# *An Attempt to Discuss Reactivities of Excited Molecules by the Molecular Orbital Method*

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(Received December 29, 1960)

In order to elucidate the mechanisms of reactions of conjugated or non-conjugated organic compounds which are in their ground state, a number of quantum mechanical, especially molecular orbital, studies have been performed and have achieved remarkable success in predicting theoretically their chemical reactivities[1-4]. In connection with the recent advance of techniques of photochemical investigation, chemical reactivities of electronically excited molecules have aroused our interest.

Because of the complicated characters and the multifariousness of reactions of excited molecules, only a few theoretical discussions have ever been made. As regards the problem of their self-dissociation, some qualitative discussions in terms of the potential energy curve have prevailed[5]. For discussing the energy transfer reaction between an excited molecule and an unexcited one, the collision theory has prevailed as a powerful tool[6]. On account of the lack in systematic experimental data and, in addition, because of the difficulties in the theoretical treatment, only a few quantum chemical studies have been presented on excited molecules involved in the addition reactions of large organic molecules. Photopolymerization of hydrocarbons has been discussed in terms of free valence of the molecules in their lowest excited state. The intramolecular orientation in the reaction of anthracene or naphthacene has been explained well[7]. But that of acenaphthylene has not been[8]; free valence of its lowest excited states is greatest at positions 5 and 6, and, on the contrary. the photodimer of the componud is produced through positions 1 and 2.

In the present paper, as was previously done with reference to the molecules in their ground state by the present authors[9,10] and by Brown[11], the reactivites of excited molecules are assumed to be parallel with the $\pi$ stabilization energy at the transition state due to the interaction of the molecule with the reagent (molecule, ion or radical) through the position of attack. Under this assumption the reactivity indexes are derived by the use of the molecular orbital method.

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## Formulation and Comparison with Experiments

Reactions of an excited molecule with an unexcited molecule are classified into several cases from the point of view of the spin multiplicity of reactants. The assumptions, the formulations and general considerations of the present molecular orbital treatments leading to the theoretical measures of reactivity will be described rather circumstantially in the first few cases, and in other cases only the indexes of reactivity derived will be given.

**Reaction of an Excited Triplet Molecule with an Unexcited Radical.**—First of all, attention is paid to the reaction of an excited triplet molecule ($^3$A) with an unexcited radical ($^2$B), where the numbers on the left shoulder refer to the multiplicity of the molecules. Here it would be rational for practical purposes in treating photochemical reactions to assume that the molecule $^3$A has only one excited electron. Then the wave functions of these molecules are written as follows:

$$\Psi(^3\mathrm{A})=\boldsymbol{A}\left[\cdots(\psi_1\alpha)^{m-3}(\psi_1\beta)^{m-2}(\psi_{01})^{m-1}(\psi_{02})^{m}\times\left\{\begin{matrix}\alpha(m-1)\alpha(m)\\ \beta(m-1)\beta(m)\\ (1/\sqrt{2})\{\alpha(m-1)\beta(m)+\beta(m-1)\alpha(m)\}\end{matrix}\right\}\right] \tag{1}$$

$$\Psi(^2\mathrm{B})=\boldsymbol{A}\left[\cdots(\phi_1\alpha)^{n-2}(\phi_1\beta)^{n-1}\left\{\begin{matrix}(\phi_0\alpha)^{n}\\ (\phi_0\beta)^{n}\end{matrix}\right\}\right]$$

where $\psi_i$ and $\phi_j$ are the molecular orbitals of molecules A and B, respectively, whose numbering is schematically shown in Fig. 1, 01 and 02 denoting the lower and the higher half-occupied levels, of A, respectively, and (0) denoting the half-occupied level of the radical B; $m$, an even integer, is the number of electrons of the molecule A and $n$, an odd number, is that of the radical B; $\boldsymbol{A}$ is the antisymmetrizing operator including the normalization constant; and each line in braces may constitute one wave function.

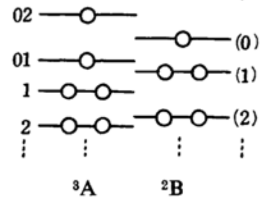

Fig. 1. Numbering of molecular orbitals.

