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# Use of Propagators in the Hückel Model. VIII. Intermolecular Interaction

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Intermolecular interactions are analyzed by the propagator method, under the tight-binding approximation. The stabilization energy or the change of charge density due to the intermolecular interaction are expressed in terms of propagators, so that the mechanism resulting above effects is satisfactorily realized. As an interesting example, the intermolecular interaction between guanine and benzo[*a*]pyrene (a famous chemical carcinogen) is investigated.

There are various types of intermolecular interactions. If interacting molecules are charged, or have permanent dipoles, the interaction between them is purely classical, due to the static coulomb potentials. If they are neutral, the induced dipole moments are responsible for their combination.[1] The hydrogen-bond is classified as one of the intermolecular interaction, but this would be a rather weak chemical bond. Another one is the charge-transfer complex proposed by Mulliken:[2] Even if the composite molecules are neutral themselves, the charge-transfer state which is energetically higher than the neutral state mixes with the latter to yield the more stable ground state.

Recently a high ability of the computer may enable us to calculate the intermolecular interaction energies on the same footing dealing with simple molecules. If this be done satisfactorily, the effects involving the above mentioned treatments would be wholly taken into account, but the concepts introduced by the respective methods will be lost. In addition, one cannot expect the computer ability to reproduce the experimental details which the common chemists are interested in.

The present analysis which is facilitated by the propagator technique is at most semiquantitaive. The interaction terms responsible for the molecular combination are assumed to have a single-particle character, i.e., are written by the so-called transfer integrals. This mechanism should be interpreted as a mutual charge transfer in Mulliken's sense.[2]

In the followings, we begin with writting the stabilization energy due to the intermolecular interaction in terms of the Green's function up to the second order of the interaction. In the first half of this paper, the first order term plays a central role in searching for the preferable conformations of the composite molecules. In the second half, adopting the unperturbed system of separated molecules, we express the stabilization energy as a second order effect due to the perturbation. This is very easily carried out by the propagator method. Then we advance one more step of approximation procedure called the closure approximation, so that the mechanism yielding the interaction effect is made very much clear. Finally the interaction between guanine and benzo[*a*]pyrene is investigated as a suggestive example for chemical carcinogenesis.

## General

As has been shown,[3] in the tight-binding approximation (Hückel approximation in the $\pi$-conjugated molecules) the bond order and the total energy are expressed, respectively, in terms of propagators as

$$q_{rs} = \frac{1}{2\pi i}\int_c dz G_{rs}(z), \tag{1}$$

$$E = Tr\frac{1}{2\pi i}\int_c dzzG(z), \tag{2}$$

where $r$ and $s$ are site indices. In the above the propagator $G$ is

$$G(z) = \frac{1}{z-H} \tag{3}$$

with

$$H = \begin{bmatrix} 0 & \beta_{12} & \beta_{13} & \cdot & \cdot \\ \beta_{21} & 0 & \beta_{23} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix}, \tag{4}$$

where $\beta_{rs}$ is a transfer integral, which is usually taken into account for the adjacent neighbors. The integration with respect to $z$ is carried out along the Coulson contour, which goes along the circuit enclosing poles referring to the occupied levels. We assume that the integration involves the spin sum. Tr(trace) means the diagonal sum, ensurering the independent character from representations.

If the Hamiltonian is separated as

$$H = H^{\circ} + v, \tag{5}$$

where $v$ is the perturbation, then Eq. 3 is rewritten as

$$\begin{aligned} G(z) &= \frac{1}{z-H} \\ &= \frac{1}{z-H^0} + \frac{1}{z-H^0}\, v\, \frac{1}{z-H} \\ &= G^0(z) + G^0(z)vG(z). \end{aligned} \tag{6}$$

In the above, we defined $G^0(z)$ for the unperturbed Hamiltonian.

