Semi-empirical Self-consistent Field Molecular Orbital Calculation of the Electronic Structure of the Base Components of Nucleic Acids

By Chikayoshi NAGATA, Akira IMAMURA, Yusaku TAGASHIRA and Masahiko KODAMA

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Investigations of the π-electronic structure of such base components as adenine, guanine, cytosine, thymine and uracil are of importance in connection with the biological activities of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Pullman⁽¹⁾ and Ladik⁽²⁾ have calculated the π-electronic structures of base components by means of the Hückel MO method, and have compared them with experimental results; various kinds of physicochemical properties of bases and nucleic acids, such as the relative stability of the base paring or the base tautomers, the positions of attack in the hydration of pyrimidine bases, etc., have been well explained. However, in the Hückel MO method an ambiguity in choosing the parameters cannot be avoided, and, furthermore, the method has failed to explain such optical properties of the bases as the absorption wavelength and the oscillator strength. That is, as was pointed out by Ladik,⁽²⁾ the calculated wavelengths are larger than the experimental results by 150 mμ or more (cf. Table II).

In view of this disagreement between the theories and experiments with absorption spectra, calculation by means of the SCF MO method may be valuable since the iterative procedure in this method is known to eliminate the parameter dependence. Veillard and Pullman⁽³⁾ have carried out semi-empirical SCF MO calculations on the bases and the base analogs, but they have not attempted to explain such optical properties of bases as their absorption wavelengths and their oscillator strengths. Recently Nesbet⁽⁴⁾ has calculated the wavelengths and oscillator strengths for adenine, guanine, cytosine and thymine and also for the base-pair, but no attempt to explain the direction of polarization has been made. Furthermore, in Veillard's treatment, no SCF MO calculations on the thymine molecule were carried out, and Nesbet has calculated the electronic structure of thymine by neglecting the methyl group. They did this bacause of the difficulty of estimating the energy of the valence state and the repulsion integral for the methyl group. The present authors have attempted in this paper to compare the calculated wavelengths, oscillator strengths and directions of polarization with the experimental results for adenine, guanine, cytosine, thymine, uracil, 9-methyladenine and 1-methylthymine. In the estimation of two-center repulsion integral, two alternative methods have been used, the Pariser-Parr⁽⁵⁾ and Mataga-Nishimoto approximations.⁽⁶⁾ Veillard and Pullman⁽³⁾ used the former method, and Nesbet,⁽⁴⁾ the latter. In our calculation, both these methods of approximation have been used and have been compared.

Calculation Procedure

In the calculation, only π-electrons have been taken into account explicitly. The Hamiltonian of the system is written in this form:

$$H=\sum_{\mu}\left\{-\frac{\hbar^2}{2m}\Delta_{\mu}+V(\mu)\right\}+\sum_{\mu>\nu}\frac{e^2}{r_{\mu\nu}} \tag{1}$$

and the molecular orbitals have been formed by a linear combination of atomic orbitals:

$$\varphi_j=\sum_{r} C_{jr}\chi_r \tag{2}$$

Then, the energies and coefficients have been determined by solving the secular equation;

$$\begin{vmatrix} F_{11}-E & F_{12}\cdots\cdots\cdots & F_{1m} \\ F_{21} & F_{22}-E\cdots\cdots\cdots & F_{2m} \\ \cdots\cdots & \cdots\cdots\cdots\cdots & \cdots\cdots \\ \cdots\cdots & \cdots\cdots\cdots\cdots & \cdots\cdots \\ F_{m1} & F_{m2}\cdots\cdots & F_{mm}-E \end{vmatrix}=0 \tag{3}$$

where

$$F_{rr}=\alpha_r+\sum_{t}^{m}P_{tt}(rr\,|\,tt)-\frac{1}{2}P_{rr}(rr\,|\,rr) \tag{4}$$

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(1) A. Pullman and B. Pullman, *Bull. soc. chim. France*, **1958**, 766; **1959**, 594.

(2) J. Ladik and T. A. Hoffmann, *Biopolymers, Symposia*, No. 1, 117 (1964).

(3) A. Veillard and B. Pullman, *J. Theoret. Biol.*, **4**, 37 (1963).

