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The Electronic Structure of Peptide and the Base Components of Nucleic Acids in the Triplet State

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The electronic structures of β-naphthol, the base components of nucleic acids, and peptide have been calculated for the ground, singlet-excited, and triplet-excited states by means of the ASMO SCF CI method. The calculated π electron density of β-naphthol agrees well with the experimental data. The π electron density, the dipole moment, and the bond order for the ground, singlet and triplet excited states have been obtained, and the characteristics of the electronic structures for the ground, singlet-excited, and triplet-excited states have been discussed in connection with the chemical behavior of the molecule.

The electronic structure of the triplet state of a molecule is of importance in connection with the mechanisms of the photochemical reaction and of the electrical conductivity of molecular crystals, and also in connection with the electron spin resonance in the triplet state. However, the calculation of the electron distribution in the triplet state of large molecules has been carried out by only a few researchers. The electron distribution of a molecule in the triplet state can be calculated by various methods. One of these is the open-shell ASMO SCF method developed by Roothaan¹⁾; it was applied to *trans*-butadiene by Lykos *et al.*²⁾ In this treatment, the electron distribution obtained gives a self-consistent field, but it is difficult to obtain the wave function of the singlet-excited state because of the orthogonality of the state to the ground state. The treatment of the triplet state is also possible by the unrestricted SCF MO method proposed by Pople and Nesbet.³⁾ Amos and Snyder calculated the zero-field splitting in the triplet states of naphthalene, anthracene, and phenanthrene by using a modified, unrestricted SCF MO method.⁴⁾ The wave function obtained by this method is not, however, the eigenfunction for the square of the total spin angular momentum, $\mathbf{S}^2$. The procedure to obtain the eigenfunction corresponding to $\mathbf{S}^2$ is very cumbersome for a large molecule.⁵⁾ Another treatment for the triplet state was that employed by Tsubomura for β-naphthol using the composite molecular orbital method. The results agreed qualitatively with the experimentally-determined basicity of the molecule.⁶⁾ He also treated the benzene monoderivatives with the same method, but this method is not suitable for such complex molecules as the base components of DNA. The closed-shell ASMO SCF CI method⁷⁾ can be employed for the calculation of the triplet-excited state as well as for the singlet-ground and excited states. In this treatment, the electronic structure of a triplet-excited state can be discriminated from one of the singlet-excited states, but the wave function obtained by this method does not give any self-consistent field.

In the present work, first, the π electron distributions of β-naphthol were calculated for the ground, excited-singlet and triplet states by the ASMO SCF CI method, and then, in order to investigate the validity of this method, the π electron densities thus obtained were compared with the experimentally-obtained basicities of the compound in the ground, excited-singlet and triplet states respectively. Moreover, such calculations were also carried out for the base components of nucleic acids, that is, for adenine, thymine, guanine, cytosine and uracil, and the π electron densities, dipole moments, and bond orders of these molecules were obtained.⁸⁾ Similar calculations were also carried out for the peptide molecule. In the course of these calculations, the effect of the spin-orbit interaction was neglected, so the wave function is the eigenfunction of $\mathbf{S}^2$; moreover, it was assumed that the bond distances in the excited states are equal to those in the ground state. The electronic structures in the excited singlet and triplet states

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1) C. C. J. Roothaan, *Rev. Mod. Phys.*, **32**, 179 (1960).

2) O. W. Adams and P. G. Lykos, *J. Chem. Phys.*, **34**, 1444 (1961).

3) J. A. Pople and R. K. Nesbet, *ibid.*, **22**, 571 (1954).

4) T. Amos and L. C. Snyder, *ibid.*, **43**, 2146 (1965).

5) P. O. Löwdin, *Phys. Rev.*, **97**, 1509 (1955).

6) H. Tsubomura, Preprint of the Discussion for the Electronic State of Molecules (1964), p. 63; K. Kimura and H. Tsubomura, Preprint of the Annual Meeting of Chemical Society of Japan, April, 1966.

7) Needless to say, the words "closed shell" indicate the SCF calculation for a closed shell and has no relation with CI calculation.

8) The findings on the excitation energy and oscillator strength will be published elsewhere.