The states of the total system consisting of the triplet A and the doublet B would be a quartet and a doublet. But the quartet, which would be proved later to be less significant in this discussion, is abandoned. The doublet wave function for $M_\mathrm{S}=1/2$* is

$$^2\Psi_{1/2}[^2(\mathrm{AB})]\equiv\Psi[0]=\boldsymbol{A}[\cdots(\psi_1\alpha)^{m-3}(\psi_1\beta)^{m-2}\cdots(\phi_1\alpha)^{m+n-2}(\phi_1\beta)^{m+n-1}(\psi_{01})^{m-1}(\psi_{02})^{m}\times(\phi_0)^{m+n}\{(\alpha\beta+\beta\alpha)\alpha-2(\alpha\alpha)\beta\}/\sqrt{6}] \tag{2}$$

where, for example, $\alpha\beta\alpha$ means $\alpha(m-1)\beta(m)\alpha(m+n)$. That for $M_\mathrm{S}=-1/2$ is not written because the energetical argument is similar. Thus the state $\Psi[0]$ is assumed to correspond to the initial system of the reaction in question. If A and B are far separated from each other, the energy of the state is the same as that of the product function $\Psi(^3\mathrm{A})\cdot\Psi(^2\mathrm{B})$. The molecular orbitals may include all $\pi$ ones and $\sigma$ ones, but in this paper we consider the reactions in company with only the $\pi$ electron excitation, and hence $\sigma$ orbitals will rationally be omitted as making an invariant framework.

At the transition state of the reaction the two molecules, $^3$A and $^2$B, will stay at a distance, making a weak interaction through the atoms at which the reaction takes place. This interaction is assumed to be a kind of $\pi-\pi$ conjugation and in this simple LCAO MO approach it will be represented by a small resonance integral $\gamma\beta$ between the atomic $\pi$ orbitals $r$ and $s$ of the reactants, A and B, respectively, where $\beta$ is the resonance integral of the C–C $\pi$ bond in benzene. This perturbation makes the initial state $\Psi[0]$ come to the direct or indirect interaction with various electronic configurations of the combined system. Of these configurations only those, which have energy matrix elements with the initial state in scope of the simple LCAO MO approximation, are taken into account. This means that the configurations (of course, doublet and $M_\mathrm{S}=1/2$) in which one electron transfers from $^3$A to $^2$B and vice versa have concern with the transition state of the reaction, whereas those which correspond to intramolecular one-electron transitions do not.

Under these assumptions the electron configurations to be taken into account are those corresponding to the following one-electron transfers, represented by $l\rightarrow m$, from an occupied or half-occupied orbital, $l$, to an unoccupied or half-occupied orbital, $m$:

$$\begin{matrix}02\rightarrow(0),\ 02\rightarrow(j'),\ 01\rightarrow(0),\ 01\rightarrow(j')\\ i\rightarrow(0),\ i\rightarrow(j'),\ (0)\rightarrow01,\ (0)\rightarrow02\\ (0)\rightarrow i',\ (j)\rightarrow01,\ (j)\rightarrow02,\ (j)\rightarrow i'\end{matrix} \tag{3}$$

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* $M_\mathrm{S}$ denotes the eigenvalue of $S_z$, the $z$ component of the spin momentum operator.