(4) R. K. Nesbet, *Biopolymers, Symposia*, **No. 1**, 129 (1964).

(5) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 (1953).

(6) N. Mataga and K. Nishimoto, *Z. physik. Chem.*, *Neue Folge*, **13**, 140 (1957).

$$F_{rs}=\beta_{rs}-\frac{1}{2}P_{rs}(rr\,|\,ss) \tag{5}$$

with

$$\begin{aligned}\alpha_r&=\int\chi_r(1)\Big(-\frac{\hbar^2}{2\,m}\Delta_1+V(1)\Big)\chi_r(1)\mathrm{d}\tau_1\\&=\int\chi_r(1)\Big(-\frac{\hbar^2}{2\,m}\Delta_1+U_r(1)\Big)\chi_r(1)\mathrm{d}\tau_1\\&\quad+\sum_{s\neq r}\int\Big[\chi_r(1)\Big\{U_s{}^0(1)-\int\frac{\chi_s{}^2(2)e^2}{r_{12}}\mathrm{d}\tau_2\Big\}\Big]\times\\&\quad\chi_r(1)\mathrm{d}\tau_1\fallingdotseq W_{2p}-\sum_{s\neq r}\{(s:rr)+(rr\,|\,ss)\}\end{aligned} \tag{6}$$

$$\beta_{rs}=\int\chi_r(1)\Big(-\frac{\hbar^2}{2\,m}\Delta_1+V(1)\Big)\chi_s(1)\mathrm{d}\tau_1 \tag{7}$$

and

$$(rr\,|\,ss)=\iint\chi_r(1)\chi_r(1)\frac{e^2}{r_{12}}\chi_s(2)\chi_s(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{8}$$

In Eq. 6, the Coulomb penetration integral $(s:rr)$ is neglected, as usual. W_{2p} is taken as equal to $-I$; I is the ionization potential of the atomic valence state. One-center repulsion integral $(rr\,|\,rr)$ is usually estimated as I-A, where A is the electron affinity. In our calculation the values of I and A have been taken from the paper of Hinze and Jaffé.⁷⁾ As was stated above, two alternative ways of estimating the two center repulsion integral have been used; the Pariser-Parr and Mataga-Nishimoto approximations. In the former method, the following equations are used: at the $R\leqq 2.8$ Å distances;

$$(rr\,|\,ss)=1/2\{(rr\,|\,rr)+(ss\,|\,ss)\}+aR+bR^2 \tag{9}$$

and at $R>2.8$ Å:

$$\begin{aligned}(rr\,|\,ss)=7.1975(1/\sqrt{R^2+1/4(R_r+R_s)^2}\\+1/\sqrt{R^2+1/4(R_r-R_s)^2})\end{aligned} \tag{10}$$

$$R_r=(4.597/Z^*)\times10^{-8}\,\text{cm.}$$

where R is the internuclear distance, and a and b are parameters determined from Eq. 10 when R is equal to 2.8 Å and 3.7 Å respectively. Z^* is the effective nuclear charge.

In the case of the Mataga-Nishimoto approximation, the following relation is used:

$$(rr\,|\,ss)=e^2/(R_{rs}+a_{rs}) \tag{11}$$

The constant, a_{rs} is determined by using the relation:

$$(rr\,|\,rr)=14.39/a=I_r-A_r \tag{12}$$

For the case of two-heteronuclear centers, i.e. carbon and nitrogen, the value of a is taken as the harmonic mean of a_C and a_N.

The above two methods of approximation have been used in our calculations, and their results have been compared with each other and also with the experimental results.

Several ways of evaluating the values of β_{rs} have been proposed[4,5,8]; Pariser-Parr's method, which determins β_{rs} from the spectroscopic data for only the nearest neighbor atomic orbitals, has especially been used. However, we used the following relation:

$$\beta_{rs}=lS_{rs} \tag{13}$$

where S_{rs} is the overlap integral between the rth π-atomic orbital and sth one, and l is a parameter, which was determined as -12.65 from the mean of the following values:

$\beta_{CO}=-2.70$ eV.	$S_{CO}=0.2063$
$\beta_{CN}=-2.39$ eV.	$S_{CN}=0.1957$

Moreover, in our calculation, β_{rs} was taken into account not only for the nearest neighbors but also for all pairs of r and s.

