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Use of Propagators in the Hückel Model. III. Stability and Reactivity

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The propagator approach is applied to the problems of chemical reactivity and stability. Subjects discussed are the ring closure and opening reactions, the Diels-Alder reaction and sigmatropic reaction for reactivity; the aromaticity, two ring compounds (such as naphthalene and azulene), and benzenoid hydrocarbons (such as anthracene and phenanthrene) for stability. Results are given in analytical formulas.

The Hückel model or the tight-binding approximation is of great use because of its mathematical simplicity in analysis of molecular electronic states and chemical reactivities. Coulson and Longuet-Higgins[1] emphasized that once the Hückel determinant is given for a system all its physical properties are derived by making analysis of the determinant, not *via* wave functions as has been done in the usual theories. The charge density, bond order and total energy are expressed by the corresponding contour integrals closely related to the Hückel determinant. The perturbation theory has been developed in terms of mutual polarizability, which are also given by similar expressions. They applied their theory to the conjugated molecules and successfully derived many rules. Recent trials of Hosoya *et al.*[2] with topological aspects seem to be inherently related to the treatment of Coulson and Longuet-Higgins.

On the other hand Fukui[3] discussed chemical reactivity and stability in view of frontier electron. In this theory, the specified orbitals called LUMO and HOMO play dominant roles in the chemical reactions, and their mutual phases qualitatively decide whether the reaction takes place or not. The last is known as the Woodward-Hoffmann rule.[4]

In the first paper[5] of this series, the Hückel theory is reformulated in terms of propagators. This is a Green's function version of Coulson's work, and has merit of giving results beyond the elementary perturbation theory. Our theory is not so easy as the usual LCAO theory, but sometimes successfully reveals physical concepts hidden in the latter. The bond order between the r-th and s-th sites, $q(r,s)$ is usually inferred to the overlap charge or the charge density at the bond. This might not be feasible if the r-th and s-th sites are far from each other. By use of a propagator the bond order is defined by

$$q(r, s) = \frac{1}{2\pi i}\int_c dz G(r, s; z). \qquad (1)$$

What this means is as follows: consider the probability amplitude which an electron at the r-th site transfers to the s-th site in any one-electron state. If we sum up such amplitude with respect to the levels occupied in the ground state, the result is $q(r, s)$. Moreover, $q(r, s)$ is divided into the contributions arising from several independent paths.[6] The bond order between the nearest sites in benzene is composed of two components which refer the shorter and longer paths in a way from the one site to the other.

Any chemical bond produced by the chemical reaction under consideration is due to the propagations of interactions. Thus the bond order plays a leading role in the following investigations, showing quantitatively what kind of route of propagation is important.

Interaction Energy

In order to investigate the stability condition in the ground state and the chemical reactivity, *i.e.*, selection of the reaction path of the chemical reaction, we derive the expression of energy stabilization due to perturbation. In the case of reactivity, we estimate the stabilization energy due to perturbation at some point along the reaction path, then at the corresponding point along the other path. Comparing these two, we can decide which one is favorable. Calculations will be performed following those in I, but are limited to the second order with respect to the perturbation. This suffices for the present case.

The total energy of the system is

$$E = \mathrm{Tr}\frac{1}{2\pi i}\int_c dz\, z\mathbf{G}(z), \qquad (2)$$

where $\mathbf{G}$ is the matrix of Green's function represented by the site indices, z the energy parameter and Tr the trace with respect to the site indices. Integration contour c is the so-called Coulson contour shown in Fig. 1. Note that the integration in Eq. 2 includes the spin sum.

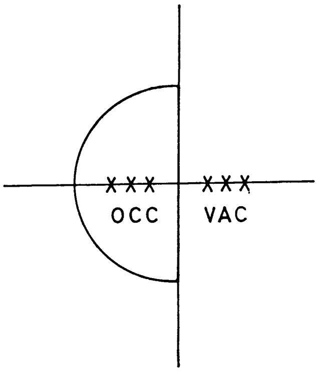

Fig. 1. Coulson's contour.

Let us consider the perturbation $\mathbf{v}$, which is a matrix represented by the site indices. The interaction energy caused by the perturbation is

$$\begin{aligned}\Delta E &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z[\mathbf{G}_0\mathbf{v}\mathbf{G}_0+\mathbf{G}_0\mathbf{v}\mathbf{G}_0\mathbf{v}\mathbf{G}_0+\cdots]\\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z\mathbf{G}_0\sum_n(\mathbf{v}\mathbf{G}_0)^n\\ &= \sum_n\frac{1}{n}\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z(\mathbf{G}_0\mathbf{v})^n. \end{aligned} \tag{3}$$

