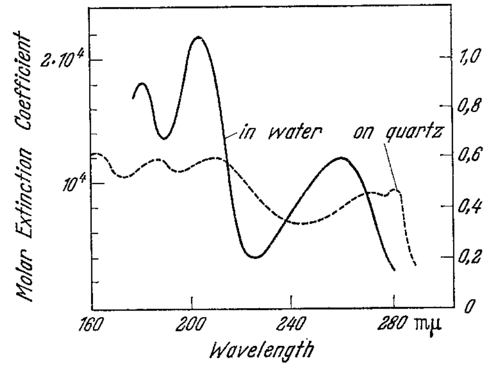

Fig. 1

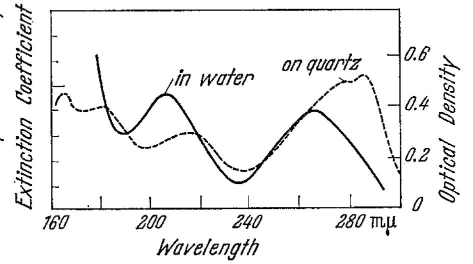

Fig. 2

Fig. 1. Absorption spectra of adenine measured with the aqueous solution and with the evaporated film

Fig. 2. Absorption spectra of thymine measured with the aqueous solution and with the evaporated film

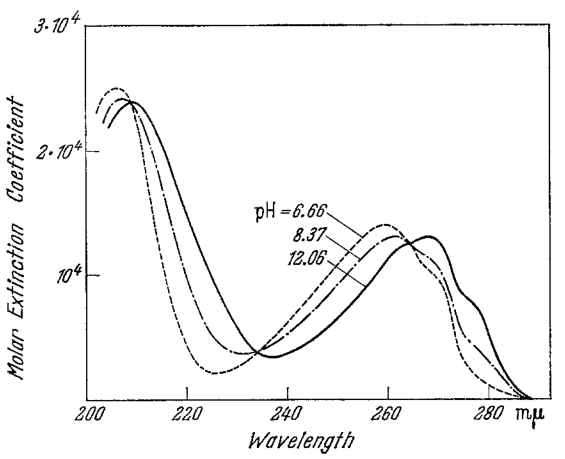

Fig. 3

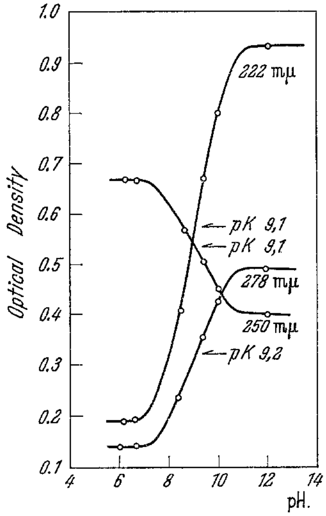

Fig. 4

Fig. 3. Absorption spectra of adenine at various pH's

Fig. 4. Adenine: variation of the intensity with pH

Experimental

Commercially available adenine and thymine were purified by vacuum sublimation.

The ultraviolet absorption spectra down to 190 mμ were measured with a Cary recording spectrophotometer, model 14M, a quartz cell of 1 cm light-path length being used for the measurements of solution spectra. A vacuum ultraviolet spectrophotometer constructed in our laboratory [26] was used for the measurements in the vacuum ultraviolet region. In this case, a quartz cell 0.01 cm thick was used for the measurements of solution spectra. The solution spectra are consistent with the results obtained by Voet et al. [28] and by Clark and Tinoco [1].

The measurements of near and vacuum ultraviolet absorption spectra were also made with thin films which were prepared by vacuum evaporation of samples on thin quartz plates. The thin films were used to extend the measurement to 160 mμ.

The observed absorption spectra are shown in Figs. 1 and 2. Furthermore the ultraviolet spectra of adenine at various pH values are recorded in Fig. 3, and the pH dependence of the intensities of the first two bands of adenine is shown in Fig. 4. The pK value of adenine was determined to be 9.2 and the spectra of the basic aqueous solution will safely be due to the adenine anion.

Theoretical

In the present study, a semi-empirical LCAO-SCF-CI method similar to Pariser, Parr, and Pople's [15, 19] was applied to the π-electron structures of adenine and thymine, Clementi's [2] SCF-AO's being used as basic atomic orbitals.

First of all, the zero-differential overlap approximation will be briefly discussed. This problem has already been discussed by Löwdin [8], McWeeny [11], Rüdenberg [23], Parr [17], Lykos [9], and Fischer-Hjalmars [3]. We will discuss the relation between the Pariser-Parr-Pople method and Roothaan's [21] LCAO-SCF method from a viewpoint somewhat different.