The oscillator strengths of the transitions from the ground state to the excited states have been calculated by using the following equation;

$$f=1.085\times10^{-5}\,\sigma_{ob}\,\boldsymbol{m}_{ob}{}^2 \tag{14}$$

where σ_{ob} is the wave number of the transition from the ground state to the excited state b. $\boldsymbol{m}_{ob}$ in Eq. 14 is given by:

$$\boldsymbol{m}_{ob}=\int\Psi_{ob}\sum_i\boldsymbol{r}_i\,\Psi_b\,\mathrm{d}\tau \tag{15}$$

in which Ψ_o and Ψ_b are the wave functions of the ground and excited states respectively, and $\boldsymbol{r}_i$ is the position coordinate of the ith electron.

Choice of Parameters

Values of W_{2p} and $(rr\,|\,rr)$ semi-empirically evaluated are tabulated in Table I.

TABLE I. SEMI-EMPIRICALLY EVALUATED VALUES OF W_{2p} AND $(rr|rr)$

r	W_{2p}	$(rr\,|\,rr)$
C	−11.16	11.13
O	−17.28	15.27
N(azo)	−14.12	12.34
N(amino)	−28.53	16.57
OH	−34.75	21.18
H_3*	−10.256	9.326

* Hyperconjugation in the methyl group is taken into account, and the group orbital of H_3 is assumed to overlap with π-orbitals.

The values of W_{2p} and $(rr\,|\,rr)$ for the carbon, oxygen and azo-nitrogen are taken from the paper of Hinze and Jaffé.⁷⁾ It is difficult to

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7) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

8) G. Leroy, *J. chim. phys.*, **60**, 1270 (1963).

choose the values of W_{2p} for such atoms as amino-nitrogen, which contribute two electrons to the π-system; many different values for this atom have been adopted by different authors.[3,9-11] In the present paper, we have adopted the value of -28.526 eV. for the W_{2p} of amino-nitrogen (that is, $N^+(t_rt_rt_r, \pi) \rightarrow N^{++}(t_rt_rt_r)$) from the following relations:

$$N^+(s^2p^2) \rightarrow N^+(t_rt_rt_r, \pi) \qquad 9.814 \text{ eV.}$$

$$N^+(s^2p^2) \rightarrow N^{++}(s^2p) \qquad 29.41 \text{ eV.}$$

$$N^{++}(s^2p) \rightarrow N^{++}(t_rt_rt_r) \qquad 8.930 \text{ eV.}$$

Similarly, the values of W_{2p} and $(rr|rr)$ for the quasi-π orbital of H_3 in the methyl group are difficult to evaluate semi-empirically, therefore, no calculation has ever been carried out for thymine and its analogs. The values adopted in our calculation are presented in Table I; the values have been determined by Morita for the SCF MO calculation of the benzenium ion by taking hyperconjugation into account.[12] By using these values, he has successfully explained the experimental results of the absorption spectra of the benzenium ion.

The values of the interatomic distances for adenine, guanine, cytosine and thymine are taken from the paper of Spencer,[13] while the values for uracil are taken from Wyckoff's table.[14] For such methylderivatives as 1-methylthymine and 9-methyladenine, the data for their parent molecules, i. e., thymine and adenine are used except for the distance of the N–CH_3 bond. The value for this N–C distance is tentatively taken as 1.46 Å, which is the distance between the carbon and the nitrogen in CH_3NH_2 molecules.

All the calculations in this paper have been carried out on the NEAC 2101 electronic computer in this Institute.

Results and Discussion

Wavelength and Oscillator Strength. — The results of the calculation of the transition energies and oscillator strengths for adenine, guanine, thymine, cytosine and uracil are presented in Table II in comparison with the experimental values. The experimental data of the absorption spectra have been given by Beaven et al.[15] For the sake of comparison, the values obtained in the Hückel MO method, taken from the paper of Ladik,[2] are also indicated. It may clearly be seen that the SCF MO treatment improves the results strikingly and that the agreement between the theoretical results and experiments is satisfactory, especially for adenine and cytosine. That is, if the 6→7 transition of adenine and 5→6 transition of cytosine are assigned to the first bands of these molecules respectively, the calculated wavelengths coincide with experimental values within the limits of 15—20 Å. Agreements between the theory and experiment for these transitions are very good also for the values of the oscillator strengths.