TABLE 1. CONFIGURATIONS CONSIDERED IN CALCULATION

Molecule	Configuration for singlet state
β-Naphthol	0—0, 6—7, 6—8, 6—9, 6—10, 6—11, 5—7, 5—8, 5—9, 5—10, 4—7, 4—8, 3—7, $\genfrac{}{}{0pt}{}{6-7}{6-7}$, $\genfrac{}{}{0pt}{}{6-8}{6-8}$, $\genfrac{}{}{0pt}{}{6-9}{6-9}$, $\genfrac{}{}{0pt}{}{6-10}{6-10}$, $\genfrac{}{}{0pt}{}{5-7}{5-7}$, $\genfrac{}{}{0pt}{}{5-8}{5-8}$, $\genfrac{}{}{0pt}{}{4-7}{4-7}$
Adenine	0—0, 6—7, 6—8, 6—9, 6—10, 5—7, 5—8, 5—9, 4—7, 4—8 4—9, 3—7, 3—8, $\genfrac{}{}{0pt}{}{6-7}{6-7}$, $\genfrac{}{}{0pt}{}{6-8}{6-8}$, $\genfrac{}{}{0pt}{}{6-9}{6-9}$, $\genfrac{}{}{0pt}{}{5-7}{5-7}$, $\genfrac{}{}{0pt}{}{5-8}{5-8}$, $\genfrac{}{}{0pt}{}{5-9}{5-9}$, $\genfrac{}{}{0pt}{}{4-7}{4-7}$
Thymine	0—0, 6—7, 6—8, 6—9, 6—10, 5—7, 5—8, 5—9, 4—7, 4—8, 3—7, 3—8, 2—7, $\genfrac{}{}{0pt}{}{6-7}{6-7}$, $\genfrac{}{}{0pt}{}{6-8}{6-8}$, $\genfrac{}{}{0pt}{}{6-9}{6-9}$, $\genfrac{}{}{0pt}{}{5-7}{5-7}$, $\genfrac{}{}{0pt}{}{5-8}{5-8}$, $\genfrac{}{}{0pt}{}{4-7}{4-7}$, $\genfrac{}{}{0pt}{}{4-8}{4-8}$
Guanine	0—0, 7—8, 7—9, 7—10, 7—11, 6—8, 6—9, 6—10, 5—8, 5—9, 5—10, 4—8, 4—9, $\genfrac{}{}{0pt}{}{7-8}{7-8}$, $\genfrac{}{}{0pt}{}{7-9}{7-9}$, $\genfrac{}{}{0pt}{}{7-10}{7-10}$, $\genfrac{}{}{0pt}{}{7-11}{7-11}$, $\genfrac{}{}{0pt}{}{6-8}{6-8}$, $\genfrac{}{}{0pt}{}{6-9}{6-9}$, $\genfrac{}{}{0pt}{}{6-10}{6-10}$
Cytosine	0—0, 5—6, 5—7, 5—8, 4—6, 4—7, 4—8, 3—6, 3—7, 3—8, 2—6, 2—7, $\genfrac{}{}{0pt}{}{5-6}{5-6}$, $\genfrac{}{}{0pt}{}{5-7}{5-7}$, $\genfrac{}{}{0pt}{}{5-8}{5-8}$, $\genfrac{}{}{0pt}{}{4-6}{4-6}$, $\genfrac{}{}{0pt}{}{4-7}{4-7}$, $\genfrac{}{}{0pt}{}{3-6}{3-6}$, $\genfrac{}{}{0pt}{}{3-7}{3-7}$, $\genfrac{}{}{0pt}{}{2-6}{2-6}$
Uracil	0—0, 5—6, 5—7, 5—8, 4—6, 4—7, 4—8, 3—6, 3—7, 3—8, 2—6, 2—7, 1—6, $\genfrac{}{}{0pt}{}{5-6}{5-6}$, $\genfrac{}{}{0pt}{}{5-7}{5-7}$, $\genfrac{}{}{0pt}{}{5-8}{5-8}$, $\genfrac{}{}{0pt}{}{4-6}{4-6}$, $\genfrac{}{}{0pt}{}{4-7}{4-7}$, $\genfrac{}{}{0pt}{}{4-8}{4-8}$, $\genfrac{}{}{0pt}{}{3-6}{3-6}$
Peptide	0—0, 2—3, 1—3, $\genfrac{}{}{0pt}{}{1-3}{2-3}$, $\genfrac{}{}{0pt}{}{2-3}{2-3}$, $\genfrac{}{}{0pt}{}{1-3}{1-3}$