The final result is as follows:

$$\begin{aligned}&\frac{1}{2}\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\mathbf{G}_0\mathbf{v}\mathbf{G}_0\mathbf{v}\\ &=\frac{1}{2}\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\frac{1}{z-\mathbf{H}_0}\mathbf{v}\frac{1}{z-\mathbf{H}_0}\mathbf{v}\\ &=\frac{1}{2}\mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z\left[\frac{1}{(z-\mathbf{H}_0)^2}\mathbf{v}\frac{1}{z-\mathbf{H}_0}\mathbf{v}\right.\\ &\quad\left.+\frac{1}{z-\mathbf{H}_0}\mathbf{v}\frac{1}{(z-\mathbf{H}_0)^2}\mathbf{v}\right]\\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z\frac{1}{z-\mathbf{H}_0}\mathbf{v}\frac{1}{z-\mathbf{H}_0}\mathbf{v}\frac{1}{z-\mathbf{H}_0}\\ &= \mathrm{Tr}\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, z\mathbf{G}_0\mathbf{v}\mathbf{G}_0\mathbf{v}\mathbf{G}_0, \end{aligned} \tag{4}$$

where the second equality arises from the partial integration and the third one from the permutation invariability in Tr.

Illustrative Example Provided that the perturbation is applied to the site a, say $v_{aa}=\varepsilon$, it follows that

$$\begin{aligned}\Delta E &= \sum_n\frac{1}{n}\,\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[G_0(a)\varepsilon]^n\\ &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z \ln(1-G_0(a)\varepsilon)^{-1} \qquad (5\mathrm{a})\\ &\simeq \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, G_0(a)\varepsilon + \frac{1}{2}\,\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z\, G_0(a)^2\varepsilon^2\\ &\equiv q(a)\varepsilon + \frac{1}{2}\Pi_{a,a}\varepsilon^2. \qquad (5\mathrm{b})\end{aligned}$$

Here $q(a)$ is the charge density at the a-th site and $\Pi_{a,a}$ is the atom-atom polarizability defined by Coulson and Longuet-Higgins.[1]

Ring Closure and Ring Opening

Let us first consider the ring closure reaction of conjugated chain. Figure 2a shows the transition state where the chain begins the ring closure reaction. The arrows at both ends stand for the basis functions, $2p\pi$ together with the phases. Note that we can put the phases in this way without loss of generality. We need not worry about one-electron state, *i.e.*, the shape of MO and its energy.

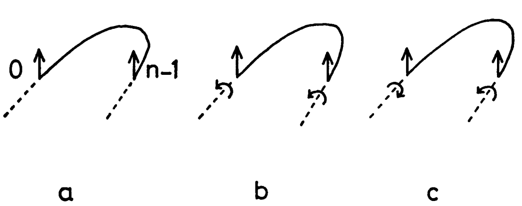

Fig. 2. Ring closure reaction.
a: Transition state, b: con-rotatory, c: dis-rotatory.

For the sake of simplicity, let us consider the case in which the chain is composed of n sites and n electrons. If the ring closure begins in the con-rotatory mode or in the dis-rotatory mode, the interaction arises between sites 0-th and (n-1)-th.

$$v_{0,n-1}=v_{n-1,0}=v\begin{cases}\text{positive for the con-rotatory}\\ \text{negative for the dis-rotatory.}\end{cases} \tag{6}$$

The extra energy due to this is given by Eq. 3. If one mode works to stabilize the system, *i.e.*, $\Delta E<0$, we can choose this mode as the desired reaction path.

Let us consider the ring opening reaction. The σ-bond in the transition state slightly rotates (Fig. 3a) in a con-rotatory mode (Fig. 3b) or in the dis-rotatory mode (Fig. 3c) to yield a small fraction of π-bond. The extra energy due to this determines which mode is preferable. Since the perturbation energy arising in these motion is classified entirely in the same way as that of ring closure reaction, *i.e.*, as Eq. 6, we see that the mathematical procedures are the same, *viz.*, if in any system the con-rotatory mode is desirable for the ring closure reaction, the same mode is also desirable for the ring opening reaction for the system in which transition state is similar to that of the previous system.

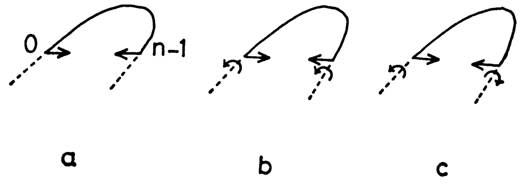

Fig. 3. Ring opening reaction.
a: Transition state, b: con-rotatory, c: dis-rotatory.