The calculated wavelength for thymine is shorter than the experimental value by about 60 mμ in the case of the Pariser-Parr approximation. This is the largest discrepancy between theory and experiment among the bases calculated in this paper. First of all, an inappropriate choice of the semi-empirical parameter for the methyl group was deemed the cause of this large discrepancy. Therefore, calculation has been carried out for demethylated thymine, and the wavelength of 198 mμ has been obtained. This result shows that the cause of the disagreement for thymine is not in the unsuitable choice of the parameter of methyl group. In general, it is known that the agreement between the calculated and experimental wavelengths for the compounds which contain two oxygens is not very good for other compounds. Thus, the calculated wavelength for parabenzoquinone gave a value 50 mμ shorter than the experimental value.[16] Many attempts have been made to improve the theoretical results by changing the values of the semi-empirical parameters, but no remarkable improvement has been achieved.[16,17] It may be expected that the theoretical wavelength for thymine can be improved in connection with these compounds.

The wavelengths and oscillator strengths for the transitions other than the maximum wavelength have been calculated; they are indicated in Table II, together with the observed values. From a comparison of these values, the following assignments may be made: the bands at 210 mμ in cytosine, 246 mμ in guanine and 207 mμ in thymine might be assigned to the transitions of 4→6 or 5→7 in cytosine, 7→9 in guanine and 5→8 in thymine respectively. The transitions of 6→8 and 5→7 in thymine may be neglected, because the calculated

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[9] S. Yomosa, *Biopolymers, Symposia*, No. 1, 1 (1964).

[10] B. Grabe, ibid., 1, 283 (1964).

[11] S. Mataga and N. Mataga, *Z. physik. Chem.*, *Neue Folge*, 19, 231 (1959).

[12] T. Morita, This Bulletin, 33, 1486 (1960).

[13] M. Spencer, *Acta Cryst.*, 12, 59 (1959).

[14] R. W. G. Wyckoff, "Crystal Structure," Supplement IV, Interscience Publishers (1959), p. 128.

[15] G. H. Beavens, E. R. Holiday and E. A. Johnson, "The Nucleic Acids," Vol. I, Ed. by E. Chargaff and J. N. Davidson, Academic Press, New York (1955), p. 493.

[16] J. W. Sidman, *J. Chem. Phys.*, 27, 429 (1957).

[17] A. Kuboyama and K. Wada, Preprint of the 17th Annual Meeting of the Chemical Society of Japan (1964), p. 496; Preprint of the Discussion for the Electronic State of Molecules (1964) p. 63.

TABLE II. COMPARISON OF THE CALCULATED WAVELENGTH AND OSCILLATOR STRENGTH WITH EXPERIMENTS

Compound	Absorption max., mμ				Oscillator strength			
	Exp.	Pariser-Parr	Mataga-Nishimoto	Hückel MO*	Exp.**	Pariser-Parr	Mataga-Nishimoto	Hückel MO*
Adenine	260.5	262(6→7)	253(6→7)	396	0.30 (13.35)	0.387	0.472	0.51
		232(6→8)	238(6→8)			0.471	0.379	
		178(5→7)	199(5→7)			0.181	0.161	
Cytosine	276	278(5→6)	289(5→6)	366	0.17 (10.0)	0.182	0.299	0.43
	210	197(4→6)	192(4→6)		(9.7)	0.616	0.689	
		181(5→7)	194(5→7)			0.618	0.601	
Guanine	275.5	299(7→8)	325(7→8)	353	(8.15)	0.395	0.361	0.44
	246	239(7→9)	268(7→9)		(10.7)	0.575	0.416	
		173(6→8)	194(6→8)			0.149	0.146	
Uracil	259	290(5→6)	300(5→6)	335	0.25 (8.2)	0.177	0.313	0.50
		185(5→7)	198(5→7)			0.622	0.616	
		188(4→6)	183(4→6)			0.611	0.516	
Thymine	264.5	200(6→7)	221(6→7)	342	0.21 (7.89)	0.730	0.993	0.50
	207	172(5→8)	175(5→8)		(9.5)	0.394	0.440	
		162(6→8)	211(6→8)			0.005	0.072	
		190(5→7)	199(5→7)			0.039	0.041	

* Theoretical values in the Hückel MO method were taken from the paper of Ladik and Hoffmann (Ref. 2).