The molecular orbitals φ_i can be written as linear combinations of Löwdin's orthogonalized orbitals

$$\varphi_i = \sum_p \chi'_p \, C'_{pi}$$

where $\chi'_p = \sum_q \chi_q \, (1 + S)^{-1/2}_{pq}$, χ_q is an SCF-AO on the atom q, and $(1 + S)$ is the overlap matrix with elements

$$S_{pq} = -\delta_{pq} + \int \chi_p(1)\, \chi_q(1)\, dv_1 \, .$$

The coefficients C'_{pi} are determined by the SCF method leading to the following equation:

$$\sum_p \langle \chi'_q \,|\, F \,|\, \chi'_p \rangle \, C'_{pi} = C'_{qi} \, \varepsilon_i$$

or

$$F' \, C' = C' \, \varepsilon' \, .$$

The elements of the matrix F' include the following six types of integrals: I'_{pp}, I'_{pq}, $(pp \,|\, pp)'$, $(pp \,|\, qq)'$, $(pq \,|\, rr)'$ and $(pq \,|\, rs)'$ where

$$I'_{pq} = \int \chi'_p(1) \, I \, \chi'_q(1) \, dv_1$$

and

$$(pq \,|\, rs)' = \iint \chi'_p(1)\, \chi'_q(1) \, \frac{1}{r_{12}} \, \chi'_r(2) \, \chi'_s(2) \, dv_1 \, dv_2 \, .$$

By expanding Löwdin's orbitals in terms of the SCF atomic orbitals and by using Mulliken's approximation for the electron repulsion integrals, the above-mentioned integrals can be represented by those over the atomic orbitals as follows:

$$\alpha_p \equiv I'_{pp} = I_{pp} - \sum_a S_{pa}\{I_{ap} - \tfrac{1}{2} S_{ap}(I_{pp} + I_{aa})\} + \tfrac{1}{4}\sum_a S_{pa}^2 (I_{pp} - I_{aa}) ,$$

$$\begin{aligned}\beta_{pq} \equiv I'_{pq} = I_{pq} &- \tfrac{1}{2} S_{pq}(I_{pp} + I_{qq}) - \tfrac{1}{2}\sum_{a\neq q} S_{pa}\{I_{aq} - \tfrac{1}{2} S_{aq}(I_{qq} + I_{aa})\} + \\ &+ \tfrac{1}{8}\sum_a S_{pa} S_{aq}(I_{qq} - I_{aa}) - \tfrac{1}{2}\sum_{a\neq p} S_{aq}\{I_{pa} - \tfrac{1}{2} S_{pa}(I_{pp} + I_{aa})\} + \\ &+ \tfrac{1}{8}\sum_a S_{pa} S_{aq}(I_{pp} - I_{aa}) ,\end{aligned}$$

$$\begin{aligned}(pp \mid pp)' &= (pp \mid pp) + \tfrac{1}{2}\sum_a S_{pa}^2 \{(pp \mid pp) - (pp \mid aa)\} , \\ (pp \mid qq)' &= (pp \mid qq) + \tfrac{1}{4}\sum_a S_{pa}^2\{(pp \mid qq) - (aa \mid qq)\} + \tfrac{1}{4}\sum_a S_{aq}^2\{(pp \mid qq) - (pp \mid aa)\} , \\ (pq \mid rr)' &= \tfrac{1}{8}\sum_a S_{pa} S_{aq}\{(qq \mid rr) + (pp \mid rr) - 2(aa \mid rr)\} , \\ (pq \mid rs)' &= S^3 \text{ terms.}\end{aligned}$$

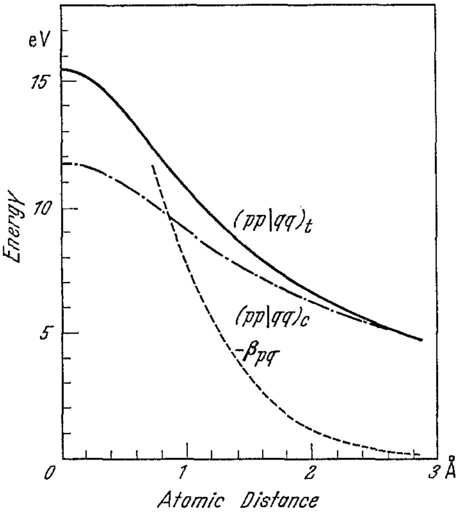

Fig. 5. The core resonance integral β_{pq} and the Coulomb repulsion integral $(pp \mid qq)$ vs. the atomic distance r_{pq}

In the π-electron system, all the terms of second or higher order concerning overlap quantities may reasonably be neglected. Accordingly the above-mentioned integrals can be reduced to the following equations:

$$\alpha_p = I_{pp}, \quad \beta_{pq} = I_{pq} - \tfrac{1}{2} S_{pq}(I_{pp} + I_{qq}) ,$$
$$(pp \mid pp)' = (pp \mid pp), \quad (pp \mid qq)' = (pp \mid qq) ,$$
$$(pq \mid rr)' = (pq \mid rs)' = 0 .$$