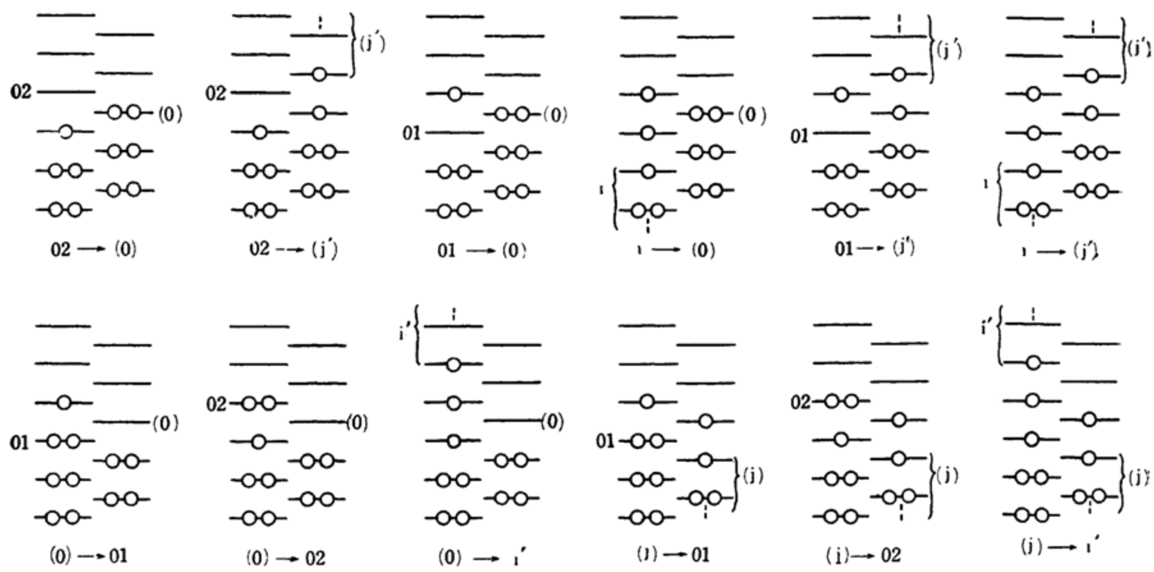


Fig. 2. Electronic configurations taken into account.

where

$i = 1, 2, \cdots$ (occupied orbitals of $^3$A)

$i' = 1', 2' \cdots$ (unoccupied orbitals of $^3$A)

$(j) = (1), (2), \cdots$ (occupied orbitals of $^2$B)

$(j') = (1'), (2'), \cdots$ (unoccupied orbitals of $^2$B)

They are schematically illustrated in Fig. 2. For an illustration, the configuration associated with the transfer 02→(0), will have the following wave function:

$$\Psi[02\rightarrow(0)] = \boldsymbol{A}[\cdots(\phi_0\alpha)^{m+n-2}(\phi_0\beta)^{m+n-1}(\psi_0\alpha)^{m+n}] \tag{4}$$

The energy matrix element between these configurations and the initial state can be expressed in terms of the integral $\gamma\beta$. For example,

$$\left|\int\Psi^*[02\rightarrow(0)]H\Psi(0)\mathrm{d}\tau\right| = |\, c_r{}^{02}d_s{}^0\gamma\beta \,| \tag{5}$$

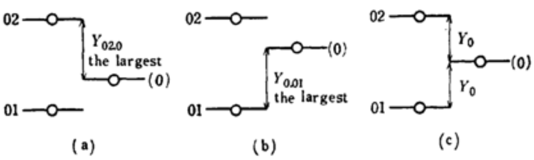
where $c_r{}^k$ and $d_s{}^l$ are the coefficient of the atomic orbitals $r$ and $s$ in the molecular orbital $k$ and $l$ of the molecules A and B, respectively.

The transition state of the reaction is the lowest energy state resulting from the interaction mentioned above. The difference in $\pi$ electronic energy, i. e. the stabilization energy, between the initial state and the transition state, was assumed in the preceding section to parallel the activation energy, of the reaction, and accordingly the reactivity of the excited molecule. This stabilization energy would be expanded in powers of $\gamma$ by regarding it to be small. There arise three main subcases according to the mutual relation of the energy levels 01 and 02 of the molecule $^3$A and (0) of the molecule $^2$B*. In the following $Y_{k,l}$ denotes the energy in units of $(-\beta)$ turned out in one electron transfer from the molecular orbital $k$ of the one molecule to the molecular orbital $l$ of the other one. That is, $Y_{k,l}$ is positive if the level $k$ is higher than the level $l$ and vice veras. Thus we reach the final reactivity indexes of excited molecules.

(a) If $Y_{02,0} > Y_{0,01} > 0$, that is, if the half-occupied level of the molecule $^2$B lies between the levels 01 and 02 of $^3$A and is nearer to 01 than to 02, as is shown in Fig. 3 (a), the stabilization energy to the second order of $\gamma$ is written in the following expression**:

$$\varDelta E = \left[Y_{02,0} + \frac{(3/2)(c_r{}^{02})^2(d_s{}^0)^2}{Y_{02,0}}\gamma^2\right](-\beta) \tag{6}$$

From this formula some general conclusions on reactivities of excited molecules may be



(a) (b) (c)

Fig. 3. Mutual relation of molecular levels.