Molecule	Configuration for triplet state
β-Naphthol	6—7, 6—8, 6—9, 6—10, 6—11, 5—7, 5—8, 5—9, 5—10, 4—7, 4—8, 3—7,
Adenine	6—7, 6—8, 6—9, 6—10, 5—7, 5—8, 5—9, 4—7, 4—8, 4—9, 3—7, 3—8,
Thymine	6—7, 6—8, 6—9, 6—10, 5—7, 5—8, 5—9, 4—7, 4—8, 3—7, 3—8, 2—7,
Guanine	7—8, 7—9, 7—10, 7—11, 6—8, 6—9, 6—10, 5—8, 5—9, 5—10, 4—8, 4—9,
Cytosine	5—6, 5—7, 5—8, 4—6, 4—7, 4—8, 3—6, 3—7, 3—8, 2—6, 2—7,
Uracil	5—6, 5—7, 5—8, 4—6, 4—7, 4—8, 3—6, 3—7, 3—8, 2—6, 2—7, 1—6,
Peptide	2—3, 1—3, $\genfrac{}{}{0pt}{}{1-3}{2-3}$

The notation $i—j$ means the singly excited configuration in which the electron in ith orbital is excited to jth orbital, and the notation $\genfrac{}{}{0pt}{}{i-j}{k-j}$, the doubly excited configuration in which the electrons in ith and kth orbitals are excited to jth orbital respectively. The notation 0—0 is ground state configuration.

for these molecules will be discussed and some interesting conclusions will be derived.

Calculation Procedure

In the calculation, only π electrons were taken into account explicitly. As a first step, the SCF MO's were obtained by using the semi-empirical ASMO SCF method.[9] In this treatment one-center Coulomb repulsion and two-center Coulomb repulsion integrals are estimated by means of the Pariser-Parr[10] and Mataga-Nishimoto[11] approximations respectively, and the differential overlap is neglected. With regard to the core Coulomb integral, the Goeppert-Mayer and Sklar approximation[12] was adopted and the penetration integrals were neglected. The resonance integral was

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[9] C. Nagata, A. Imamura, Y. Tagashira and M. Kodama, This Bulletin, **38**, 1639 (1965).

