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The Stereoselection Rule for Electrocyclic Interactions

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A general stereoselection rule governing the electrocyclic interactions has been proposed with a molecular orbital rationale. The reactions discussed from a unified point of view cover the ring-closure of polyenes, the Diels-Alder additions, 1, 4-dipolar additions, the Cope and the Claisen rearrangements, the hydrogen and the proton migrations, 1, 3-dipolar additions, the ring-opening of cyclic olefins, the deamination of cyclic unsaturated imines, 1, 2-noncycloadditions, 1, 2-eliminations, the nucleophilic displacement with allylic rearrangements, and other cyclic intermediate or complex formations. The relation to the molecular orbital symmetry has been also discussed.

The molecular orbital (MO) theory, which has early proved itself suitable for interpreting the chemical reactivity, is exhibiting its usefulness also in the problem of the stereoselectivity. In particular, the symmetry property of MO has been intimately connected to the steric course of chemical reactions. One of the present authors first pointed out the importance of the symmetry of the highest occupied (HO) MO of dienes and the lowest vacant (LV) MO of dienophiles for the occurrence of the Diels-Alder reaction.[1] The MO symmetry was correlated with the stereoselectivity in the ring-closure of linear polyenes and in the ring-opening of cyclic olefins first by Woodward and Hoffmann,[2] and later by Longuet-Higgins and Abrahamson,[3] and by Fukui.[4] Woodward and Hoffmann[2] considered the symmetry of HO only, while Fukui[1,4] HO and LV for discussing the interaction of two systems.

These particular orbitals were coincident with those which played an important role in the MO theory of chemical reactivity of both saturated and unsaturated compounds, called the frontier orbitals by the present authors.[5,6] The physical basis on which these orbitals were distinguished from the others in the course of interaction with a reagent was clearly disclosed.[7] However, the discrimination of HO in the Woodward-Hoffmann interpretation[2] should be given a theoretical basis anew, since they considered the overlap stabilization of two π-atomic orbitals (AO) at both ends of the conjugated chain and it is hence evident that all of the π-MO's must deservedly contribute to such a sort of stabilization energy.

The MO theoretical interpretation was made also for other stereochemical problems. The selection rules in such cyclic additions as Diels-Alder, 1, 3-dipolar, and 1, 2-*cis* types,[1,8,9,12] in hydrogen migration,[10,12] in the Claisen and Cope rearrangements,[8,9,12] in noncycloadditions like 1, 2-*trans*,[9,11,12] and in 1, 2-*trans*-eliminations[12] were discussed theoretically.[13]

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[1] K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," ed. by P.-O. Löwdin and B. Pullman, Academic Press Inc., New York, N. Y. (1964), p. 513.

[2] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[3] H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

[4] K. Fukui, *Tetrahedron Letters*, **1965**, 2009.

[5] a) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); b) K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, *ibid.*, **22**, 1433 (1954); see also many other papers cited in Ref. 1.

[6] a) K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **33**, 1201 (1960); b) K. Fukui, H. Kato and T. Yonezawa, *ibid.*, **34**, 442 (1961); c) K. Fukui, H. Kato and T. Yonezawa, *ibid.*, **34**, 1111 (1961); see also many other papers cited in K. Fukui, "Modern Quantum Chemistry," Vol. 1, ed. by O. Sinanoğlu, Academic Press Inc., New York, N. Y. (1965), p. 49.

[7] a) K. Fukui, T. Yonezawa and C. Nagata, This Bulletin, **27**, 423 (1954); b) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957); c) K. Fukui, T. Yonezawa and C. Nagata, *ibid.*, **27**, 1247 (1957); d) R. D. Brown, *J. Chem. Soc.*, **1959**, 2224, 2232; e) K. Fukui, K. Morokuma, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **32**, 1743 (1960).

[8] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[9] K. Fukui, This Bulletin, **39**, 498 (1966).

[10] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

[11] K. Fukui, *Tetrahedron Letters*, **1965**, 2427.

[12] K. Fukui and H. Fujimoto, This Bulletin, **39**, 2116 (1966).

[13] Other problems were discussed in a similar fashion: a) for the stereoselectivity in E2 reactions, see K. Fukui and H. Fujimoto, *Tetrahedron Letters*, **1965**, 4303; b) for *endo-exo* selection in cyclic additions, see R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965); c) for the stereochemistry of the transition state of the Cope rearrangements, see R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4389 (1965); K. Fukui and H. Fujimoto, *Tetrahedron Letters*, **1966**, 251; and d) for the stereochemistry of excited configuration of conjugated chains, see R. Hoffmann and R. A. Olofson, *J. Am. Chem. Soc.*, **88**, 943 (1966). (Dr. Hoffmann kindly sent a manuscript to us prior to publication.)