In both cases, the extra energy ΔE in Eq. 3 due to perturbation to the second order is

$$\begin{aligned}\Delta E &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[G_n(0,\, n-1)v_{n-1,0}+G_n(n-1,\, 0)v_{0,n-1}]\\ &\quad+\frac{1}{2}\,\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[G_n(0,\, n-1)v_{n-1,0}G_n(0,\, n-1)v_{n-1,0}\\ &\quad+G_n(n-1,\, 0)v_{0,n-1}G(n-1,\, 0)v_{0,n-1}]\\ &\quad+\frac{1}{2}\,\frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[G_n(0)v_{0,n-1}G_n(n-1)v_{n-1,0}\\ &\quad+G_n(n-1)v_{n-1,0}G_n(0)v_{0,n-1}] \qquad (7\mathrm{a})\\ &= \frac{1}{2\pi \mathrm{i}}\int_c \mathrm{d}z[2vG_n(0,\, n-1)+v^2G_n(0,\, n-1)G(n-1,\, 0)\\ &\quad+v^2G_n(0)G_n(n-1)]. \qquad (7\mathrm{b})\end{aligned}$$

Each term in Eq. 7b, shown in detail in Eq. 7a, has its own structure: the first order term indicates a path going round the system once, the path indicated by the second terms in Eq. 7a goes round the system twice, and the final second order term corresponds to the interaction going back and forth between the ends. Let us examine each term in detail.

The matrix elements of Green's function in Eq. 7a are given in the second paper[7] of this series, as

$$G_n(0) = G_n(n-1) = \frac{\sin n\theta}{\sin(n+1)\theta}, \tag{8}$$

$$G_n(0, n-1) = G_n(n-1, 0) = \frac{\sin\theta}{\sin(n+1)\theta}, \tag{9}$$

$$z = 2\cos\theta. \tag{10}$$

If we map the Coulson contour in z-plane onto θ-plane by means of the relation (10), the contour in θ-plane turns round twice the corresponding points in z-plane. This is why we introduced the factor, 1/2.(7)

As an example, let us take the system with n sites and n electrons, n being even. The first order energy in Eq. 7b is

$$\Delta E^{(1)} = -4\frac{1}{4\pi \mathrm{i}}\int_c \mathrm{d}\theta \frac{\sin^2\theta}{\sin(n+1)\theta}v. \tag{11}$$

The poles of the propagator are given by

$$\theta_r = \frac{\pi r}{n+1}, \qquad r=\pm 1, \pm 2, \cdots, \pm(n+1), \tag{12}$$

in which the single particle states from $r=\pm 1$ to $r=\pm n/2$ are doubly occupied. The result of calculation is

$$\begin{aligned}\Delta E^{(1)} &= -\frac{8v}{(n+1)}\sum_{r=1}^{n/2}(-1)^r \sin^2\theta_r \\ &= -\frac{4v}{(n+1)}\left\{\sum_{r=1}^{n/2}(-1)^r + 1/2\right. \\ &\qquad \left. + \frac{(-1)^{n/2}}{2}\sec \pi/(n+1)\right\}.\end{aligned} \tag{13}$$

The second order energy arising from the path going round the system twice is

$$\begin{aligned}\Delta E^{(2,q)} &= -2\frac{1}{4\pi \mathrm{i}}\int_c \mathrm{d}\theta \frac{\sin^3\theta}{\sin^2(n+1)\theta}\frac{v^2}{\beta} \\ &= \frac{-3}{2(n+1)^2}\left\{\operatorname{cosec} \pi/2(n+1)\right. \\ &\qquad \left. + \operatorname{cosec} 3\pi/2(n+1)\right\}\frac{v^2}{\beta}.\end{aligned} \tag{14}$$

The resonance integral β which was scaled to unity in evaluating G, is recovered by dimensional analysis. The resonance integral β is negative. Another second order term is

$$\begin{aligned}\Delta E^{(2,c)} &= -2\frac{1}{4\pi \mathrm{i}}\int_c \mathrm{d}\theta \frac{\sin\theta \sin^2 n\theta}{\sin^2(n+1)\theta}\frac{v^2}{\beta} \\ &= \frac{(2n-1)}{2(n+1)^2}\left\{\operatorname{cosec} \pi/2(n+1)\right. \\ &\qquad \left. + \operatorname{cosec} 3\pi/2(n+1)\right\}\frac{v^2}{\beta}.\end{aligned} \tag{15}$$

Thus we get

$$\begin{aligned}\Delta E &= \Delta E^{(1)} + \Delta E^{(2,q)} + \Delta E^{(2,c)} \\ &= \frac{-4}{n+1}\left\{\sum_{r=1}^{n/2}(-1)^r + 1/2 + \frac{(-1)^{n/2}}{2}\sec \pi/(n+1)\right\}v \\ &\quad + \frac{n-2}{(n+1)^2}\left\{\operatorname{cosec} \pi/2(n+1) + \operatorname{cosec} 3\pi/2(n+1)\right\}\frac{v^2}{\beta}.\end{aligned} \tag{16}$$

Due to the fact that $n>2$ in the actual molecules the second order terms in Eqs. 16 and 20 are negative, irrespective of the sign of v. The second order term has nothing to do with the determination of the reaction path, except for slight stabilization of the system as regards energy. The first order term should dominantly affect the progress of the reaction. The reaction proceeds if the quantity in the curly bracket has the same sign as that of v in the first order term.