** Numerals in parenthesis are $\varepsilon \times 10^{-3}$, where ε is the absorption coefficient.

oscillator strengths of these transitions are very small, i. e., 0.005 and 0.038 respectively.

It is difficult to determine the relative merits of the Pariser-Parr and Mataga-Nishimoto approximations.

The Direction of Polarization.—It may be of interest to compare the polarized absorption spectra of bases with the theoretically-determined directions of polarization. As far as we are aware, the experimental data for the polarized absorption spectra of bases or their analogs have been obtained only for 9-methyladenine and 1-methylthymine. That is, Stewart and Davidson[18] have obtained the polarized absorption spectra of the single crystal of 9-methyladenine, 1-methylthymine and the A-T dimer.[18] As a result, for 1-methylthymine the first absorption band has been shown to polarize close to the N_1–C_4 axis, and the second band, approximately perpendicular to the first, and for 9-methyladenine the direction of polarization has been determined along the shorter axis, D_4–C_5. From the results for 9-methyladenine, Stewart and Davidson also assumed that the main band of adenine ($\lambda_{max}=261$ mμ) should be assigned to a short-axis polarized band and the weak shoulder ($\lambda_{max}=267$ mμ), to a long-axis band

The theoretical treatment of Tinoco and DeVoe[19] has led to the same assignment; that is, by using the Hückel MO method they have assigned the 6→8 transition to the main band of adenine and the 6→7 transition to the shoulder band. On the other hand, Mason has attributed the intense absorption (261 mμ) in adenine to a long-axis polarized band.[20] Thus, the assignments of the transitions in adenine and 9-methyladenine contradict to one another; in view of this contradiction, it may be worth while to determine the directions of polarization for adenine and 9-methyladenine by means of the SCF MO calculation and to compare them with the experimental values.

As may be seen in Fig. 1, the theoretically-predicted direction of polarization of the 7→9 transition for 9-methyladenine is close to the C_4–C_5 axis (short-axis polarized), whereas the 7→8 transition is nearly perpendicular to the direction of the 7→9 transition. This is true in both methods of approximations, the Pariser-Parr and Mataga-Nishimoto methods. When these results are compared with those of the experiment of Stewart and Davidson,[18] it may

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[18] R. F. Stewart and N. Davidson, *J. Chem. Phys.*, **39**, 255 (1963).

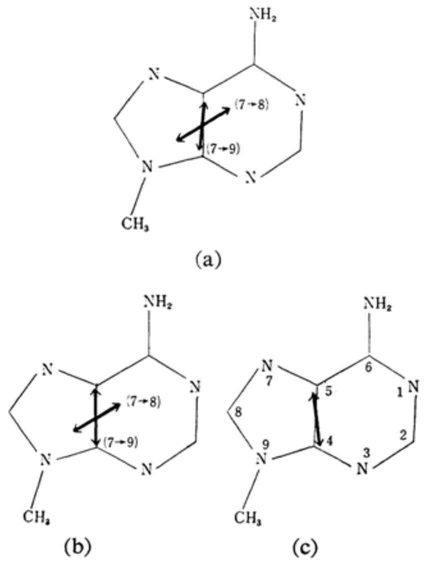
[19] H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, **4**, 518 (1962).

[20] S. F. Mason, *J. Chem. Soc.*, **1954**, 2071.