Assuming the core Hamiltonian I to be the sum of the kinetic operator and core potentials $U_k^{+Z_k}$ approximated by GOEPPERT-MAYER and SKLAR [*5*], we can obtain the core integrals α_p, I_{pq} and β_{pq} as follows:

$$\alpha_p = W_p - (Z_p - 1)(pp \mid pp) - \sum_{k\neq p} Z_k (pp \mid kk) ,$$
$$I_{pq} = -\langle p \mid -\tfrac{1}{2}\Delta \mid q\rangle + \langle p \mid -\tfrac{1}{2}\Delta + U_p^{+Z_p} \mid q\rangle + \langle p \mid -\tfrac{1}{2}\Delta + U_q^{+Z_q} \mid q\rangle - \sum_{k\neq p,q} Z_k (pq \mid kk) ,$$
$$\beta_{pq} = -\langle p \mid -\tfrac{1}{2}\Delta \mid q\rangle + \tfrac{1}{2} S_{pq}(W_p + W_q) + S_{pq}(pp \mid qq) ,$$

where W_p is the orbital energy of the AO χ_p and may be approximated as the negative of the first ionization potential from a suitable valence state. The resonance integrals β_{pq} may be shown to be negative in terms of PARISER's [*16*] relation.

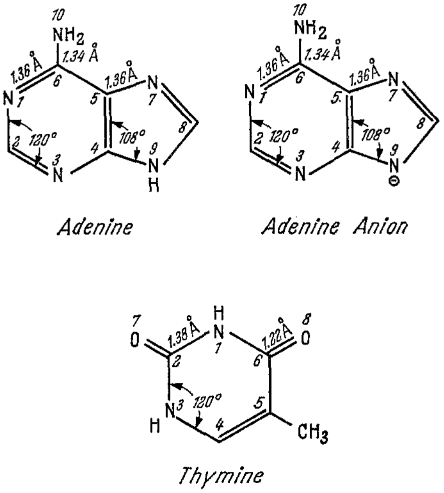

Fig. 6

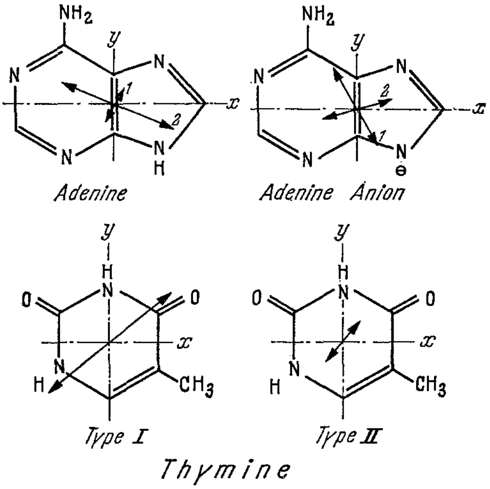

Fig. 7

Fig. 6. The geometries and numberings of adenine, adenine anion and thymine

Fig. 7. Calculated directions ofthe polarizations of adenine, adenine anion and thymine (types I and II). In adenine and adenine anion, number 1 is of the first excitation and 2 of the second excitation

The atomic integrals were evaluated from formulae analyzed by ROOTHAAN [22]. The correlation energy of a pair of $2p\pi$ electrons was taken into account according to FISCHER-HJALMARS' [4] method.

$$(pp\,|\,pp)_c = (pp\,|\,pp)_t - V_{\text{corr}} \quad , \quad (pp\,|\,qq)_c = (pp\,|\,qq)_t - V_{\text{corr}} S_{pq} \, ,$$

where V_{corr} for a pair of $2p\pi$ electrons is to a good approximation constant for the first row elements, and its values should be close to 3.5 eV. The subscript t means that the integrals are numerical values obtained by ROOTHAAN's formulae.

In Fig. 5, the resonance and the Coulomb repulsion integrals calculated by the above equations are given as functions of the distance r_{pq} between two carbon atoms p and q.

Table 1. *Calculated and observed excitation energies (ΔE in eV) and oscillator strengths (f) for the neutral Adenine and the Adenine anion*

Adenine				Adenine anion			
obs.[a]		calc.		obs.[a]		calc.	
ΔE	f	ΔE	f	ΔE	f	ΔE	f
				4.46	$\sim 5 \cdot 10^{-4}$	($n \rightarrow \pi^*$)	
4.61	$\sim 10^{-3}$	4.45	0.006	4.61	0.15	4.41	0.09
4.73	0.27	4.81	0.21	4.93	0.07	4.70	0.05
5.98	0.40	5.61	0.39	5.90	0.63	6.15	0.37
6.77	0.26	6.77	0.61				
		6.90	0.50				
7.56[b]		7.15	0.21				
		7.42	0.49				

---

[a] The observed values are taken from the spectra of adenine at pH = 6.66 and the adenine anion at pH = 12.06.

[b] The value observed with the evaporated film on a quartz plate.

The above-mentioned theoretical procedure has been applied to the π-electron structures of adenine and thymine. Concerning adenine, the calculation was made with the anion beside the neutral molecule in order to understand the pH dependence of the intensity of the spectra. As for thymine, two types of calculations were made. Type I is concerned with the keto type thymine and in type II the core integrals α_p were taken as parameters and were changed in wide ranges in order to consider the deformation of the σ-skeleton due to the hydrogen-bond formation with solvent molecules or due to other solvation effects.