Let us examine the case with odd n sites and n electrons. In this case, the single particle states, $r=\pm 1$ to $\pm(n-1)/2$, are doubly occupied and those with $n=\pm(n+1)/2$ are singly occupied. The spin summation should be carefully done. Terms corresponding to the previous ones are

$$\Delta E^{(1)} = \frac{-4}{n+1}\left\{\sum_{r=1}^{(n+1)/2}(-1)^r + \frac{1}{2} - \frac{(-1)^{(n+1)/2}}{2}\right\}v = 0, \tag{17}$$

$$\Delta E^{(2,q)} = \frac{-3}{2(n+1)^2}\left\{\cot\frac{\pi}{2(n+1)} + \cot\frac{3\pi}{2(n+1)}\right\}\frac{v^2}{\beta}, \tag{18}$$

$$\Delta E^{(2,c)} = \frac{2n-1}{2(n+1)^2}\left\{\cot\frac{\pi}{2(n+1)} + \cot\frac{3\pi}{2(n+1)}\right\}\frac{v^2}{\beta}. \tag{19}$$

Thus

$$\begin{aligned}\Delta E &= \Delta E^{(1)} + \Delta E^{(2,q)} + \Delta E^{(2,c)} \\ &= \frac{n-2}{(n+1)^2}\left\{\cot\frac{\pi}{2(n+1)} + \cot\frac{3\pi}{2(n+1)}\right\}\frac{v^2}{\beta}.\end{aligned} \tag{20}$$

The first order term vanished identically, the second order term having a similar character as previous ones.

Since the first order term predominantly affects the electrocyclic interaction, we will reexamine this more carefully. Denote the number of sites by n, which is even or odd, and the number of electrons by M, which is less than $2n$. Let us investigate the cases where M is $4m$, $4m+2$, $4m+1$, and $4m+3$.

(*i*) $M = 4m$

$$\begin{aligned}\Delta E^{(1)} &= -\frac{8v}{n+1}\sum_{r=1}^{2m}(-1)^r \sin^2\theta_r \\ &= \frac{4v}{n+1}\sum_{r=1}^{2m}(-1)^r \cos 2\pi r/(n+1) \\ &= -\frac{2v}{n+1}\left\{1 - \frac{\cos(4m+1)\pi/(n+1)}{\cos \pi/(n+1)}\right\}.\end{aligned} \tag{21a}$$

Note that

$$1 - \frac{\cos(4m+1)\pi/(n+1)}{\cos\pi/(n+1)} > 0. \tag{21b}$$

(*ii*) $M=4m+2$ Similar calculation yields

$$\Delta E^{(1)} = \frac{2v}{n+1}\left\{1 - \frac{\cos(4m+3)\pi/(n+1)}{\cos\pi/(n+1)}\right\}. \tag{22a}$$

Note that

$$1 - \frac{\cos(4m+3)\pi/(n+1)}{\cos\pi/(n+1)} > 0. \tag{22b}$$

(*iii*) $M = 4m+1$

$$\begin{aligned}\Delta E^{(1)} &= \frac{v}{(n+1)\cos\pi/(n+1)} \\ &\quad \times [\cos(4m+1)\pi/(n+1) - \cos(4m+3)\pi/(n+1)] \\ &= \frac{2v}{n+1}\tan\pi/(n+1)\sin(4m+2)\pi(n+1).\end{aligned} \tag{23a}$$

Note that $\tan\pi/(n+1)>0$, but

$$\sin(4m+2)\pi/(n+1)\begin{cases} >0 & \text{for } 1<M<n \\ =0 & \text{for } M=n \\ <0 & \text{for } \mathrm{n}<M<2n. \end{cases} \tag{23b}$$

$(iv) M = 4m+3$

$$\Delta E^{(1)} = \frac{-2v}{n+1}\tan \pi/(n+1)\sin(4m+4)\pi/(n+1) \tag{24a}$$

with

$$\sin(4m+4)\pi/(n+1)\begin{cases} >0 & \text{for } 1<M<n \\ =0 & \text{for } M=n \\ <0 & \text{for } n<M<2n. \end{cases} \tag{24b}$$

It is desirable to clarify the fact that in the ring closure and ring opening reactions, it is not the number of sites but the number of electrons which control the reactivity of these reactions.[8] The results obtained are summarized in Table 1.