Expanding $G(z)$ as in Eq. 6 and keeping up to the second order term of $v$, we can obtain changes of energy and bond order. The energy change due to $v$ is

$$\begin{aligned}\Delta E &= \mathrm{Tr}\frac{1}{2\pi i}\int_c dz z(G-G^0) \\ &\doteqdot \mathrm{Tr}\frac{1}{2\pi i}\int_c dz z(G^0vG^0+G^0vG^0vG^0) \\ &= \mathrm{Tr}\frac{1}{2\pi i}\int_c dz(G^0v+\frac{1}{2}G^0vG^0v)\,. \end{aligned} \tag{7}$$

The last result is obtained by partial integration in the second line. If the perturbation $v$ is independent of $z$, the first term of Eq 7 is evaluated as

$$\Delta E^{(1)} = 2\sum_{rs} q_{rs}v_{sr} \tag{8}$$

by the use of Eq. 1. The numerical factor 2 is due to the spin sum. If we use the representation diagonalizing the Hamiltonian $H^0$, $G^0(z)$ is written as

$$G^0(z) = \sum_i \frac{|i><i|}{z-\varepsilon_i}\,,\ (H^0|i>=\varepsilon_i|i>)\,. \tag{9}$$

We can evaluate the second term of Eq. 7 as follows:

$$\begin{aligned}\Delta E^{(2)} &= \frac{1}{2\pi i}\int_c dz\frac{1}{2}\sum_{rstu}\sum_{ij}\frac{<r|i><i|s>}{z-\varepsilon_i}v_{st}\frac{<t|j><j|u>}{z-\varepsilon_j}v_{ur} \\ &= 2\sum_{rstu}\sum_{i}^{occ}\sum_{j}^{un}<r|i><i|s>v_{st}<t|j><j|u>v_{ur}/(\varepsilon_i-\varepsilon_j)\,. \end{aligned} \tag{10}$$

This result is also rewritten in terms of polarizabilities.[4)]

The similar expression for the bond order is also obtained as well. The above expressions are useful for the case of the interaction $v$ being intramolecular, and in the intermolecular case are replaced by a little more complicated expressions.

Now we advance the approximation procedure (so-called the closure approximation) one more step in Eq. 10. If the denominators are replaced by their average,

$$\Delta\varepsilon \simeq <\varepsilon_j-\varepsilon_i>_{av}\,(>0), \tag{11}$$

we can carried out the summation with respect to $i$ and $j$ to obtain

$$\Delta E^{(2)} = -\frac{1}{2}\frac{1}{\Delta\varepsilon}\sum_{rstu} q_{rs}v_{st}\hat{q}_{tu}v_{ur}\,, \tag{12}$$

where

$$q_{rs} = 2\sum_i^{occ}<r|i><i|s> \tag{13}$$

is the so-called the bond order, and

$$\begin{aligned}\hat{q}_{tu} &= 2\sum_i^{un}<t|i><i|u> \\ &= 2\delta_{tu}-q_{tu}\,. \end{aligned} \tag{14}$$

The last line is obtained from the completeness relation.

We can understand from Eq. 12 that the additional energy arises from going round a circuit as $r\to s\to t\to u\to r$, which are constructed of bond orders and interaction matrix elements.

As an illustrative example, we ask which is energetically more stable, anthracene or phenanthrene. First we note that the energy difference between them occurs from the second order terms. Observing Fig. 1, we can immediately obtain (noticing that $\Delta\varepsilon>0$), for anthracene

$$\Delta E^{(2)} = -\frac{1}{\Delta\varepsilon}q_{79}v_{9,14}\hat{q}_{14,2}v_{27} = 0\,, \tag{15}$$

since $q_{79}=\hat{q}_{14,2}=0$, and for phenanthrene

$$\Delta E^{(2)} = -\frac{1}{\Delta\varepsilon}\hat{q}_{69}v_{9,14}q_{14,1}v_{16}<0\,, \tag{16}$$

since $q_{14,1}>0$, and $\hat{q}_{69}>0$. Therefore phenanthrene is more stable than anthracene.

## Mutual Orientation of Interacting Molecules

Let us imagine that two conjugated ring molecules, $A$ and $B$ approach with each other, and a bond indicated by a solid line in Fig. 2 takes place between them. If molecular planes are mutually parallel, this bond is a $\sigma$-type between $\pi$-orbitals of $A$ and $B$ molecules. The mutual phases of $\pi$ atomic orbitals of both molecules are put so that all resonance integrals are attractive. This situation seems appropriate for the beginning of intermolecular reaction. Problem is: Where is the next bond formed (not necessarily restricted only one) to get a firmer combination between? The answer will be provided by Eq. 8. Since we can consider the above molecular compound, $A$—$B$ as a whole system because

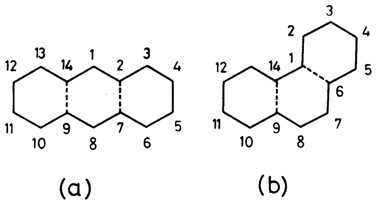

Fig. 1. (a) Anthracene and (b) phenanthrene molecules.