The geometrical structures of the molecules are taken as is shown in Fig. 6. They are a little different from those determined by SPENCER [*24*] and by PAULING and COREY [*18*] by the aid of the X-ray crystal analysis technique. The simplification of our geometrical model may be expected to exert no serious effect on the theoretical results. In actual calculations the resonance integral β_{pq} was taken as an adjustable parameter. In the Appendix are given the integral values necessary for the SCF and CI calculations and the detailed presentations of the SCF-MO's, and of the finally obtained state energies and wave functions. All singly excited configurations within 3 eV above the lowest excited configuration were taken into account in our CI calculations. All the above-mentioned calculations are made by an electronic computer, Facom 202 in our Institute.

Table 2. *Calculated and observed transition energies (ΔE in* eV*) and oscillator strengths (f) for Thymine*

obs.		calc.			
		(type I)		(type II)	
ΔE	f	ΔE	f	ΔE	f
4.68[a]	0.21	5.34	0.88	4.81	0.09
6.05[a]	0.31	6.20	0.09	5.74	0.23
6.9[b]		6.54	0.34	7.38	1.16
7.6[b]		6.76	0.05	7.76	0.35

[a] The values are taken from the spectrum of neutral solution.

[b] The values measured with evaporated film on quartz plate.

The calculated transition energies and oscillator strengths for the adenine, adenine anion and thymine (types I and II) are summarized in Tabs. 1 and 2 together with the experimental values. The theoretically predicted directions of polarization of the first two transitions for the adenine and adenine anion, and the first transition for the thymine (types I and II) are indicated in Fig. 7.

Discussion

Adenine

As is clearly seen in Fig. 1, the neutral adenine shows a spectrum consisting of five bands in the wavelength region of 300 mμ to 160 mμ. Their energies and oscillator strengths are given in Tab. 1 together with the corresponding theoretical values. This table shows that the experimental and theoretical results of the adenine molecule and the anion are in good agreement with the observed results. Therefore, it may be said that the assignments of the bands were conclusively made by the present theoretical consideration.

According to the observed absorption spectrum of the adenine molecule, there exist two bands in the 260 mμ region, a stronger band at 261 mμ and a shoulder at 269 mμ. Whether the latter band may be assigned to the $n \rightarrow \pi^*$ transition or the $\pi \rightarrow \pi^*$ transition was discussed seriously by several workers [*12*] and the question still remains to be solved. The present experimental and theoretical studies show that these two bands are due to the $\pi \rightarrow \pi^*$ transition. One of the reasons for this is that the present theoretical consideration on the π-electron structures can explain satisfactorily the appearance of the two $\pi \rightarrow \pi^*$ transition bands in the 260 mμ region for both the adenine molecule and anion (see Tab. 1). In particular, the phenomenon that in the anion the longer wave length band at 269 mμ is stronger than the shorter wave length band at 257 mμ while the reverse is the case in the neutral molecule, can be well explained theoretically. The second reason supporting the above assignment is that, as is clearly seen in Fig. 3, a new weak band due to the $n \rightarrow \pi^*$ transition appears at 278 mμ for the anion in addition to the two bands in the 260 mμ region. It is reasonable that the band disappears for the neutral molecule, because the $n \rightarrow \pi^*$ transition band is usually known to shift toward shorter wave lengths by protonation.

MASON found a weak absorption band at about 300 mμ in the spectrum of 9-methyl purine in cyclohexane. STEWART et al. attributed the band at about 300 mμ of 9-methyl-ademine 1-methyl-thymine hydrogen-bonded complex to the $n \rightarrow \pi^*$ transition with the transition moment perpendicular to the molecular plane. These weak absorption bands at about 300 mμ are likely to correspond to the $n \rightarrow \pi^*$ transition band of the adenine anion observed by the present authers.

The theoretically determined polarization of the 269 and 261 mμ band (Fig. 7) are almost parallel to the short and long axes, respectively. This is in agreement with the polarized absorption spectrum obtained by STEWART et al. with 9-methyl adenine, which shows that the first band at 275 mμ is short axis polarized and the second band at 255 mμ is long axis polarized. On the other hand, MASON attributed the former band to a long axis polarized band in view of the fact that the spectra of several 2- and 8-substituted purine derivatives such as 2-aminopurine and 8-mercaptopurine are greatly red shifted compared with adenine (6-aminopurine) and unsubstituted purine. Therefore, our calculation for neutral adenine seems to support STEWART's assignments, as does the calculation of BERTHOD et al. [*1*].

The spectrum of the film has five absorption bands in the region of 300 mμ to 160 mμ. All the bands show red shift compared with the spectrum in neutral solution and the shift of the first band is extremely great. Two peaks in the 280 mμ region seem to correspond to two peaks at 269 and 261 mμ in solution.