TABLE 1. CONDITIONS FOR $\Delta E^{(1)} < 0$

M[a]	[b]	Sign of v	Reaction path[c]
$4m$		+	con
$4m+2$		−	dis
$4m+1$	$0<M<n$	−	dis
	$M=n$		
	$n<M<2n$	+	con
$4m+3$	$0<M<n$	+	con
	$M=n$		
	$n<M<2n$	−	dis

a) Number of electrons. b) Relation between M and the number of sites, n. c) con: con-rotatory, dis: dis-rotatory.

In order to confirm the previous general results the details of small systems are given in Table 2. Care should be taken on signs of $\Delta E^{(1)}$ and $\Delta E^{(2)}$, remembering that β is negative. Our predictions as to whether the reactions is con-rotatory or dis-rotatory are made only from the first order term, $\Delta E^{(1)}$. Agreements with those from the Woodward-Hoffmann rule are almost satisfactory. For cases written as non-selective or that indicating disagreements between two predictions, there has been no experimental result,[4] so far we are aware of.

Diels-Alder Reaction

The simplest Diels-Alder reaction is shown in Fig. 4. As transition states for this sort of reaction, we adopt two types (Fig. 5a). In both models, the phases of basic orbitals can be chosen, without a loss of generality, such that the perturbing interactions are negative (attractive).

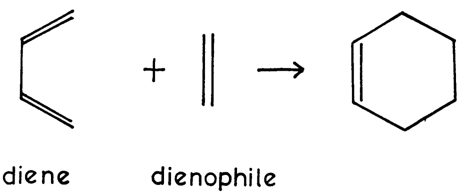

Fig. 4.

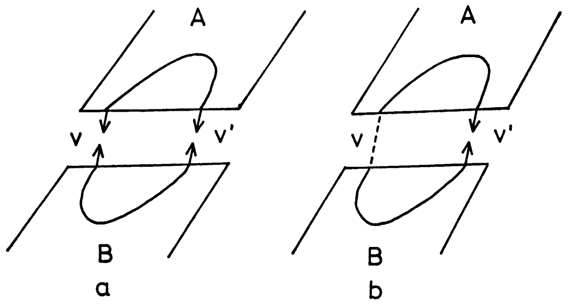

Fig. 5. Diels-Alder reaction.
a: Two interactions, b: single interaction.

Let us investigate the case in which two interactions v and v' coexist (Fig. 5a). We will show that this is not acceptable. For the sake of simplicity, we assume that the combining two species A and B are the same consisting of n sites and n electrons.

The extra energy due to perturbation Eq. 3, up to the second order is

$$\begin{aligned}\Delta E &= (v^2+v'^2)\frac{1}{2\pi i}\int_c \mathrm{d}z\, G_n(0)G_n(n-1) \\ &\quad + 2vv'\frac{1}{2\pi i}\int_c \mathrm{d}z\, G_n^2(0, n-1) \\ &= (v^2+v'^2)\frac{-2}{4\pi i}\int_c \mathrm{d}\theta\, \frac{\sin\theta\sin^2 n\theta}{\sin^2(n+1)\theta} \\ &\quad + 2vv'\frac{-2}{4\pi i}\int_c \mathrm{d}\theta\, \frac{\sin^3\theta}{\sin^2(n+1)\theta}.\end{aligned} \tag{25}$$

Calculations are carried out in a similar way to that for the second order terms $\Delta E^{(2)}$.

If n is even, the levels up to $n/2$ are doubly occupied, so that

$$\begin{aligned}\Delta E &= \frac{1}{2(n+1)^2\beta}[\operatorname{cosec}\pi/2(n+1) + \operatorname{cosec} 3\pi/2(n+1)] \\ &\quad \times [(2n-1)(v^2+v'^2) - 6vv'],\end{aligned} \tag{26a}$$

TABLE 2. RING CLOSURE AND RING OPENING REACTION

n[a]	M[b]	Species	$\Delta E^{(1)}$	$\Delta E^{(2)}$	Prediction	W-H rule[c]
3	2	+ion	v	$\sqrt{2}v^2/8\beta$	dis	dis
	3	neutral	0	$\sqrt{2}v^2/8\beta$	non-selective	con
	4	−ion	$-v$	$\sqrt{2}v^2/8\beta$	con	con
4	3	+ion	$(5-3\sqrt{5})v/10$	$3\sqrt{5}v^2/25\beta$	con	con
	4	neutral	$-\sqrt{5}v/5$	$4\sqrt{5}v^2/25\beta$	con	con
	5	−ion	$(5-3\sqrt{5}v/10$	$3\sqrt{5}v^2/25\beta$	con	dis
5	4	+ion	$-2v/3$	$(3+\sqrt{3})v^2/12\beta$	con	con
	5	neutral	0	$(3+\sqrt{3})v^2/12\beta$	non-selecitve	dis
	6	−ion	$2v/3$	$(3+\sqrt{3})v^2/12\beta$	dis	dis

a) Number of sites. b) Number of electrons. c) Predictions from the Woodward-Hoffmann rule.

and for $v=v'$

$$\Delta E = \frac{2(n-2)}{(n+1)^2}[\operatorname{cosec}\pi/2(n+1) + \operatorname{cosec}3\pi/2(n+1)]\frac{v^2}{\beta}. \tag{26b}$$

By means of dimensional analysis, we write explicitly β put to unity in evaluating propagators of the original system.