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

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

[12] M. Goeppert-Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

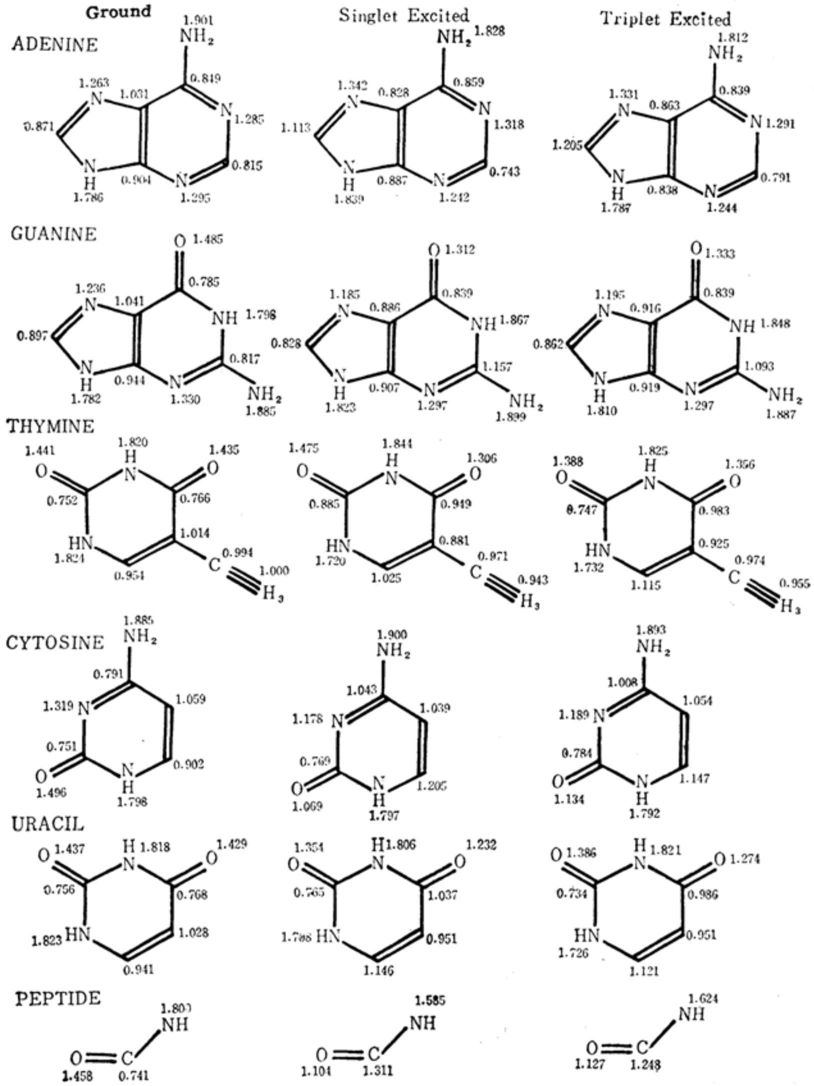

Fig. 1. Total π electron densities in ground, singlet excited and triplet excited states of base components of nucleic acids and peptide.

assumed to be proportional to the overlap integral. The estimated values for these integrals are the same as those in our previous paper.⁹⁾

The matrix elements appearing in the calculation of the configuration interaction were evaluated with the same approximation as that used in the ASMO SCF method by using the above-stated SCF molecular orbitals. In our calculation, not only the singly-excited configurations, but also the doubly-excited ones were taken into consideration. The configurations adopted for β-naphthol, the base components of nucleic acids, and peptide are listed in Table 1. Needless to say, in the ground and the singlet excited states, the total wave function is represented by a linear combination of the wave functions of the ground and various singly- and doubly-excited configurations; on the other hand, in the triplet-excited states, the total wave function is a linear combination of singly-excited configurations.¹³⁾ Moreover, the matrix element between singly-excited singlet configurations differs from that between the triplet configurations because of its spin function. Because of these circumstances, in the treatment of configuration interactions the total wave function of the excited singlet state differs from that of the excited triplet state. The total wave function of the *i*th excited singlet or triplet state (including the ground state) is represented as follows;

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13) In peptide the doubly-excited configurations in which two electrons excited from or to different energy levels are included in the form of a linear combination in the triplet state.

$$\Psi_i = \sum_j d_{ij}\psi_j \tag{1}$$

where ψ_j is the wave function corresponding to the j th configuration, and where d_{ij} is the coefficient of the wave function of the jth configuration. The summation covers all the configurations considered. The total π electron densities and the bond orders of the ith excited state can be calculated by the following formulas:

$$Q^i_r = \sum_j (d_{ij})^2 q^{(j)}_r \tag{2}$$

where:

$$q^{(j)}_r = \sum_k (C_{kr})^2 \tag{3}$$

and:

$$P^i_{rs} = \sum_j (d_{ij})^2 p^{(j)}_{rs} \tag{4}$$

where:

$$p^{(j)}_{rs} = \sum_k C_{kr}C_{ks} \tag{5}$$

In these equations, C_{kr} is the coefficient of the rth atomic orbital in the kth molecular orbital obtained in the ASMO SCF treatment, and the summation in Eqs. (3) and (5) covers all the occupied orbitals in the jth configuration, so $q^{(j)}_r$ indicates the total π electron density on the rth atom in the jth configuration and $p^{(j)}_{rs}$ is the bond order between the rth and sth atoms in the jth configuration. Using these formulas, the total π electron densities and bond orders of the ground, excited-singlet and excited-triplet states were obtained.

Results and Discussion

π Electron Density. In order to investigate the validity of this method, the π electron densities of β-naphthol in the ground, excited-singlet and triplet states were calculated, and the π electron density of the hydroxy substituent was compared with the pK values of β-naphthol in the ground, excited-singlet and excited-triplet states (Table 2). As is shown in the table, the less the electron density, the less the pK value. Therefore, the method and the approximation used in the present paper seem to be appropriate for the calculation of the π electron densities of the ground, excited-singlet, excited-triplet states.