Thymine

As is shown in Tab. 2, the calculated oscillator strengths based on type I cannot explain the observed relative intensities between 264 mμ and 205 mμ bands. According to the observed results, the former is weaker than the latter, while the calculated oscillator strengths are 0.88 and 0.09, respectively. Furthermore, the discrepancy between the observed and theoretical transition energies is also considerably large for type I. The agreement between the observed and theoretical values is greatly improved for type II in which a change in the α_p values due to the hydrogen-bond formation or due to other solvation effects is allowed for. That is to say, the $|\alpha_p|$ values of the $C = O$ oxygen atom and the $N - H$ nitrogen atoms are respectively taken to be larger and smaller in type II than the corresponding values in type I. These changes in the $|\alpha_p|$ values can be reasonably explained by considering the formation of hydrogen bonds in which the $C = O$ and $N - H$ groups act as proton acceptor and donor, respectively. From this, it may be inferred that the thymine molecule interact strongly with the solvent molecules through the hydrogen-bond and the electronic structure of thymine in solution is different from that of the free molecule. The theoretically determined direction of the polarization of the first $\pi \to \pi^*$ transition band is well coincident with the experimental data obtained by Stewart and Davidson [25] (Fig. 7).

The spectrum of the evaporated film has four bands in the region of 300 mμ to 160 mμ. All the bands show red shift compared with the spectrum in neutral solution and the shift of the first band is extremely large.

Appendix

Table I. *Coulomb integral values used for the* SCF-CI *calculations of adenine, adenine anion and thymine* (types I and II)

r	(CC | CC)
0.00 Å	11.76 eV
1.36	7.74
1.38	7.68
2.20	5.72
2.35	5.45
2.40	5.36
2.72	4.87
2.76	4.82
3.56	3.88
4.53	3.11

r	(NN | NN)
0.00 Å	15.08 eV
2.20	6.04
2.25	5.93
2.33	5.76
2.35	5.72
2.40	5.62
2.95	4.74
3.48	4.06
3.70	3.81
4.06	3.49
4.50	3.16

r	(CC | NN)
1.34 Å	8.23 eV
1.36	8.16
1.38	8.01
2.20	5.89
2.25	5.79
2.33	5.63
2.35	5.59
2.40	5.50
2.72	4.97
2.76	4.90
3.48	4.00
3.54	3.92
3.56	3.91
3.70	3.78
4.06	3.47
4.25	3.32
4.53	3.12

r	(OO | OO)
0.00	17.72
4.48	3.18

r	(CC | OO)
1.22	8.96
2.25	5.86
3.50	3.99
3.98	3.54

r	(NN | OO)
2.25	5.99
3.98	3.56

Table II. *The numerical calculations for adenine*

α) Adenine molecular orbitals obtained from the SCF *calculation*[a, b]

ε_i (eV)*	i	C'_{ki} $k = 1$	$= 2$	$= 3$	$= 4$	$= 5$	$= 6$	$= 7$	$= 8$	$= 9$	$= 10$
−17.05	1	0.0630	0.0560	0.1282	0.3204	0.1985	0.1309	0.1775	0.2938	0.8217	0.1557
−16.10	2	0.1809	0.0650	0.0176	−0.0080	0.1427	0.3740	0.0231	−0.0727	−0.2531	0.8559
−13.53	3	0.3954	0.3704	0.4299	0.2759	0.3583	0.2165	0.1886	−0.0367	−0.3084	−0.3718
−12.44	4	−0.1695	−0.2829	−0.3380	−0.1060	0.3325	0.0731	0.6622	0.3886	−0.2328	−0.0778
−10.90	5	−0.6558	−0.1685	0.4049	0.4442	0.2167	−0.2422	0.0066	−0.1538	−0.1642	0.1551
− 9.99	6	−0.0290	0.3511	0.4145	−0.2241	−0.4454	−0.3529	0.3228	0.4233	−0.0935	0.1969
− 2.06	7	−0.1114	−0.3381	0.3043	−0.4672	−0.1243	0.4850	−0.4123	0.5684	−0.1346	−0.1291
0.37	8	−0.4350	0.2659	0.2212	−0.6167	0.1891	0.3719	0.1016	−0.2708	0.2094	−0.0964
1.36	9	0.2355	−0.5820	0.3545	−0.0315	−0.3574	0.1515	0.4085	−0.3883	0.0979	−0.0348
3.83	10	−0.3004	0.3162	−0.2850	0.4230	−0.5263	0.4594	0.2061	−0.0778	−0.0638	−0.0948
α_k (eV)		−72.54	−65.30	−73.90	−78.76	−79.67	−77.12	−75.31	−67.81	−81.36	−74.88

* ε_i: energy of the i-th molecular orbital; k: the numbering of OAO's (see Fig. 6); α_k: core coulomb integrals.

[a] The core resonace integrals β are taken as follows, β_{CC} ($r = 1.36$ Å) $= -2.40$ eV, β_{CN} ($r = 1.36$ Å) $= -2.00$ eV, β_{CN} ($r = 1.34$ Å) $= -2.20$ eV.

[b] Values of W_p are taken as follows, W_p (carbon) $= -11.22$ eV, W_p (nitrogen) $= -14.51$ eV.