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* Some rare cases, for instance, $Y_{0,02} > 0$ or $Y_{01,0} > 0$, are not included for the sake of brevity.

** In general the stabilization energies for each $M_S$ component may differ from each other. In the surroundings of reaction no magnetic field being applied, no specialization of the component is possible and the mean of all components would be significant as a real stabilization energy. In this case the energy for $M_S = 1/2$ is the same as that for $M_S = 1/2$; also the mean energy becomes the same.

TABLE I. RATE CONSTANT AND $\pi$ STABILIZATION ENERGY OF POLYMERIZATION OF STYRENE

| Reaction[a)] | Rate constant[b)] $k$ (l. mol$^{-1}$ sec$^{-1}$) | $\pi$ Stabilization energy (in units of $-\beta$) |
|---|---|---|
| $R\cdot + {}^3A \rightarrow RA\cdot$ | $\sim 10^{11}$ | $0.414 + 0.801\,\gamma^2$ (position 9)<br>$0.414 + 0.400\,\gamma^2$ (position 1)<br>$0.414 + 0.200\,\gamma^2$ (position 2) |
| $R\cdot + A \rightarrow RA\cdot$ | $3.4 \times 10^2$ | $0.926\,\gamma^2$ |
| $R\cdot + M \rightarrow R\cdot$ | $1.2 \times 10^2$ | $0.932\,\gamma^2$ |
| $RA\cdot + M \rightarrow R\cdot$ | 0.8 | $0.739\,\gamma^2$ |

a) Abbreviations, $R\cdot$: polymer radical of styrene; ${}^3A$: triplet anthracene; A: anthracene; M: styrene.

b) Taken from Ref. 10.

derived. In most reactions between unexcited molecules, terms first appear in the second order of $\gamma$, whereas in Eq. 6 the term in zero order exists. The appearance of the zero order term is universal in all the following cases and subcases, making clear the reason why the reactions including excited molecules proceed so fast. The difference in reactivity of several excited molecules would thus dominantly be decided by this term. The intramolecular orientation, on the other hand, depends on the term in the second order. More minutely, so far as attention is paid to the lowest excitation of the molecule A as is expected in real photochemical reactions of conjugated molecules, the atom where $(c_r^{02})^2$, the frontier electron density for a nucleophilic attack in the ground state, is the greatest is the most reactive in an excited molecule. The coefficient (3/2) is characteristic to the triplet A molecule. If the molecule A is excited in the singlet state it amounts to (1/2), as will be mentioned in the next section. The difference would not necessarily mean the difference in reactivity of these two states, since the approximation is too simple to discuss at this point, on which there will be some discussion in a later section.

To the transition state the electron configuration corresponding to the one-electron transfer $02 \rightarrow (0)$ has the greatest contribution, since the other configurations have the first contribution to $\Delta E$ in the fourth order. Therefore, the direction of charge transfer is from molecule A to molecule B.

(b) If $Y_{0,01} > Y_{02,0} > 0$, i. e., if the half-occupied level of ${}^2B$ lies between the levels 02 and 01, and nearer to 02 than to 01, as shown in Fig. 3 (b), then

$$\Delta E = \left[ Y_{0,01} + \frac{(3/2)(c_r^{01})^2 (d_s^0)^2}{Y_{0,01}} \gamma^2 \right] (-\beta) \quad (7)$$

In this subcase also the rate of reaction is great and the intramolecular orientation of the excited molecule is controlled by $(c_r^{01})^2$, the frontier electron density for an electrophilic attack in the ground state. The most contributive configuration in this subcase corresponds to the transition $(0) \rightarrow 01$, resulting in a charge transfer from B to A.

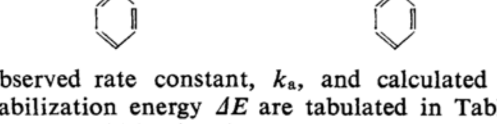
(c) If $Y_0 \equiv Y_{02,0} = Y_{0,01} > 0$, i. e., if the level (0) is just in the midst of the levels 01 and 02, as shown in Fig. 3 (c), then

$$\Delta E = \left[ Y_0 + \frac{(3/2)\,[(c_r^{01})^2 + (c_r^{02})^2]\,(d_s^0)^2}{Y_0} \gamma^2 \right] \times (-\beta) \quad (8)$$

A large rate constant is confirmed also in this subcase, and $[(c_r^{01})^2 + (c_r^{02})^2]$, the frontier electron density for a radical attack in the ground state, comes to the point.