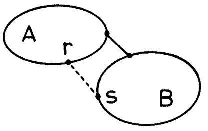

Fig. 2. Schematic diagrame of two interacting molecules.

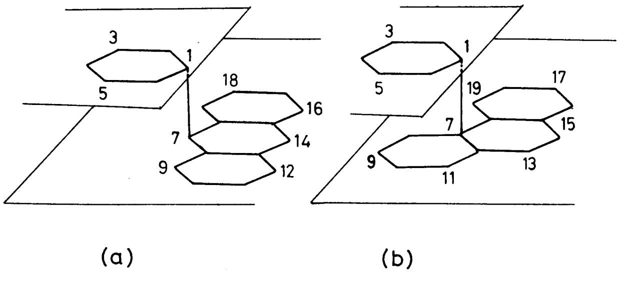

Fig. 3. Schematic diagrames of composite molecule between (a) benzene-anthracene and (b) benzene-phenanthrene.

Table 1. Bond Orders of Benzene-Anthracene Pair

| (a) | | (b) | | (c) | | (d) | |
|---|---|---|---|---|---|---|---|
| Site | $q_{rs}$ | Site | $q_{rs}$ | Site | $q_{rs}$ | Site | $q_{rs}$ |
| 2-8 | −0.125 | 2-7 | −0.095 | 2-7 | −0.090 | 2-8 | −0.164 |
| 2-14 | 0.146 | 2-9 | −0.098 | 2-8 | −0.177 | 2-9 | −0.199 |
| 4-8 | 0.097 | 2-13 | −0.082 | 2-10 | −0.091 | 2-14 | 0.084 |
| 4-14 | −0.131 | 2-14 | 0.135 | 2-12 | 0.066 | 4-8 | 0.128 |
| | | 2-20 | −0.119 | 2-13 | −0.083 | 4-9 | 0.160 |
| | | 4-14 | −0.122 | 2-14 | 0.081 | | |
| | | 4-20 | 0.093 | 2-20 | −0.076 | | |
| | | | | 4-7 | 0.073 | | |
| | | | | 4-8 | 0.136 | | |
| | | | | 4-10 | 0.067 | | |
| | | | | 4-13 | 0.061 | | |
| | | | | 4-14 | −0.070 | | |

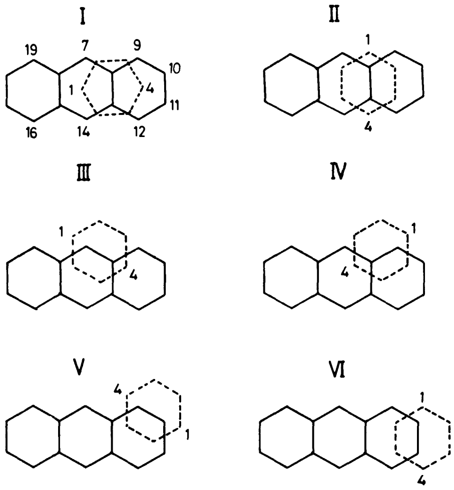

Fig. 4. Various conformations of benzene-anthracene pair.

Table 2. Bond Orders of Benzene-Phenanthrene Pair

| Site | $q_{rs}$ | Site | $q_{rs}$ |
|---|---|---|---|
| 2-8 | −0.122 | 2-14 | 0.083 |
| 2-10 | 0.089 | 4-8 | 0.093 |
| 2-12 | −0.1110 | 4-12 | 0.085 |

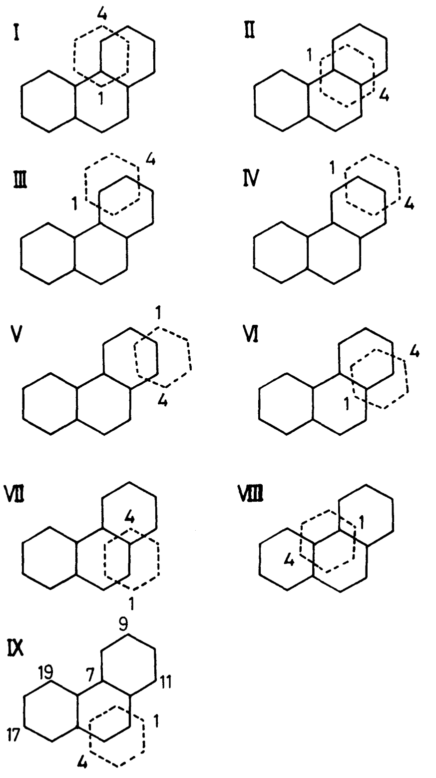

Fig. 5. Various conformations of benzene-phenanthrene pair.