β) Adenine: state energies, wave function and transition moments[a]

Energy (eV)		(6 − 7)	(6 − 8)	(6 − 9)	(6 − 10)	(5 − 7)	(5 − 8)	(5 − 9)	(4 − 7)	X	Y
4.446	1	0.1860	0.7380	−0.1014	−0.0527	−0.5258	0.0430	−0.3397	−0.1182	−0.021	−0.122
4.808	2	0.8429	−0.2009	0.1277	0.0818	0.0549	0.4696	−0.0512	−0.0006	0.625	−0.316
5.610	3	−0.2213	0.4343	0.5545	0.0407	0.5219	0.3608	−0.0340	−0.2238	−0.877	−0.173
6.767	4	−0.3635	−0.3172	0.4005	−0.4178	−0.6004	0.4801	−0.0487	0.1082	−0.047	1.016
6.898	5	0.2162	−0.0478	0.6830	0.0877	−0.0981	−0.6197	−0.2013	0.2066	0.908	−0.056
7.148	6	−0.0849	0.1732	−0.1309	0.1978	0.1830	0.1823	−0.2306	0.8869	−0.542	−0.210
7.420	7	0.1251	0.3057	0.1383	−0.0329	−0.1764	−0.0084	0.8822	0.2475	0.237	−0.834
8.295	8	−0.0654	0.0046	−0.0527	0.9691	−0.1155	−0.0131	0.0805	−0.1836	0.157	0.252

[a] Column 1 gives the eigenvalues with reference to zero energy for the ground state. Column 2 numbers the wave functions, and columns 3 − 10 list the coefficients of the wave functions. Columns 11 and 12 show the X and Y components of the transition moments between the excited states and the ground state.

Table III. *The numerical calculations for adenine anion*

α) *Adenine anion molecular orbitals obtained from the* SCF *calculation*[a, b]

ε_i (eV)*	i	C'_{ki} $k = 1$	$= 2$	$= 3$	$= 4$	$= 5$	$= 6$	$= 7$	$= 8$	$= 9$	$= 10$
−12.226	1	0.1994	0.0867	0.0540	0.0691	0.1515	0.3955	0.0621	0.0269	0.0308	0.8720
− 9.484	2	0.3191	0.3531	0.4151	0.3812	0.3174	0.1582	0.2728	0.2420	0.2992	−0.3280
− 7.972	3	−0.4717	−0.4239	−0.2191	0.1495	0.2182	−0.1023	0.4138	0.4069	0.3485	0.1054
− 6.318	4	0.4028	−0.1315	−0.5122	−0.3229	0.2633	0.3633	0.3443	0.0608	−0.2607	−0.2496
− 4.239	5	0.3615	0.1369	−0.2621	−0.2158	−0.5152	−0.0972	−0.1239	0.4313	0.5066	0.0485
− 3.593	6	−0.1015	0.3484	0.2566	−0.3662	−0.1697	−0.3322	0.5471	0.2545	−0.3783	0.1488
5.920	7	0.2048	0.2932	−0.4521	0.2698	0.2261	−0.5888	0.1615	−0.3674	0.1101	0.1546
6.863	8	0.4841	−0.6123	0.2333	0.3225	−0.3006	−0.2275	0.2159	−0.0299	−0.1986	0.0575
9.080	9	0.0823	0.4313	−0.1348	0.2311	0.2720	−0.2193	−0.4562	0.6196	−0.4510	0.0484
10.478	10	−0.2226	0.2610	−0.3207	0.5590	−0.4996	0.3314	0.1911	0.0295	−0.2559	−0.0682
α_k (eV)		−69.05	−61.52	−67.97	−70.60	−73.78	−73.12	−69.27	−59.65	−66.28	−71.72

* ε_i: energy of the i-th molecular orbital; k: the numbering of OAO's (see Fig. 6); α_k: core coulomb integrals.

[a] The core resonance integrals β are taken as follows, β_{CC} ($r = 1.36$ Å) $= -2.40$ eV, β_{CN} ($r = 1.36$ Å) $= -2.50$ eV, β_{CN} ($r = 1.34$ Å) $= -2.70$ eV.

[b] Values of W_p are taken like those of adenine.

β) *Adenine anion: state energies, wave function and transition moments*[a]

Energy (eV)		(6 − 7)	(6 − 8)	(6 − 9)	(5 − 7)	(5 − 8)	(5 − 9)	(4 − 7)	(4 − 8)	X	Y
4.414	1	0.9147	−0.0483	0.0433	−0.1767	−0.3351	−0.0254	0.0897	−0.0835	−0.243	0.429
4.698	2	0.1491	0.5678	0.0372	0.7887	−0.0359	0.0088	0.0282	−0.1726	−0.326	0.109
6.151	3	0.0371	0.6072	−0.0149	−0.4364	0.3786	−0.0274	0.5417	0.0409	0.749	0.359
6.739	4	−0.2618	−0.1995	0.5018	0.0855	0.7430	−0.1118	−0.2268	−0.1285	−0.677	0.537
7.022	5	0.1021	−0.4904	−0.3592	0.3535	0.2602	0.1296	0.6371	0.0690	−1.207	−0.210
7.426	6	−0.1355	−0.0649	0.4004	−0.0756	−0.1456	0.7130	0.2069	−0.4890	0.593	−0.356
8.040	7	0.0943	0.0659	−0.6635	−0.1339	0.2689	0.1527	−0.3444	−0.5607	0.131	0.773
8.426	8	0.1831	0.1328	−0.1227	0.0222	0.1728	0.6615	−0.2811	0.6220	−0.124	0.913

[a] Column 1 gives the eigenvalues with reference to zero energy for the ground state. Column 2 numbers the wave functions, and columns 3 − 10 list the coefficients of the wave functions. Columns 11 and 12 show the X and Y components of the transition moments between the excited states and the ground state.