TABLE III. COMPARISON OF THE CALCULATED WAVELENGTH AND OSCILLATOR STRENGTH WITH EXPERIMENTS FOR 9-METHYLADENINE AND 1-METHYLTHYMINE

Compound	Absorption max., mμ			Oscillator strength		
	Exp.*	Pariser-Parr	Mataga-Nishimoto	Exp.*	Pariser-Parr	Mataga-Nishimoto
9-Methyladenine	261	263(7→8)	254(7→8)	0.28	0.377	0.479
	206	231(7→9)	238(7→9)	0.62	0.482	0.389
		199(7→10)	204(7→10)		0.188	0.191
		180(6→8)	200(6→8)		0.199	0.165
		178(6→9)	184(6→9)		0.435	0.447
		164(6→10)	172(6→10)		0.358	0.408
1-Methylthymine	273	200(7→8)	222(7→8)	0.19	1.007	0.985
	207	162(7→9)	213(7→9)	0.28	0.005	0.074
		154(7→10)	165(7→10)		0.098	0.125
		190(6→8)	199(6→8)		0.042	0.049
		172(6→9)	175(6→9)		0.396	0.428
		129(6→10)	138(6→10)		0.203	0.087

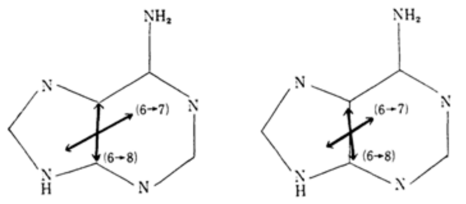
* These are spectra in solution. Spectra in crystal state are 275 and 230 mμ for 1-methylthymine and 275, 255 and 230 mμ for 9-methyladenine (Ref. 18).



(a)

(b) (c)

Fig. 1. Comparison of the predicted direction of polarization of 9-methyladenine with the experiment: (a) Calculation according to Mataga-Nishimoto and (b) Pariser-Parr approximations. (c) Experiment of Stewart and Davidson (Ref. 18).

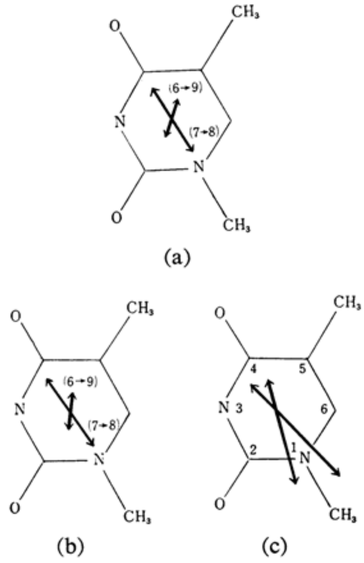


(a) (b)

Fig. 2. Predicted directions of polarization of adenine: (a) Mataga-Nishimoto approximation and (b) Pariser-Parr approximation.

be seen that the intense band which is polarized to the C_4-C_5 axis may be assigned to the second transition, 7→9. Similarly, the first (6→7) transition of adenine is predicted to polarize to the long-axis, and the second (6→8) transition, to be short-axis polarized (Fig. 2). If Stewart's assignment for adenine were true, 6→7 and 6→8 transitions in adenine should be assigned to the weak shoulder (267 mμ) and to the main band (261 mμ) respectively. However, as has been stated above, Mason[20] attributed the long-axis polarized band to the main band of adenine. From this point of view, the 6→7 transition may reasonably be assigned to the main band. In these controversial circumstances, it is difficult to determine which assignment is true for adenine and 9-methyladenine. From a comparison of the calculated transition energy and the experimental results, the main band of adenine was assigned to the 6→7 transition; in this point Mason's assignment is supported. Thus, the first and the second bands of 9-methyladenine (261 mμ and 206 mμ respectively) may be assigned to the 7→8 and 7→9 or 7→10 transitions (Table III). As may be seen in Table III, the 7→9, 7→10, 6→8, 6→9 and 6→10 transitions in 9-methyladenine have nearly the same energies of absorption; therefore, the absorption of 206 mμ may consist of these transitions. The magnitude of the oscillator strength of this absorption may well be understood if it is assigned as above.