So far as alternant hydrocarbons are concerned, however, the equality $(c_r^{01})^2 = (c_r^{02})^2$ holds in the simple LCAO MO approximation, so that in all subcases and the following cases the most reactive position in a molecule in its lowest excited state is the same as that in the ground state. This explains the great reactivity of meso position of anthracene. Further experimental studies are anticipated with respect to the intramolecular orientation in nonalternant hydrocarbons and heterocyclic compounds where the equality mentioned above no more exists.

Here a comparison with experimental data may be given. Excited triplet anthracene was reported by Norrish et al.[12)] to enter into the chain of polymerization of styrene in the following way:



$$\sim\sim CH_2\text{-}\underset{C_6H_5}{CH}\cdot + A^* \xrightarrow[\text{(step a)}]{} \sim\sim CH_2\text{-}\underset{C_6H_5}{CH}\text{-}A\cdot \quad (9)$$

Observed rate constant, $k_a$, and calculated $\pi$ stabilization energy $\Delta E$ are tabulated in Table I. The stabilization in the reaction a is calculated by using Eq. 8. Those of other reactions in which only molecules in their ground state participate are given by the usual formula for stabilization energy[10)]:

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[12)] V. S. Anderson and R. G. W. Norrish, *Proc. Roy. Soc.*, **A251**, 1 (1959); R. G. W. Norrish and J. P. Simons, ibid., **A251**, 4 (1959).

$$\Delta E=\left[\sum_{j}^{\text{unocc}}\sum_{i}^{\text{all}}\nu_i-\sum_{j}^{\text{occ}}\sum_{i}^{\text{all}}(2-\nu_i)\right]\times\frac{(c_r^{\,i})^2(d_s^{\,j})^2}{Y_{ji}}\gamma^2(-\beta) \tag{10}$$

where $\nu_i$ is the number of electrons in the $i$th molecular orbital of A. The extraordinary great magnitude of rate constant of reaction a is well understood in connection with the presence of the zero order term. Further, the position 9 is the most active, at which anthracene would enter into the polymer chain. An appropriate choice of the value of $\gamma$ $(=0.7)$ makes the $\log k_a-\Delta E$ plots practically linear.

The wave functions (Eq. 1) of $^3$A and $^2$B may be combined so as to construct a quartet instead of the doublet (Eq. 2). The quartet state has matrix elements with some configurations in Eq. 3, only to give the stabilization energy in the second order. Because of the lack of the zero order terms and, accordingly, because of the instability of the transition state, reactions would not be considered to proceed by way of the quartet transition state.

**Reaction of an Excited Singlet Molecule with an Unexcited Radical.**—The reaction of an excited singlet molecule ($^1$A) with an unexcited radical ($^2$B) can be discussed in a way similar to that of a triplet molecule ($^3$A) mentioned in the preceding reaction. The doublet wave function for $M_S=1/2$ of the combined system is, in place of Eq. 2 in the triplet case,

$$\Psi[0]=\boldsymbol{A}[\cdots(\psi_{01})^{m-1}(\psi_{02})^{m}(\psi_0)^{m+n}\times\{(\alpha\beta-\beta\alpha)\alpha\}/\sqrt{2}] \tag{11}$$

Also, we are led to the same equations as Eqs. 3, 4 and 5, excepting that the numerical coefficient in the second term should be read (1/2) in this case, instead of (3/2). The meanings of the frontier electron density and the direction of charge transfer in each subcase are entirely the same as in the last case; and therefore discussions may be omitted for brevity.