Table IV. *The numerical calculations for thymine (type I)*

α) *Thymine (type I) molecular orbitals obtained from the* SCF *calculation*[a], [b]

ε_i (eV)*	i	C'_{ki} $k = 1$	$= 2$	$= 3$	$= 4$	$= 5$	$= 6$	$= 7$	$= 8$
−18.467	1	0.5517	0.3493	0.6594	0.2289	0.1414	0.1943	0.1494	0.0799
−17.030	2	−0.7051	−0.0288	0.6283	0.1892	−0.0020	−0.2374	−0.0152	−0.1219
−14.104	3	−0.1580	−0.2993	−0.0570	0.3703	0.5057	0.4396	−0.3185	0.4412
−12.439	4	−0.3267	0.3684	−0.2176	0.0224	0.1489	0.1652	0.7564	0.2969
−11.429	5	−0.0840	−0.0300	0.2503	−0.4913	−0.4764	0.2131	−0.1352	0.6303
− 1.519	6	−0.1269	0.0346	0.1434	−0.6383	0.4138	0.4564	−0.0288	−0.4175
− 0.148	7	0.1384	−0.7833	0.1623	0.0403	−0.1524	0.1713	0.5236	−0.1126
1.929	8	−0.1562	0.1905	−0.1018	0.3518	−0.5298	0.6343	−0.1030	−0.3341
α_k (eV)		−79.39	−72.07	−76.96	−63.58	−62.80	−68.55	−65.41	−62.87

* ε_i: energy of the i-th molecular orbital; k: the numbering of OAO's (see Fig. 6); α_k: core coulomb integrals.

[a] The core resonance integrals β are as follows, β_{CC} ($r = 1.38$ Å) $= -2.40$ eV, β_{CN} ($r = 1.38$ Å) $= \beta_{CO}$ ($r = 1.22$ Å) $= -2.00$ eV.

[b] Values of W_p are taken as follows, W_p (carbon) $= -11.22$ eV, W_p (nitrogen) $= -14.51$ eV, W_p (oxygen) $= -17.79$ eV.

β) *Thymine (type I): state energies, wave function and transition moments*[a]

Energy (eV)		(5 − 6)	(5 − 7)	(5 − 8)	(4 − 6)	(4 − 7)	(3 − 6)	X	Y
5.347	1	0.9742	−0.1042	0.0573	−0.1154	0.1230	−0.0919	−1.165	−0.727
6.201	2	0.0739	−0.1139	0.0912	0.8196	0.3567	0.4175	−0.385	0.086
6.541	3	−0.1957	−0.5062	−0.0090	−0.3613	0.7571	−0.0391	−0.424	0.629
6.764	4	−0.0131	0.7680	0.4322	−0.1588	0.4421	0.0514	−0.275	−0.065
7.399	5	0.0595	−0.0109	−0.0927	−0.3965	−0.1357	0.9012	0.169	0.104
7.722	6	−0.0597	−0.3606	0.8905	−0.0444	−0.2655	0.0317	0.253	−0.019

[a] Column 1 gives the eigenvalues with reference to zero energy for the ground state. Column 2 numbers the wave functions, and columns 3 − 8 list the coefficients of the wave functions. Columns 9 and 10 show the X and Y components of the transition moments between the excited states and the ground state.

Table V. *The numerical calculations for thymine (type II)*

α) *Thymine (type II) molecular orbitals obtained from the* SCF *calculation*[a]

ε_i (eV)*	i	C'_{ki}							
		$k = 1$	$= 2$	$= 3$	$= 4$	$= 5$	$= 6$	$= 7$	$= 8$
−19.327	1	0.1089	0.0415	0.0186	0.0315	0.0903	0.3082	0.0149	0.9390
−15.219	2	0.3816	0.5775	0.4134	0.2383	0.1676	0.1663	0.4588	−0.1640
−12.326	3	0.0710	−0.2371	0.2375	0.4570	0.5191	0.2737	−0.5540	−0.1487
−11.106	4	−0.6255	0.0140	0.5084	0.3501	−0.0602	−0.4195	0.1054	0.1919
− 9.213	5	−0.3520	−0.1889	−0.4263	0.1405	0.5381	0.1572	0.5668	−0.0595
1.094	6	−0.4226	0.0666	0.3914	−0.6029	0.0874	0.5257	−0.0379	−0.1218
1.677	7	0.1383	−0.6186	0.2348	0.2376	−0.4766	0.3716	0.3383	−0.0828
4.667	8	−0.3530	0.4309	−0.3519	0.4136	−0.4077	0.4328	−0.1847	−0.0849
α_k (eV)		−70.67	−68.84	−65.81	−58.57	−61.20	−68.51	−65.41	−74.41

---

* ε_i: energy of the i-th molecular orbital; k: the numbering of OAO's (see Fig. 6); α_k: core coulomb integrals.