of the bond described by the solid line, it is expected that the next bond (indicated by the dotted line in Fig. 2) will arise between $r$ and $s$ sites where $\Delta E^{(1)}$ of Eq. 8 is negative and as large as possible in its absolute value. In other words, $v_{rs}$ being negative, $q_{rs}$ should be positive and as large as possible.

We give two examples: Benzene-anthracene pair and benzene-phenanthrene pair. As is shown in Fig. 3(a), benzene and anthracene approach with each other keeping their molecular plane parallel, and make a bond between the *1*-site of benzene and the *7*-site of anthracene. The calculated results of which absolute values are considerably large are shown in Table 1a. Observing the data we can expect new bonds between sites *2* and *14*, or between sites *4* and *8*. If we consider that the new bond is likely under the condition that the original *1-7* bond does not shift so much, it should be concluded that the pair under consideration is stable at the conformation, I or III in Fig. 4.

From the symmetry consideration it is enough to select the anthracene sites *7-10* to make similar treatments. From Table 1b which refers to the *1-8* original bond, we expect again the conformation III. Table 1c corresponding to the *1-9* original bond suggests conformations II and IV. Finally from Table 1d referring to the original *1-10* bond we can expect the conformation V. Unexpectedly we can not find the conformation VI from Table 1d.

From the preceding considerations we find that, in every compound, benzene rings avoid the face-to-face structure as if the steric effect be satisfactorily taken into account. This fact is already pointed out by one of the present authors.[5]

The entirely same investigation is also applied to the benzene-phenanthrene pair. From the symmetry consideration the phenanthrene sites combining with the benzene *1*-site are selected to be *7—13* in Fig. 3(b). As an example we evaluate bond orders in the case of the pair with the *1-7* original bond. The results are shown in Table 2. From this it is easy to presume that conformations I and II in Fig. 5 are likely. Similar considerations for cases involving sites *8—13* in phenanthrene lead to various conformations III—VII in Fig.5.

### Intermolecular Interaction

If we take the separated molecules, $A$ and $B$ as the unperturbed system, the additional energy is of the second order to the perturbation $v$. We find a little more complicated expression than that of Eq. 7, as

$$\Delta E^{(2)} = Tr \frac{1}{2\pi i}\int_c dz G_A{}^0 v_{AB} G_B{}^0 u_{BA} \ , \tag{17}$$

where the factor 1/2 in the first line of Eq. 7 cancels out with the factor arising in interchanging $A$ and $B$ in the above. Then the straightforward calculation yields:

$$\begin{aligned}\Delta E^{(2)} = {} & 2 \sum_{rs}^{A} \sum_{tu}^{B} \\ & \left\{ \sum_{iA}^{\mathrm{occ}} \sum_{\mu B}^{\mathrm{un}} \frac{1}{\varepsilon_{iA} - \varepsilon_{\mu B}} [<r|i><i|s>]^A v_{st}^{AB} [<t|\mu><\mu|u>]^B v_{ur}^{BA} \right. \\ & \left. + \sum_{\mu A}^{un} \sum_{iB}^{occ} \frac{1}{\varepsilon_{iB} - \varepsilon_{\mu A}} [<r|\mu><\mu|s>]^A v_{st}^{AB} [<t|i><i|u>]^B v_{ur}^{BA} \right\}\end{aligned} \tag{18}$$

where the numerical factor 2 is due to the spin sum.