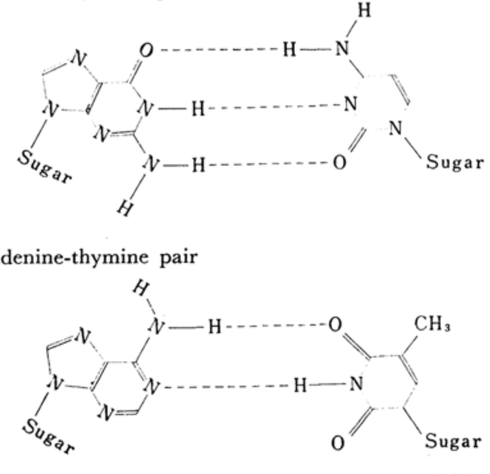
TABLE 2. THE ELECTRON DENSITY ON HYDROXY SUBSTITUENT OF β-NAPHTHOL AND pK VALUE FOR GROUND, SINGLET EXCITED AND TRIPLET EXCITED STATES

	Ground state	Singlet excited state	Triplet excited state
π Electron density	1.974	1.956	1.964
pK Value*	9.5	3.1	8.1

* G. Jackson and G. Porter, *Proc. Roy. Soc.*, **A260**, 13 (1961).

Similarly, the π electron densities and the bond orders of the base components of nucleic acids were calculated; they are shown in Fig. 1. At a glance, it may be seen that there is a tendency for the values of the electron distribution of the excited triplet state to be intermediate between that of the ground state and that of the singlet-excited state; this is especially true of the peptide molecule. This tendency explains well such experimental results as those concerning basicity.[14] The difference in electronic structure between the ground state and the excited-triplet state is of especial importance in elucidating the difference in chemical reactivity between the ground and the excited states. In this connection, the electronic structures of the base pair in DNA in the ground, and in the lowest singlet and the triplet-excited states[15] are worth noticing. The π electron distribution of the base components may be altered when they are paired with the complementary base components in DNA, but it has been found that the alteration is so small[16] that the general conclusion is not altered. For this reason, the discussion of the base-pair of DNA will be given by using the π electron distributions of the base components. As may be seen in Figs. 1 and 2, in the guanine-cytosine base pair the π electron densities on all proton-accepting atoms in the singlet

Adenine-cytosine pair



Adenine-thymine pair

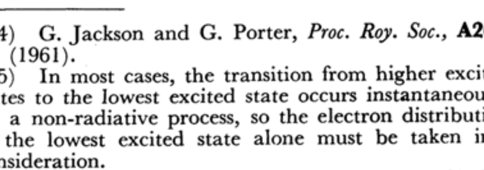


Fig. 2. Base pairs in DNA by Watson-Crick model.

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[14] G. Jackson and G. Porter, *Proc. Roy. Soc.*, **A260**, 13 (1961).

[15] In most cases, the transition from higher excited states to the lowest excited state occurs instantaneously *via* a non-radiative process, so the electron distribution of the lowest excited state alone must be taken into consideration.

[16] B. Pullman and A. Pullman, *Biochim. biophys. Acta*, **36**, 343 (1959).

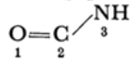
and the triplet-excited states are less than in the ground state; that is, the proton-accepting power decreases when the molecule is in the ground state. For instance, the π electron densities on carbonyl oxygen in cytosine are 1.496, 1.069, and 1.134 in the ground, singlet-excited and triplet-excited states, respectively. Moreover, in the guanine-cytosine base pair all the proton-donating atoms in the excited state have larger π electron densities than those in the ground state; in other words, the proton-donating power in the ground state is stronger than that in the excited states. Both these results mean that in the guanine-cytosine base pair scarcely proton tunneling occurs in the excited states. On the other hand, the circumstances are reversed for the adenine-thymine base pair; that is, these all proton-donating atoms in the ground state have more electron densities than those in the excited state, and all proton-accepting atoms have smaller π electron densities in the ground state than in the excited states except for the carbonyl oxygen of thymine in the triplet state. Therefore, in the adenine-thymine base pair proton tunneling can more easily occur in the excited singlet and triplet states than in the ground state. According to our previous paper,[17] proton tunneling lead to the misduplication of DNA; that is, in the case of excitation of an electron by light the misduplication of DNA by means of the proton tunneling can more easily occur in the adenine-thymine pair than in the guanine-cytosine pair. The similar calculation was carried out by Ladik by the Hückel MO method.[18] In his calculations, contrary to our conclusion, the guanine-cytosine base pair has more chances to tunnel in the excited state than in the ground state. The Hückel MO approximation is considered to be not reliable, as has been pointed out by Ladik.[17] However, at the present stage, which conclusion is correct can not be determined because of the lack of experimental data. In the future, the data on the chemical behavior of the base pair in the excited state and of the biological action connected with it should be sought for.