The calculated optical indexes for 1-methylthymine are also shown in Table III, in comparison with the experimental results. The calculated oscillator strength of the first band, i. e., the 7→8 transition, is the largest, and that of the 6→9 transition is next largest. The strengths of the other transitions are relatively weak compared with these two transitions, and, as may be seen in Fig. 3, the directions of these transitions agree well with the experimentally-determined values. With regard to the transition energy, agreement between theory and experiment is very poor, as in the case of thymine itself; in this case, the results of the Mataga-Nishimoto approximation are better than those of the Pariser-Parr method.



(a)

(b) (c)

Fig. 3. Comparison of the predicted direction of polarization of 1-methylthymine with the experiment: (a) Calculation according to the Mataga-Nishimoto and (b) Pariser-Parr approximations. (c) Experiment of Stewart and Davidson (Ref. 18).

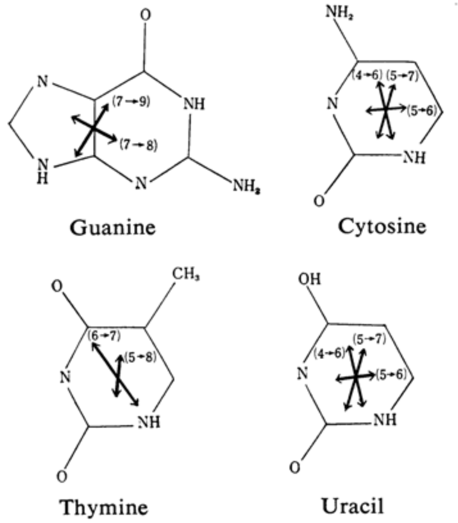


Fig. 4. Predicted directions of polarization of guanine, cytosine, thymine and uracil (Pariser-Parr approximation).

Similarly, the theoretically-determined direction of the polarization for guanine, thymine, cytosine and uracil are indicated in Fig. 4. Although the experiments have not yet been carried out for these compounds, the theoretical results may give an insight into the direction of the polarization and the assignment of the optical transition. In determining the direction of polarization, calculations were carried out by means of the Pariser-Parr approximation. The results using the Mataga-Nishimoto approximation are nearly the same in all these molecules. DeVoe and Tinoco,[19] from their Hückel MO calculation, have predicted the directions of polarization of these molecules and of adenine. It is worth noticing that their results are very similar to those of our SCF MO treatment. Therefore, it may be said that the direction of the transition moments is not sensitive to the degree of approximation.

The Orbital Energy and the π-Electron Distribution. — The energies of the highest-occupied and lowest-vacant orbitals are indicated in Table IV. The meanings of the orbital energy in the Hückel and SCF MO methods are not necessarily the same, but it may be of interest to compare the relative magnitudes of the orbital energies obtained by the two methods. The order of the energies

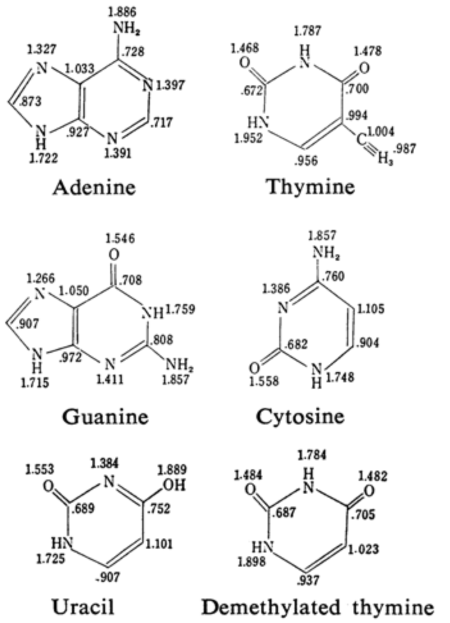
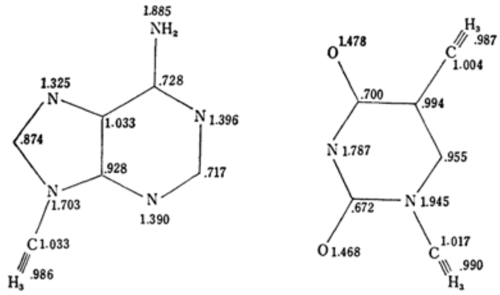


Fig. 5. π-Electron distributions of bases by means of SCF MO method (Pariser-Parr approximation).