Now we want to take the closure approximation. Replacing the energy denominators in the above by suitable averages, for example

$$\Delta\varepsilon_{BA} \simeq <\varepsilon_{\mu B} - \varepsilon_{iA}>_{av}, \ \Delta\varepsilon_{AB} \simeq <\varepsilon_{\mu A} - \varepsilon_{iB}>_{av}, \tag{19}$$

we obtain

$$\Delta E^{(2)} = \frac{-1}{2} \sum_{rs}^{A} \sum_{tu}^{B} \left\{ \frac{1}{\Delta\varepsilon_{BA}} q_{rs}^A v_{st}^{AB} q_{tu}^B v_{ur}^{BA} + \frac{1}{\Delta\varepsilon_{AB}} q_{rs}^A v_{st}^{AB} q_{tu}^B v_{ur}^{BA} \right\} \tag{20}$$

where $q_{rs}^B$ is the bond order and (see Eq. 14)

$$\hat{q}_{tu}^B = 2\delta_{tu} - q_{tu}^B \, . \tag{21}$$

Next we evaluate the change of bond order due to $v$. To this end we begin with the expansion

$$G_B = G_B^0 + G_B^0 v^{BA} G_A^0 v^{AB} G_B^0 + \cdots \tag{22}$$

and obtain

$$\begin{aligned}\Delta q_{rs}^B &= \frac{1}{2\pi i}\int_c dz (G_B - G_B^0) \\ &= \sum_{s's''t't''} \frac{1}{2\pi i}\int_c dz G_{B,rs'}^0 v_{s's''}^{BA} G_{A,s''t'}^0 v_{t't''}^{AB} G_{B,t''s}^0 \, .\end{aligned} \tag{23}$$

Substituting Eq. 9 in the above, and integrating along the Coulson contour, we obtain the result:

$$\begin{aligned}\Delta q_{rs}^B = 2 \sum_{s't''}^{A} \sum_{s''t'}^{B} & \left\{ \sum_{iB}^{occ} \sum_{jA}^{occ} \sum_{kB}^{un} \frac{-2}{(\varepsilon_{kB} - \varepsilon_{iB})(\varepsilon_{kB} - \varepsilon_{jA})} \right. \\ & + \sum_{iB}^{coo} \sum_{jA}^{un} \sum_{kB}^{occ} \frac{-1}{(\varepsilon_{jA} - \varepsilon_{iB})(\varepsilon_{jA} - \varepsilon_{kB})} \\ & + \sum_{iB}^{occ} \sum_{jA}^{un} \sum_{kB}^{un} \frac{2}{(\varepsilon_{jA} - \varepsilon_{iB})(\varepsilon_{kB} - \varepsilon_{iB})} \\ & \left. + \sum_{iB}^{un} \sum_{jA}^{occ} \sum_{kB}^{un} \frac{1}{(\varepsilon_{iB} - \varepsilon_{jA})(\varepsilon_{kB} - \varepsilon_{jA})} \right\} \\ \times <r|i><i|s'>^B v_{s's''}^{BA} & <s''|j><j|t'>^A v_{t't''}^{AB} <t''|k><k|s>^B .\end{aligned} \tag{24}$$

Now we employ the closure approximation in the above and obtain

$$\begin{aligned}\Delta q_{rs}^B = \frac{1}{4} \sum_{s't''}^{B} \sum_{s''t'}^{A} & \left\{ \frac{-2}{\Delta\varepsilon_{BB}\Delta\varepsilon_{BA}} q_{rs'}^B v_{s's''}^{BA} q_{s''t'}^A v_{t't''}^{AB} \hat{q}_{t''s}^B \right. \\ & + \frac{-1}{\Delta\varepsilon_{AB}\Delta\varepsilon_{AB}} q_{rs'}^B v_{s's''}^{BA} \hat{q}_{s''t'}^A v_{t't''}^{AB} q_{t''s}^B \\ & + \frac{2}{\Delta\varepsilon_{AB}\Delta\varepsilon_{BB}} q_{rs'}^B v_{s's''}^{BA} \hat{q}_{s''t'}^A v_{t't''}^{AB} \hat{q}_{t''s}^B \\ & \left. + \frac{1}{\Delta\varepsilon_{BA}\Delta\varepsilon_{BA}} \hat{q}_{rs'}^B v_{s's''}^{BA} q_{s''t'}^A v_{t't''}^{AB} \hat{q}_{t''s}^B \right\} .\end{aligned} \tag{25}$$

Here we again stress that the change of bond order does arise from additional contributions of some reaction pathes which are constructed of bond orders and interaction matrix elements. We can get, with a little sacrifice of accuracy in Eq. 24, a very transparent physical insight of the phenomena under consideration.

We present numerical results in the followings. The parameters used here are:

1. The distance of molecular planes (e.g. between benzene and anthrathene planes) is assumed to be 2 in the unit of the benzene bond distance (1.39 Å).
2. The values of $v_{rs}$ are estimated to be reciprocally proportional to the cube of the *r-s* distance, and are assumed to be zero for cases with distances larger than 8. Then a multicative factor *2* is applied because of the $\sigma$-bond character of $v_{rs}$.