The π electron densities of the peptide molecule in the ground and excited states are remarkably different from each other. From the values of the electron densities at the nitrogen atom, the magnitude of the basicity of the peptide molecule is assumed to be of the following order; the ground> the excited triplet> the excited singlet. As was stated above, the π electron densities of the excited singlet state obtained by means of the closed-shell ASMO SCF method are not different from those of triplet-excited states. The π electron densities of peptides in the excited singlet and triplet states obtained by the ASMO SCF CI method are compared with the values by the ASMO SCF method (Table 3). Except for the value at the nitrogen atom, the values obtained by the ASMO SCF method can be considered to be averages of the values in the singlet and triplet states obtained by the ASMO SCF CI method.

TABLE 3. THE π ELECTRON DENSITY OF PEPTIDE FOR SINGLET EXCITED AND TRIPLET EXCITED STATES OBTAINED BY ASMO SCF CI METHOD AND THE CORRESPONDING EXCITED STATE BY ASMO SCF METHOD

Atom*	Singlet excited state by ASMO SCF CI	Triplet excited state by ASMO SCF CI	Excited state by ASMO SCF
1	1.104	1.127	1.110
2	1.311	1.248	1.253
3	1.585	1.624	1.637

* The numbering of peptide molecule is as follows.



Dipole Moments. In Table 4, the dipole moments of β-naphthol, base components of nucleic acids and peptide are tabulated. The dipole moment of β-naphthol in the triplet state is very close to the value in the ground state; on the other hand, the dipole moment of guanine in the triplet state is slightly different from that in the singlet state. For adenine, thymine, and peptide, dipole moments in the triplet state are smaller than the values in the other two states.

TABLE 4. DIPOLE MOMENT OF β-NAPHTHOL, BASE COMPONENTS OF NUCLEIC ACIDS AND PEPTIDE FOR THE GROUND, SINGLET EXCITED AND TRIPLET EXCITED STATES (in Debye unit)

Molecule	Ground state	Singlet excited state	Triplet excited state
β-Naphthol	0.450	0.706	0.474
Adenine	2.470	3.134	1.227
Guanine	6.039	3.746	4.157
Thymine	3.511	4.996	2.729
Cytosine	6.063	0.884	2.067
Uracil	3.411	1.759	2.227
Peptide	2.876	5.651	1.568

Bond Order. The bond orders of the molecules in the ground, singlet and triplet excited states are indicated in Fig. 3. The bond order can generally be considered to be correlated with the strength of the bond; that is, the greater the bond order, the stronger the corresponding bond. In this sense, the change in the bond order represents the change in the strength of the bond, that is, the reactivity for some kinds of chemical reaction. As may be seen in Fig. 3, in general, the calculated

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[17] C. Nagata, A. Imamura, K. Fukui and H. Saito, *Gann*, **54**, 401 (1963).

[18] J. Ladik, *J. Theoret. Biol.*, **6**, 201 (1964).