If n is odd, the levels up to $(n-1)/2$ are doubly occupied and the $(n+1)/2$-th is singly occupied, thus

$$\Delta E = \frac{1}{2(n+1)^2\beta}[\cot\pi/2(n+1) + \cot 3\pi/2(n+1)] \times [(2n-1)(v^2+v'^2) - 6vv']. \tag{27a}$$

For $v=v'$ we have

$$\Delta E = \frac{2(n-2)}{(n+1)^2}[\cot\pi/2(n+1) + \cot 3\pi/2(n+1)]\frac{v^2}{\beta}. \tag{27b}$$

Since β is negative, ΔE given by Eqs. 26b and 27b are negative, indicating that the Diels-Alder reaction is possible if two species are like those given in Fig. 5a. The result shows that the combined system is more stable than the original, not explaining the selection rule of Diels-Alder reaction.

Let us consider the model in Fig. 5b. Simultaneous interactions considered in Fig. 5a hardly seem to happen, instead a two step process like Fig. 5b is more probable. In the first step, A and B combine, due to v, yielding a long chain. In the second step, the chain starts the ring closure interaction due to the v' interaction. Note that in this model v' has always negative sign.

If we assume that the first step is rate-determining, the rules investigated for the ring closure reaction can be applied. Only the cases with negative v in Table 1 are allowed:

1) The case $M=4m$ is forbidden.
2) The case $M=4m+2$ is allowed.
3) For the case $M=4m+1$
   if $0<M<n$, the reaction is allowed,
   if $n<M<2n$, the reaction is forbidden,
   where n is the number of sites.
4) For the case of $M=4m+3$
   if $0<M<n$, the reaction is forbidden,
   if $n<M<2n$, the reaction is allowed.

The Cope and Claisen rearrangements are also treated in a similar way.

Sigmatropic Reaction

Let us consider the reaction shown in Fig. 6. This has been pointed out by Berson[9] as an example that the Woodward-Hoffman rule does not hold exactly. The Woodward-Hoffmann rule suggests the reaction path shown in Fig. 6a rather than that in Fig. 6b. In view of symmetry, the highest occupied orbital of the allyl type radical is described by displaying the phases of the atomic orbitals of both ends.

As has been done in the Diels-Alder reaction, we make use of the models shown in Figs. 7a and 7b for the transition states in Figs. 6a and 6b, respectively. v_a and v_b are examined since v_a' and v_b' have no significant contribution. The interactions, v_a and v_b are split into σ- and π-components, the parallel or perpendicular components with respect to the binding axis. Both components of v_a are positive, v_a being repulsive. The σ-component of v_b is negative and the π-one is positive. The migrating radical in the reaction is the methyl type one. This suggests that if we consider the steric effect, the methyl type radical might migrate above the allyl radical considerably nearer in the case of Fig. 7b than in the case of Fig. 7a. If this is the case, it is possible that the π-component becomes predominant and v_b is repulsive. Thus i) $v_a>0$, ii) $v_b>0$, if the migrating radical moves considerably close to the allyl radical.

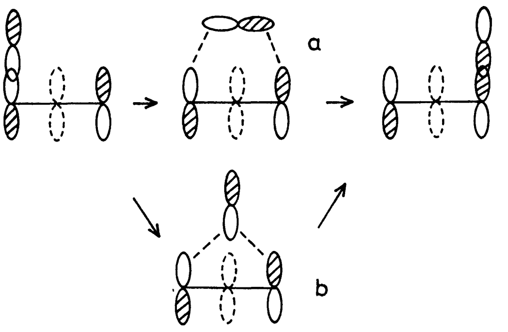

Fig. 6. Sigmatropic reaction.
The highest occupied orbital of the allyl type radical is described by displaying the phases of the atomic orbitals at the both ends.

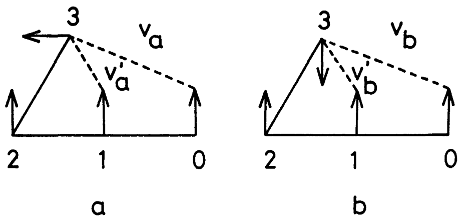

Fig. 7. Models for the transition states of the sigmatropic reaction.
Figures 7a and 7b correspond to the Figs. 6a and 6b respectively, but here arrows indicate the phases of the basic atomic orbitals.