**Reaction of an Excited Tripled Molecule with an Unexcited Molecule.**—The reaction of an excited triplet molecule ($^3$A) with an unexcited singlet molecule ($^1$B)* now comes to our attention. Discussions are almost alike, so that the only important formulas would be summarized in this case and in the following case. The numbering of molecular orbitals is illustrated in Fig. 4. The states of the combined system at the initial stage of reaction are represented by a set of three triplet wave functions, one with $M_S=1$, one with $M_S=0$ and the other with $M_S=-1$, as follows:

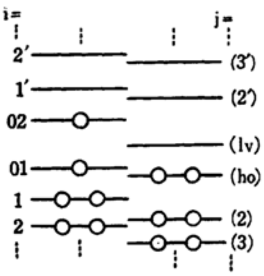

Fig. 4. Numbering of molecular orbitals. lv and ho mean the lowest unoccupied and the highest occupied orbitals, respectively.

$$\left.\begin{aligned}
{}^3\Psi_1&=\boldsymbol{A}[\cdots(\psi_{01})^{m+n-1}(\psi_{02})^{m+n}\\
&\quad\times\alpha(m+n-1)\alpha(m+n)]\\
{}^3\Psi_0&=\boldsymbol{A}[\cdots(\psi_{01})^{m+n-1}(\psi_{02})^{m+n}\\
&\quad\times(\alpha(m+n-1)\beta(m+n)\\
&\quad+\beta(m+n-1)\alpha(m+n)\}/\sqrt{2}]\\
{}^3\Psi_{-1}&=\boldsymbol{A}[\cdots(\psi_{01})^{m+n-1}(\psi_{02})^{m+n}\\
&\quad\times\beta(m+n-1)\beta(m+n)]
\end{aligned}\right\} \tag{12}$$

Electronic configurations which are taken into account in the perturbation calculation are summarized in Fig. 5 with illustrations. Each $M_S$ component of the functions 12 will have matrix elements with the same $M_S$ component of the wave functions for the configurations

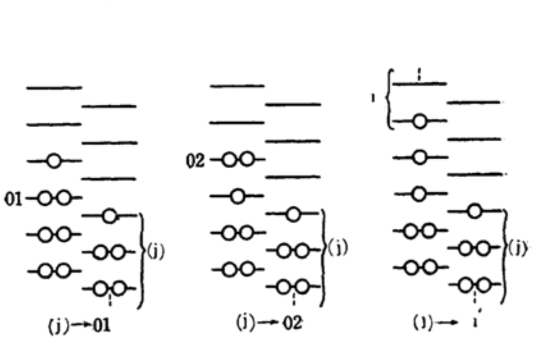

Fig. 5. Electronic configurations taken into account.
$i=1,2,\cdots$ (occupied orbitals of $^3$A); $i'=1',2',\cdots$ (unoccupied orbitals of $^3$A); $j=$ ho, 2, $\cdots$ (occupied orbitals of $^1$B); and $j'=$lv, 2', $\cdots$ (unoccupied orbitals of $^1$B).

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* The singlet molecule $^1$B may be an ion whose spin is singlet.

TABLE II. $\pi$ STABILIZATION ENERGY IN PHOTODIMERIZATION OF POLYACENES AND ACENAPHTHYLENE

| Compound | Pairs of positions to react with | $\pi$ Stabilization energy (in units of $-\beta$) |
|---|---|---|
| Anthracene | 9-9, 10-10 (central) | $0.547\,\gamma$ |
| | 1-1, 4-4 (end) | $0.273\,\gamma$ |
| Naphthacene | 5-5, 12-12 (central) | $0.417\,\gamma$ |
| | 1-1, 4-4 (end) | $0.159\,\gamma$ |
| Pentacene | 6-6, 13-13 (central) | $0.400\,\gamma$ |
| | 5-5, 14-14 | $0.299\,\gamma$ |
| | 1-1, 4-4 (end) | $0.100\,\gamma$ |
| Acenaphthylene | 1-1, 2-2 | $0.568\,\gamma$ |
| | 5-5, 6-6 | $0.375\,\gamma$ |

in Fig. 5. Then the stabilization energy* is obtained as follows, according to the mutual relation of energy levels:

(a) If $Y_{02,\mathrm{lv}}$ is positive and the most positive of all $Y$'s, then

$$\Delta E=\left[Y_{02,\mathrm{lv}}+\frac{(c_r^{02})^2(d_s^{\mathrm{lv}})^2\gamma^2}{Y_{02,\mathrm{lv}}}\right](-\beta) \tag{13}$$

This is the case for most electrophilic reagents (cations) serving as $^1$B.