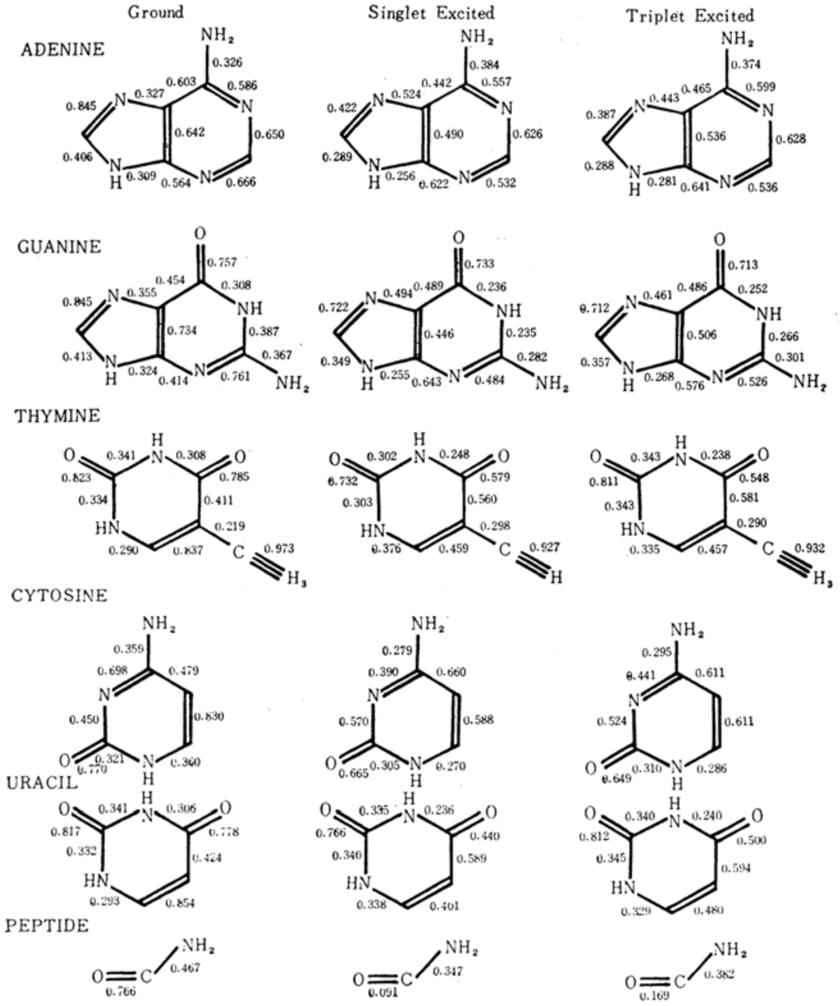
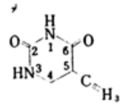


Fig. 3. π Bond orders in ground, singlet excited and triplet excited states of base components of nucleic acids and peptide.

TABLE 5. BOND ORDERS OF PYRIMIDINE DERIVATIVES IN GROUND AND EXCITED STATES

Molecule	Bond order of C_4–C_5 bond		
	Ground state	Singlet excited state	Triplet excited state
Thymine	0.837	0.459	0.457
Uracil	0.854	0.401	0.480
Cytosine	0.830	0.588	0.611



bond orders in the excited state are smaller than those in the ground state, so the molecule in the excited state may be expected to be more unstable than that in the ground state. However, in some bonds such as the C–NH_2 bond in adenine, the excited state has a larger bond order than the ground state. Therefore, the tendency of the bond order to alter with the change in the state is multifarious. It is interesting to notice that in the thymine molecule, the C_4–C_5 bond has greatly different bond orders in its ground and excited states (Table 5). Hence, in the excited states the bond may be expected to become very weak, so that bond breakage may easily occur. It is this bond that plays an important role in thymine dimer formation by photoirradiation.[19] In connection with this, uracil is also known to form photodimers easily; on the other hand, cytosine does so scarcely at all. According to Table 5, in which the bond orders of C_4–C_5 bonds of thymine,

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[19] R. Beukers and W. Berends, *Biochim. biophys. Acta,* **41**, 550 (1960).

uracil and cytosine in the ground, singlet-excited and triplet-excited states are tabulated, the bond of cytosine in the excited state is stronger than those of thymine and uracil. This finding agrees with the experimental data. From this data, however, the question as to whether the dimer formation occurs *via* the singlet-excited state or *via* the triplet-excited state is still unsolved.

Some of the calculations were carried out on an IBM 7090 computer with the permission of the UNICON committee, to the members of which the authors are grateful. This investigation was partly supported by a grant of the Japanese Ministry of Education.