In Table 3, we have shown the calculated results of various conformations of benzene-anthracene pair. The first column presents the types of pairs as displayed in Fig. 4. The energy changes of the second column are given in the unit of $|\beta|$. The minus sign indicates the system to be stable. The values of the first line is obtained by the closure approximarion, Eq. 20, while the second line by the relation without approximation, Eq. 18. Agreements between them are remarkable, though the values themselves are rather qualitative. The following columns present the changes of charge densities at various benzene sites. As to these, the agreements between the first and second lines are not so satisfactory as in the case of energy. This is a

Table 3. Changes of Energy and Charge Densities of Various Types of Benzene-Anthracene Pair

| | $\Delta E$ | $\Delta q_{rr}$ of benzene | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| I | −0.0436 | 0.047 | −0.007 | −0.043 | 0.089 | −0.043 | −0.007 |
| | −0.0591 | 0.059 | −0.017 | −0.019 | 0.049 | −0.019 | −0.017 |
| II | −0.0584 | 0.044 | −0.016 | −0.016 | 0.044 | −0.021 | −0.021 |
| | −0.0723 | 0.030 | −0.013 | −0.013 | 0.030 | −0.013 | −0.013 |
| III | −0.0457 | 0.023 | 0.026 | 0.011 | −0.015 | −0.008 | −0.021 |
| | −0.0629 | 0.024 | 0.034 | 0.008 | −0.001 | −0.009 | −0.006 |
| IV | −0.0714 | −0.012 | 0.003 | 0.017 | 0.025 | −0.006 | −0.009 |
| | −0.0842 | −0.000 | −0.005 | 0.028 | 0.023 | 0.003 | −0.021 |
| V | −0.0122 | 0.011 | 0.011 | 0.010 | 0.018 | −0.006 | −0.036 |
| | −0.0074 | 0.001 | 0.017 | 0.022 | 0.018 | −0.016 | −0.033 |
| VI | −0.0115 | 0.021 | 0.003 | 0.003 | 0.021 | −0.020 | −0.020 |
| | −0.0156 | 0.011 | 0.006 | 0.006 | 0.011 | −0.016 | −0.016 |

Table 4. Changes of Energy and Charge Densities of Various Types of Benzene-Anthracene Pair

| | $\Delta E$ | $\Delta q_{rr}$ of benzene | | | | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 |
| I | −0.0447 | 0.006 | −0.014 | 0.017 | 0.025 | 0.001 | −0.008 |
| | −0.0436 | 0.016 | −0.014 | 0.024 | 0.023 | 0.010 | −0.020 |
| II | −0.0434 | 0.036 | −0.013 | −0.014 | 0.037 | −0.003 | −0.031 |
| | −0.0451 | 0.023 | −0.013 | −0.009 | 0.027 | −0.014 | −0.017 |
| III | −0.0524 | 0.006 | 0.017 | 0.008 | 0.021 | −0.006 | −0.029 |
| | −0.0635 | 0.004 | 0.019 | 0.018 | 0.020 | −0.016 | −0.027 |
| IV | 0.0036 | 0.021 | 0.005 | 0.005 | 0.021 | −0.021 | −0.020 |
| | 0.0045 | 0.010 | 0.011 | 0.011 | 0.011 | −0.020 | −0.018 |
| V | −0.0382 | 0.017 | 0.009 | 0.011 | 0.011 | −0.034 | −0.006 |
| | −0.0434 | 0.015 | 0.019 | 0.018 | 0.003 | −0.030 | −0.016 |
| VI | −0.0593 | −0.013 | −0.010 | −0.007 | 0.026 | 0.018 | 0.005 |
| | −0.0693 | −0.002 | −0.022 | 0.001 | 0.025 | 0.029 | 0.001 |
| VII | −0.0325 | 0.032 | −0.005 | −0.010 | −0.009 | 0.008 | 0.021 |
| | −0.0334 | 0.030 | 0.013 | −0.017 | −0.000 | 0.002 | 0.031 |
| VIII | −0.0591 | −0.005 | 0.003 | 0.003 | −0.005 | 0.025 | 0.025 |
| | −0.0720 | 0.014 | −0.005 | −0.005 | 0.014 | 0.023 | 0.023 |
| IX | −0.0261 | 0.014 | 0.015 | 0.015 | 0.014 | −0.021 | −0.021 |
| | −0.0279 | 0.010 | 0.023 | 0.023 | 0.010 | −0.022 | −0.022 |

well-known trend in quantum chemistry. We can say, the values of the second lines are more reliable.