[a] The core resonance integrals β are taken as follows, β_{CC} (r = 1.38 Å) = β_{CN} (r = 1.38 Å) = −2.50 eV, β_{CO} (r = 1.22 Å) = −2.80 eV.

β) *Thymine (type II): state enercies, wave function and transition moments*[a]

Energy (eV)		(5 − 6)	(5 − 7)	(5 − 8)	(4 − 6)	(4 − 7)	(3 − 6)	X	Y
4.814	1	0.8922	0.0177	0.0013	−0.0191	0.4376	0.1090	0.319	0.348
5.744	2	−0.0192	0.8992	−0.0724	−0.4281	−0.0031	−0.0505	−0.546	0.408
7.375	3	−0.1045	0.3983	−0.1872	0.8618	0.2148	0.0816	−1.226	0.546
7.555	4	−0.4222	−0.1030	−0.0618	−0.2443	0.7453	0.4383	−0.313	−0.659
8.175	5	0.1075	0.0632	0.0429	0.0193	−0.4421	0.8870	0.401	0.866
8.483	6	−0.0540	0.1337	0.9767	0.1172	0.1070	0.0006	−0.337	0.555

---

[a] Column 1 gives the eigenvalues with reference to zero energy for the ground state. Column 2 numbers the wave functions, and columns 3 −8 list the coefficients of the wave functions. Coulmns 9 and 10 show the X and Y components of the transition moments between the excited states and the ground state.

References

[1] Berthod, H., C. Giessner-Prettre, and A. Pullman: Theoret. chim. Acta **5**, 53 (1966).
[1a] Clark, L. B., and I. Tinoco, Jr.: J. Amer. chem. Soc. **87**, 11 (1965).
[2] Clementi, E, C. C. J. Roothahn, and M. Yoshimine: Physic. Rev. **127**, 1618 (1962).
[3] Fischer-Hjarmars, I.: J. chem. Physics **42**, 1962 (1965).
[4] — In: Molecular Orbitals in Chemistry, Physics and Biology, ed. P. O. Löwdin, and B. Pullman, p. 370. New York: Academic Press 1964.
[5] Goeppert-Mayer, M., and A. L. Sklar: J. chem. Physics **6**, 645 (1938).
[6] Ladik, J., and T. A. Hoffman: Biopolymer Symp. **1**, 117 (1964).
[6a] —, and K. Appel: Theoret. chim. Acta **4**, 132 (1966).
[7] Löwdin, P. O.: J. chem. Physics **18**, 365 (1950).
[8] — Advan. Physics **5**, 111 (1956).
[9] Lykos, P. G.: J. chem. Physics **35**, 1249 (1961).
[10] Mason, S. F.: J. chem. Soc. (London) **1960**, 219; **1954**, 20 and references therein.
[11] McWeeny, R.: Proc. Roy. Soc. (London) A **227**, 288 (1955); A **237**, 355 (1956).
[12] Nagata, C., A. Imamura, Y. Tagashira, and M. Kodama: Bull. chem. Soc. Japan **38**, 1938 (1965).
[13] Nakanishi, K., N. Suzuki, and F. Yamazaki: Bull. chem. Soc. Japan **34**, 53 (1961).
[14] Nesbet, R. K.: Biopolymer Symp. **1**, 129 (1964).
[15] Pariser, R., and R. G. Parr: J. chem. Physics **21**, 466, 767 (1953).
[16] — J. chem. Physics **21**, 568 (1953).
[17] Parr, R. G.: Quantum Theory of Molecular Electronic Structure. New York: Benjamin 1963.
[18] Pauling, L., and R. B. Corey: Arch. Biochem. Biophys. **65**, 164 (1956).
[19] Pople, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
[20] Pullman, A., and B. Pullman: Bull. soc. chim. France **1958**, 766; **1959**, 594.
[21] Roothaan, C. C. J.: Rev. mod. Physics **23**, 69 (1951).
[22] — J. chem. Physics **19**, 1445 (1951).
[23] Ruedenberg, K.: J. chem. Physics **34**, 1861 (1961).
[24] Spencer, M.: Acta Cryst. **12**, 59 (1959).
[25] Stewart, R. F., and N. Davidson: J. chem. Physics **39**, 255 (1963).
—, and L. H. Jensen: J. chem. Physics **40**, 2071 (1964).
[26] Tsubomura, H., K. Kimura, K. Kaya, J. Tanaka, and S. Nagakura: Bull. chem. Soc. Japan **37**, 418 (1964).
[27] Veillard, A., and B. Pullman: J. theoret. Biol. **4**, 37 (1963).
[28] Voet, D., W. B. Gratzer, R. A. Cox, and P. Doty: Biopolymers **1**, 193 (1963).

Prof. Dr. S. Nagakura
The Institute for Solid State Physics
The University of Tokyo
Azabu Minato-ku, Tokyo, Japan