TABLE IV. THE ENERGIES OF THE HIGHEST OCCUPIED AND LOWEST VACANT ORBITALS OF BASES (in eV.)

Compound	Energies of the highest occupied levels		Energies of the lowest vacant levels	
	Pariser-Parr	Mataga-Nishimoto	Pariser-Parr	Mataga-Nishimoto
Thymine	−12.045	−10.131	−1.450	−1.861
Uracil	−10.472	−9.419	−1.332	−2.109
Cytosine	−10.460	−9.401	−1.145	−1.914
Adenine	−9.513	−9.029	+0.132	−0.980
Guanine	−9.236	−8.289	−0.314	−1.305



9-Methyladenine 1-Methylthymine

Fig. 6. π-Electron distributions of 9-methyladenine and 1-methylthymine (Pariser-Parr approximation).

of the highest-occupied level of bases is written, in the order of decreasing energy, as follows; guanine>adenine>cytosine>uracil. This order is in accordance with that obtained by Veillard and Pullman,³⁾ and also with the results of the Hückel MO method.¹˒²⁾ For thymine, however, the results by the SCF MO and Hückel MO methods are not in accord; in the former method, the energy of the highest-occupied level of this molecule is the lowest among the bases, but the latter method gives a value between those of cytosine and adenine.

The π-electron distributions of adenine, thymine, guanine, cytosine, uracil, 9-methyladenine and 1-methylthymine are shown in Figs. 5 and 6. The relative magnitude of the π-electron density for guanine and cytosine is the same as that of the SCF MO calculation of Veillard and Pullman³⁾ and also that of the Hückel MO calculation by Pullman,¹⁾ but for adenine the relative magnitude is in disagreement; that is, the order is $N_1>N_3>N_7$ in our calculation, whereas it is $N_7>N_1>N_3$ in Veillard and Pullman.³⁾ The protonation has been known to occur at the N_1 position of adenine,²¹˒²²⁾ and this fact is in accord with the results of the present authors.

As may be seen in Figs. 5 and 6, the electron densities for 9-methyladenine and 1-methylthymine are nearly the same as those of its parent molecules, adenine and thymine. Thus, the changes in the π-electron distributions due to the methyl substitution are known to be small. The changes in the transition wavelengths due to the methyl substitution are zero and 10 mμ for 9-methyladenine and 1-methylthymine respectively (cf. Tables II and III). The fact that there is no shift due to the methyl substitution in adenine seems very curious; the spectra of adenine and 9-methyladenine should be measured under the same conditions.

Summary

SCF MO calculations have been carried out for adenine, guanine, thymine, cytosine, uracil, 9-methyladenine and 1-methylthymine. In evaluating the two-center repulsion integral, the Pariser-Parr and Mataga-Nishimoto approximations have both been used, and the results compared with each other and with the experimental data on the optical properties. In the calculation of thymine, 9-methyladenine, and 1-methylthymine, the hyperconjugation of the methyl group has been taken into account. The calculated wavelength and the oscillator strength of the singlet-singlet transition for the above-mentioned molecules explain the experimental values well except for thymine and 1-methylthymine. The theoretically-determined directions of the polarization of the transition moments have been compared with the experimental results for adenine, 9-methyladenine and 1-methylthymine. With regard to the direction of the polarization of the transition moments of the first and the second absorptions of adenine and 9-methyladenine, the results are questionable. From the theoretical point of view, it is difficult to determine which assignment is correct, however, in view of the wavelength and the oscillator strength, the first absorption may

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21) J. M. Broomhead, *Acta Cryst.*, **1**, 324 (1948); **4**, 92 (1951).

22) W. Cochram, ibid., **4**, 81 (1951).

reasonably be assigned to the long-axis polarized band. The calculated and the experimentally-determined direction of polarization for 1-methylthymine agree well with each other. The energies of the highest and lowest vacant orbitals and the π-electron densities for the molecules treated in the present paper have been calculated and compared with the results obtaied by the Hückel MO method.

Division of Biophysics,
National Cancer Center Research Institute
Tsukiji, Chuo-ku, Tokyo