We have carried out calculations for the type VI, not acceptable in the previous treatment, and find that this is not so stable, as is type V.

The calculations for the various types of the benzene-phenathrene pair are given in Table 4. The results are almost satisfactory as was seen in the case of benzene-anthracene pair. If we regard phenanthrene as a prototype of benz[*a*]pyrene (a famous chemical carcinogen), we can find stable structures in which the benzene molecule sits on areas extending over the so-called Bay, K, and L regions.

## Benzo[*a*]pyrene-Guanine Pair

Benzo[*a*]pyrene is a famous chemical carcinogen, of which activity has been widely discussed connecting with its structure or its derivatives produced by the metabolic reactions.6) Though recent studies rather stress the metabolic effect, we come back to an old-fashioned view of chemical carcinogenesis, based on the direct combination of carcinogen with nucleotide.

Replacing benzene and phenanthrene in the previous section by guanine and benzo[*a*]pyrene, respectively, we carry out the same treatment as before. However, in this time we have not tried to optimize the mutual orientation of these molecules, but begin with assuming several conformations as described in Fig. 6, which are presumed from the investigation of the benzene-phenanthrene pair. Empirical parameter added to previous ones are

$$\alpha(\ddot{\mathrm{O}})=2.0\beta,\quad \alpha(\ddot{\mathrm{N}})=1.5\beta,\quad \alpha(\dot{\mathrm{N}})=0.5\beta \qquad (26)$$

where the dotts represent the number of $\pi$ electrons given by these atoms.

Strictly speaking, it is inadequate to disregard cytosine bonded with guanine by hydrogen bonds (see Fig. 7). We have to imagine cytosines at the appropriate positions in conformations I—V of Fig. 6. Calculated results are in Table 5. In each row, the numerals of the first line are obtained by the closure approximation (Eqs. 20 and 25), and those of the second line are without this approximation. Therefore the latter is a little

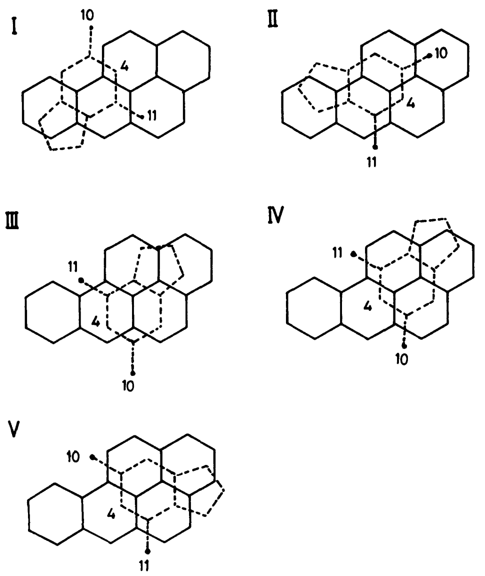

Fig. 6. Various conformations of guanine-benzo[*a*]-pyrene pair.

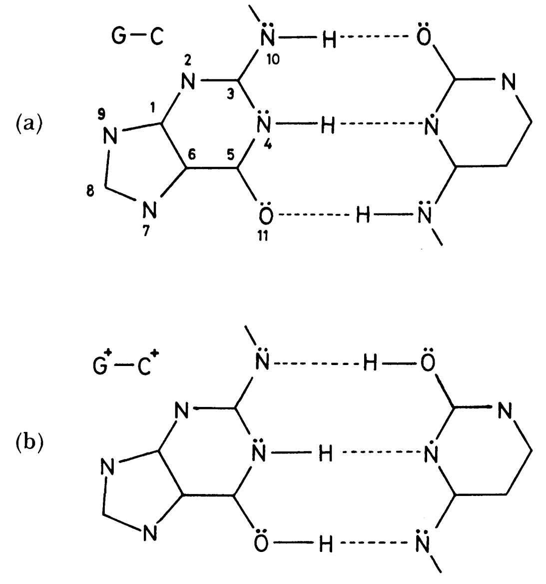

Fig. 7. Conformations of guanine-cytosine pair.