For the cases of Figs. 7a and 7b, we obtain ΔE in Eq. 3 in the first order approximation;

$$\Delta E = \mathrm{Tr}\frac{1}{2\pi i}\int_c \mathrm{d}z\,\mathbf{Gv} = 2\left\{\frac{v_a}{2\pi i}\int_c \mathrm{d}z\,G_4(0,3) + \frac{v'_a}{2\pi i}\int_c \mathrm{d}z\,G_4(1,3)\right\}, \tag{28}$$

for the cases of Fig. 7a. Replacing v_a and v_a' by v_b and v_b', respectively, we get the expression for Fig. 7b. G_4 (0, 3) is the 0-3 matrix element of the chain propagator with four sites. In Eq. 28, the second integral is the bond order between the starred sites of the conjugated chain, vanishing identically. The remaining term gives

$$\Delta E_a(\Delta E_b) = \frac{2\sqrt{5}}{5}v_a(v_b),\ v_a(v_b)>0. \tag{29}$$

The reaction mechanism infers the first case in Table 1, in other words, the formation of the Möbius ring presented in the next section. Accordingly our theory explains the possibility of two reaction paths.

Aromaticity

Let us examine the stability conditions in the ground state of the conjugated systems. The question what aromaticity is has been discussed for a long time. We consider it as a problem of energy stabilization when the conjugated chain becomes a ring by connection of both ends.[10]

Let the interaction between two ends be v. The following conclusions are obtained from Table 1.

A. The ring with the negative v or the Hückel ring is more stable than the original chain, under the conditions where

i) $M=4m+2$

ii) $M=4m+1$ and $0<M<n$

iii) $M=4m+3$ and $n<M<2n$,

where n is the number of sites.

B. The ring with positive v or the Möbius ring is preferable under the conditions that

i) $M=4m$

ii) $M=4m+1$ and $n<M<2n$

iii) $M=4m+3$ and $0<M<n$.

Naphthalene and Azulene

The stability of compounds consisting of two rings is of interest. Naphthalene and azulene are well-known examples. Two ring compounds consisting of ten atoms are presented (Fig. 8).

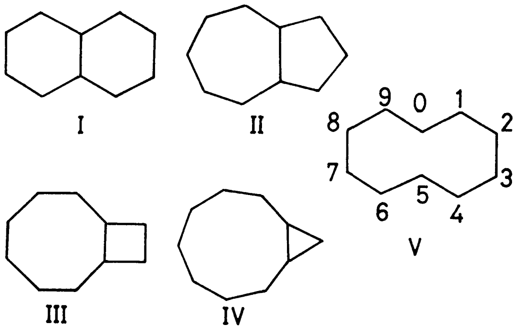

Fig. 8. Two ring compounds (I—IV) composed of cyclodecapentaene (V).

Compounds I—IV are derived from various perturbations put in cyclodekapentaene V as follows:

$$v' = \begin{cases} v'_{05} \text{ for I} \\ v'_{04} \text{ for II} \\ v'_{03} \text{ for III} \\ v'_{02} \text{ for IV.} \end{cases} \tag{30}$$

The stabilization energies in these cases are mainly due to the first order term:

$$\left.\begin{matrix} \Delta E(\text{I}) \\ \Delta E(\text{II}) \\ \Delta E(\text{III}) \\ \Delta E(\text{IV}) \end{matrix}\right\} = 2v' \frac{1}{2\pi i}\int_c dz \begin{Bmatrix} G_{10}\,(0,5) \\ G_{10}\,(0,4) \\ G_{10}\,(0,3) \\ G_{10}\,(0,2) \end{Bmatrix} = 2v' \begin{Bmatrix} q_{10}(0,5) \\ q_{10}(0,4) \\ q_{10}(0,3) \\ q_{10}(0,2). \end{Bmatrix} \tag{31}$$

The problems are reduced to the evaluation of the corresponding bond orders. The bond order $q_n(0, k)$ in this case is

$$q_n(0,k) = \frac{2}{n}\frac{\sin(k\pi/2)}{\sin(k\pi/n)}, \tag{32}$$

from which it follows that

$$\begin{aligned} q_{10}(0,5) &= 1/5 \\ q_{10}(0,4) &= 0 \\ p_{10}(0,3) &= -(\sqrt{5}-1)/5 \\ q_{10}(0,2) &= 0. \end{aligned} \tag{33}$$

Naphthalene is the most stable, azulene and IV next, III being the most unstable.

Anthracene and Phenanthrene

In order to clarify the distinction between anthracene and phenanthrene in view of stabilization, a simple method has been worked out for generalization to larger benzenoid hydrocarbons.