(b) If $Y_{\mathrm{ho},01}$ is positive and the most positive of all $Y$'s, then

$$\Delta E=\left[Y_{\mathrm{ho},01}+\frac{(c_r^{01})^2(d_s^{\mathrm{ho}})^2\gamma^2}{Y_{\mathrm{ho},01}}\right](-\beta) \tag{14}$$

Most nucleophilic reagents (anions) as $^1$B are included in this subcase.

(c) If $Y_{02,\mathrm{lv}}=Y_{\mathrm{ho},01}$, and they are positive (then of course the most positive), then, putting them equal to $Y_0$,

$$\Delta E=\left[Y_0+\frac{\{(c_r^{02})^2(d_s^{\mathrm{lv}})^2+(c_r^{01})^2(d_s^{\mathrm{ho}})^2\}\gamma^2}{Y_0}\right]\times(-\beta) \tag{15}$$

Such a conjugated molecule as has its lowest excitation energy smaller than the excitation energy to the triplet of the molecule A would be classified in this subcase.

(d) If all $Y$'s are negative, then

$$\Delta E=\left[\sum_j^{\mathrm{unocc}}\sum_i^{\mathrm{all}}\nu_i-\sum_j^{\mathrm{occ}}\sum_i^{\mathrm{all}}(2-\nu_i)\right]\frac{(c_r^i)^2(d_s^j)^2\gamma^2}{Y_{ji}}\times(-\beta) \tag{16}$$

In this subcase the stabilization energy begins in the second order terms, predicting a slow rate in the process of reaction.

(e) If $Y_{02,\mathrm{lv}}=0$ and the others are negative, then

$$\Delta E=\left[\,|\,(c_r^{02})(d_s^{\mathrm{lv}})\,|\,\gamma+\left\{\sum_j^{\mathrm{unocc}}\sum_i^{\mathrm{all}}\nu_i-\sum_j^{\mathrm{occ}}\sum_i^{\mathrm{all}}(2-\nu_i)\right\}'\frac{(c_r^i)^2(d_s^j)^2\gamma^2}{2Y_{ji}}\right](-\beta) \tag{17}$$

where the mark $'$ on the summation tells to omit the set ($j=\mathrm{lv}$, $i=02$).

(f) If $Y_{\mathrm{ho},01}=0$ and others are negative, then, similarly

$$\Delta E=\left[\,|\,(c_r^{01})(d_s^{\mathrm{ho}})\,|\,\gamma+\left\{\sum_j^{\mathrm{unocc}}\sum_i^{\mathrm{all}}\nu_i-\sum_j^{\mathrm{occ}}\sum_i^{\mathrm{all}}(2-\nu_i)\right\}'\frac{(c_r^i)^2(d_s^j)^2\gamma^2}{2Y_{ji}}\right] \tag{18}$$

$'$ indicating the neglect of the set ($j=\mathrm{ho}$, $i=01$).

(g) If $Y_{02,\mathrm{lv}}=Y_{\mathrm{ho},01}=0$ and others are negative, we obtain

$$\Delta E=\left[\sqrt{(c_r^{02})^2(d_s^{\mathrm{lv}})^2+(c_r^{01})^2(d_s^{\mathrm{ho}})^2}\,\gamma+\left\{\sum_j^{\mathrm{unocc}}\sum_i^{\mathrm{all}}\nu_i-\sum_j^{\mathrm{occ}}\sum_i^{\mathrm{all}}(2-\nu_i)\right\}'\times\frac{(c_r^i)^2(d_s^j)^2\gamma^2}{2Y_{ji}}\right](-\beta) \tag{19}$$

neglecting in the summation the sets ($j=\mathrm{ho}$, $i=01$) and ($j=\mathrm{lv}$, $i=02$) In the latter three subcases the stabilization is of the first order, and for the lowest excited molecule the frontier electron density controls a main part of the reactivity indexes. The subcase g includes reactions of an excited molecule with an unexcited molecule of the same kind.

The photodimerization of aromatic hydrocarbons has been considered to pass through the following mechanism:

$$\mathrm{A}^*+\mathrm{A}\xrightarrow[\text{(step b)}]{}(\mathrm{AA}^*)\xrightarrow[\text{(step c)}]{}\mathrm{AA} \tag{20}$$

Though the detail of the intermediate (AA*) is not clear, assuming the present type of complex for the transition state of step b, one can discuss the reactivity of this reaction as belonging to the subcase g. In Table II calculated values of the $\pi$ stabilization energy are collected. In that table, reagents are assumed to make two weak bondings through two meso positions, as illustrated in Fig. 6; the assumption of one bonding would only need to divide the values by the factor 2.