Table 5. Changes of Energy and Charge Densitiesof Various Types of Guanine-Benzo[*a*]pyrene Pair

| | $\Delta E$ | $\Delta q_{rr}$ of guanine | | |
|---|---|---|---|---|
| | | 4-$\ddot{\mathrm{N}}$ | 10-$\ddot{\mathrm{N}}$ | 11-$\ddot{\mathrm{O}}$ |
| I | 0.0018 | | | |
| | 0.0191 | | | |
| II | 0.0065 | | | |
| | 0.0179 | | | |
| III | −0.1649 | 0.122 | −0.029 | 0.046 |
| | −0.0953 | 0.039 | 0.004 | 0.020 |
| IV | −0.1401 | 0.136 | −0.020 | 0.021 |
| | −0.1235 | 0.038 | 0.001 | 0.013 |
| V | −0.1195 | 0.153 | −0.041 | 0.023 |
| | −0.0609 | 0.051 | −0.027 | 0.014 |

more reliable, even though it is quite crude from the quantitative viewpoints. However we may insist that if we pass from column to column, or from row to row, the trends observed there tell us something true. The types I and II are not energetically stable. The conformation adopted in a current investigation,[7] is an almost face-to-face structure, because of the maximum overlap between $\pi$ orbitals of the composite molecules being achieved. As mentioned before, this is not necessarily favorable for molecular compounds.

The conformations III—V are stable, where the mutual arrangement of guanine and cytosine is opposite in the direction to that of I and II. In these stable structure we estimated the changes of charge densities at the positions relating to the hydrogen bonds. We proceed discussions based upon the data of the second lines in Table 5. In Fig. 7(a), we present the normal guanine-cytosine pair in which three hydrogen bonds are there. We can see that, in Table 5, a considerably large increase of charge arises at the *10*-$\ddot{\mathrm{N}}$ (the upper most $\ddot{\mathrm{N}}$ in Fig. 7(a)). This shifts the proton of NH group in guanine toward the oxygen of cytosine, and results in shitfing the proton of the NH group in cytosine toward the oxygene of guanine. As a result, we have a new pair denoted G*-C* in Fig. 7(b). It is understood that, in the new pair, the original two hydrogen bonds are lost, and only a weak hydrogen bond remains, and this conformation might be a source of mutation.

One may say the above consideration is old, and seems almost denied. The O- or OH- substituted benzo[*a*]pyrene produced by the metabolic reaction strongly binds the nucleotide, so that the order of nucleotide is confused to arise the mutation. However we may argue the present investigation especially of the mutual orientation between composite molecules is still suggestive in the further investigation to chemical carcinogen.

## Concluding Remarks

In the present work, the intermolecular interaction is treated as a perturbation of the sigle-particle character between molecules. We have assumed that the intermolecular distance and other geometrical factors are almost predetermined by other mechanical sources, e.g., the van der Waals interaction and so on. In other words, we consider that two molecules come near to an appropriate position and the charge exchange begins to work between them.

In the usual treatments, the local interactions are taken into account for predominantly determining geometrical structure of the molecular complex, i.e., the maximum overlap between atomic orbitals of composite molecules being achieved. This consideration inevitably leads to the face-to-face structure for the present systems, and then an undesirable feature is avoided by introducing a steric effect of it. Really the structure experimentally observed is not of a face-to-face type, but is that the benzene ring of one molecule shifts by about a half of width relatively to that of the other moledule. What we have claimed here is follows: This preferable structure is explained energetically, that is to say, the additional energy producing a stable structure is arisen by the product of the transfer integral between sites under consideration and the coresponding long-range bond order. The latter that is hiden before introducing the perturbation is a decisively important factor to determin geometrical structure.

Next, supposing that the geometrical structure of a couple of molecules is given by the previous analysis, we treat the intermolecular interaction as a second order perturbation problem with respect to transfer matrix elements. The propagator technique enable us to obtain the complicated results very easily. The resultant expression is reinterpreted by introducing the closure approximation: The stabilization aises as an effect from a closed path constructed of bond orders and interaction matrix elements. We should like to stress a deep understanding of the bond order of a quantum mechanical and wave-functional character.

As a final example, interaction between guanine and benzo[*a*]pyrene is investigated. This is rather old-fashioned, but might be helpfull in remembering a conformational investigation apt to be missed in the recent studies.

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