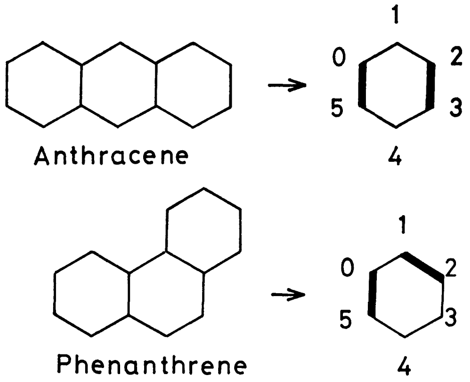

Fig. 9.

We rewrite anthracene and phenanthrene, as in Fig. 9, by means of structures with bold bonds which indicate the adjacent benzene rings in each compound. Anthracene is considered as a fictitious benzene in which the 0-5 and 2-3 bonds have the effective resonance integrals, β_{eff}, instead of the original β. If we put

$$v = \beta_{\text{eff}} - \beta, \tag{34}$$

and use Eq. 3 up to the second order, ΔE for anthracene is given by

$$\begin{aligned} \Delta E_{\text{A}} = \frac{1}{2\pi i}\int_c dz\{&2v[G(0,5)+G(2,3)]+v^2[G(0)G(5) \\ &+G(2)G(3)+G(0,5)G(5,0) \\ &+G(2,3)G(3,2)]+2v^2[G(0,2)G(3,5) \\ &+G(0,3)G(2,5)]\}. \end{aligned} \tag{35}$$

In a similar way, ΔE for phenanthrene is given by

$$\begin{aligned} \Delta E_{\text{P}} = \int_c dz\{&2v[G(0,5)+G(1,2)]+v^2[G(0)G(5) \\ &+G(1)G(2)+G(0,5)G(5,0) \\ &+G(1,2)G(2,1)]+2v^2[G(0,1)G(2,5) \\ &+G(0,2)G(1,5)]\}. \end{aligned} \tag{36}$$

The difference between ΔE_A and ΔE_P arises from the second order terms,

$$\Delta E_A - \Delta E_P = \frac{1}{2\pi i}\int_c dz\, 2v^2[G(0,2)G(3,5)+G(0,3)G(2,5) -G(0,1)G(2,5)-G(0,2)G(1,5)]. \qquad (37)$$

It is instructive to trace the routes indicated by combining propagators and v of Eq. 37. We can easily evaluate this and find

$$\Delta E_A - \Delta E_P = -(0.17+0.35)v^2/\beta = -0.25v^2/\beta. \qquad (38)$$

Because of the negative sign of β, the value of Eq. 38 is positive, with a small magnitude. Thus phenanthrene should be more stable than anthracene. This is in line with the observation. The result is independent of the sign of v. Generalization to a larger system is straigtforward (Fig. 10).

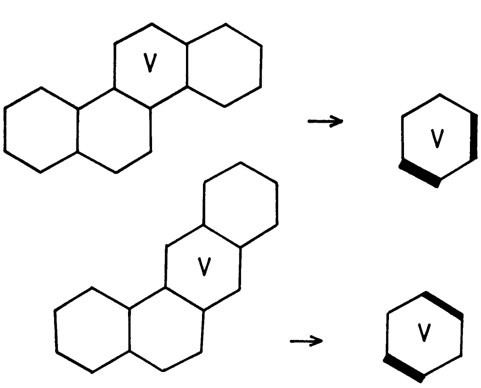

Fig. 10. Shorthand display of the benzenoid.

β_{eff} in Eq. 34 is interpreted as an average of the operator, $|s\rangle\beta_{st}\langle t|$, with respect to the ground state of the system in question,

$$|0\rangle = \prod_i^{\mathrm{occ}} |i\rangle. \qquad (39)$$

Namely

$$\beta_{st:\mathrm{eff}} = \beta_{st}\sum_i \langle s|i\rangle\langle i|t\rangle = \beta_{st}\frac{1}{2\pi i}\int_c dz\, G(s,t;z). \qquad (40)$$

This relation reproduces the original β_{st} in the diatomic chain. Using Eq. 40 in the benzene ring, we obtain

$$\beta_{\mathrm{eff}} = 0.667\beta. \qquad (41)$$

This is in line with the fact that in anthracene or phenanthrene, the corresponding bond length is slightly greater than that of benzene.

Concluding Remarks

Propagator theory has been successfully applied to the problems of chemical reactivity and stability. No use was made of wave functions or LCAO coefficients. Even if the concept of orbital is established, the orbital is not a physical quantity. The final result should be presented only in terms of the coupling constants in the Hamiltonian. In this respect our theory is nearer to that of Coulson than that of Fukui and Woodward-Hoffmann.

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