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* Each $M_S$ component gives the same stabilization energy, and the mean is, therefore, the same.

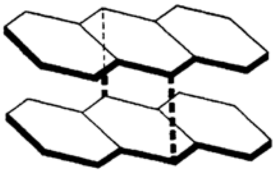
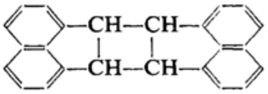


Fig. 6. Model of transition state of photodimerization of anthracene.

Anthracene is well known to make a photodimer at 9 and 10 positions, in accord with our calculation. Also in other polyacenes the most central meso-positions have the largest stabilization energy. This result is compatible with the experiment[13]. Bowen and Marsh[14] studied the photodimerization of acenaphthylene, finding that the structure of the photodimer was



This finding was first theoretically discussed by Crawford and Coulson[8]. They calculated the free valence of this molecule in its lowest excited state and found that the values of positions 5 and 6 (0.62) are greater than those of positions 1 and 2 (0.57), which conflicted with the above experimental results. Thus they stated that the free valence is not a sufficient guide to reactivity. Recently this experiment has been interpreted successfully by the present authors in terms of the frontier electron density for a radical reaction[15]. The frontier electron density of positions 1 and 2 is greater than that of positions 5 and 6. In that paper the excited acenaphthylene was regarded as an ordinary radical reagent attacking an acenaphthylene molecule in the ground state. At this time it would be interesting to apply the present theory which involves an explicit consideration of the excitation. This belongs to the subcase g. As is seen in Table II the stabilization energy of the reaction through pairs of positions 1-1 and 2-2 is greater than that through 5-5 and 6-6, in accordance with the experiment.

In intermolecular comparison it is said that the ease of photodimerization is greater in pentacene than in anthracene[13]. But this is not a direct comparison of the rate constant $k_b$ of the step b but a rough estimation from the amount of dimers produced. The total rate of dimer formation would be affected not only by the rate constant $k_b$ but also by various competitive reactions such as the collisional or spontaneous degradation of the excited A molecule, dissociation of (AA*), and so forth. To measure and compare the rate constant with calculated stabilization energy would be interesting.

**Reaction of an Excited Singlet Molecule with an Unexcited Molecule.**—The method and the results of the treatment for this kind of reaction is exactly the same as that in the last case if only the wave function, Eq. 12, is replaced by the following equation:

$$^{1}\Psi_0=\boldsymbol{A}[\cdots(\psi_{01})^{m+n-1}(\psi_{02})^{m+n}\{\alpha(m+n-1)\times\beta(m+n)-\beta(m+n-1)\alpha(m+n)\}/\sqrt{2}] \quad (21)$$

Eqs. 13 to 20 are also valid in this case.

**Reaction of an Excited Molecule with Another Excited Molecule.**—We derived also the equations giving the stabilization energy in a reaction of an excited molecule (singlet or triplet) with another excited molecule (singlet or triplet) in a similar way. But as they are less meaningful for practical purposes and rather intricate, we do not give their explicit forms. It would be noteworthy that in this case also the frontier electron densities decide the intramolecular orientation.

## Discussion

We have derived formulas giving the $\pi$ stabilization energy and the reactivity index, discussing the rate of reactions of excited molecules. But we do not, at all, regard this theory as complete but merely as a simple pioneering attempt in the molecular orbital method; the assumptions included may have to be subjected to some improvements in future. For discussing the difference in rate constant caused by the difference in multiplicity of states, interactions of electrons should be explicitly taken into account. For discussing various dissociation reactions, attention would have to be paid to $\sigma$ electrons in the bond to be broken. Furthermore, in order to understand all the figures of reactions of an excited molecule, discussions on relations between various elementary steps involved in the reaction would be expected.

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[13] For example, M. Nakagawa, "Gendai Kagaku", III-D, Iwanami, Tokyo (1956); M. Koizumi and M. Shiba, ibid., I-E, (1956).

[14] E. L. Bowen and J. D. F. Marsh, *J. Chem. Soc.*, **1947**, 109.

[15] K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **34**, 37 (1961).