The present paper intends to supply a universal stereoselection rule governing these stereochemical phenomena by a unified principle. The rule is given in a surprisingly simple form, making it at the same time possible to understand the reason why only HO does appear to act a discriminative part.[14]

The Electrocyclic Interaction

Woodward and Hoffmann[2] used the term "electrocyclic reactions" in their first elegant generalization of the stereochemical phenomena in the ring-closure of conjugated polyenes and the ring-opening of cyclic olefins. Here we consider a chain-like connected sequence of n AO's containing an even number, let it be $2m$, of electrons,[15] and define the "electrocyclic interaction" of these electrons in case of the approach of both ends of the chain to form a cyclic system. These AO's are not limited to the carbon 2p AO only, but may include nitrogen, oxygen, or other p AO's, 1s AO of hydrogen, or even any type of hybridized orbital to constitute a sigma skeletal chain of which we can adopt the usual approximation that the resonance integrals between non-neighbored AO's are neglected. It is important to choose these AO's as real functions.

The MO's are composed of the linear combination of these AO's which are named $\phi_1, \phi_2, \ldots, \phi_n$ from one end of the chain. The secular determinant in the Hückel MO treatment[16] is given by the following formula:

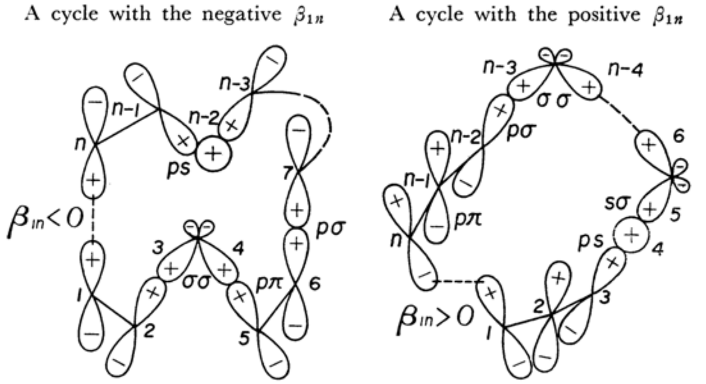
$$\Delta^{(0)}(\varepsilon) =$$

$$\begin{vmatrix} \alpha_1-\varepsilon & \beta_{12} & 0 & \cdots & 0 & 0 \\ \beta_{12} & \alpha_2-\varepsilon & \beta_{23} & \cdots & 0 & 0 \\ 0 & \beta_{23} & \alpha_3-\varepsilon & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & \alpha_{n-1}-\varepsilon & \beta_{n-1n} \\ 0 & 0 & 0 & \cdots & \beta_{n-1n} & \alpha_n-\varepsilon \end{vmatrix} \qquad (1\text{-a})$$

in which $\alpha_1, \alpha_2, \ldots$ are the Coulomb integrals being all negative, and $\beta_{12}, \beta_{23}, \ldots$ are the resonance integrals. The sign (or direction) of AO's is assumed to be chosen so as to make all β_{ii+1}'s ($i=1, 2, \ldots, n-1$) possess negative values. The interaction between the two termini may be characterized by introducing a parameter β_{1n} into the determinant as its $(1, n)$ and $(n, 1)$ elements. The secular determinant becomes

$$\Delta(\varepsilon) = \Delta^{(0)}(\varepsilon) - \beta_{1n}^2 \Delta_{11,nn}^{(0)}(\varepsilon) - 2(-1)^n \beta_{1n}\beta_{12}\beta_{23}\cdots\beta_{n-1n} \qquad (1\text{-b})$$

in which $\Delta_{11,nn}^{(0)}$ is the minor of $\Delta^{(0)}$ obtained by removing the first and the nth columns and rows. The sign of β_{1n}, negative or positive, is made to stand for the direction of interaction of chain ends. Provided such a selection of direction is sterically permitted in this interaction, the reaction will take place through the one of steric paths which gives the lower electronic energy. The comparison of energy is easily made by solving the secular determinant. The secular determinants corresponding to the negative and the positive


A cycle with the negative β_{1n}

A cycle with the positive β_{1n}

Fig. 1. The electrocyclic interactions with the negative and the positive β_{1n}'s. The signs (+) and (−) imply the positive and the negative parts of the real AO wave functions.

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[14] Hoffmann and Woodward (Ref. 8) as well as Longuet-Higgins and Abrahamson (Ref. 3) used correlation diagrams in place of the HO MO symmetry criterion employed in Ref. 2.

[15] An unequivocal way of taking such a sequence of AO's will be possible with respect to any system if we select the one which is most sensibly affected by the difference in the steric course.

[16] More elaborate treatments will be no more than a nuisance in the present case in which only the things essential are necessary. It is well known that the results of prediction of chemical reactivity by relevant MO-theoretical indices are not essentially affected by the roughness of the Hückel MO calculation.

β_{1n}'s are expressed by $\Delta^{(N)}(\varepsilon)$ and $\Delta^{(P)}(\varepsilon)$ respectively.

We replace the argument ε by α_0+z to obtain the functions of z, $D^{(N)}(z)$ and $D^{(P)}(z)$, corresponding respectively to $\Delta^{(N)}(\varepsilon)$ and $\Delta^{(P)}(\varepsilon)$, so that both of the equations, $D^{(N)}(z)=0$ and $D^{(P)}(z)=0$, come to possess m negative and $(n-m)$ positive roots.

We try to compare the sum of the negative roots between the cases of negative and positive β_{1n}'s which are put, for the purpose of comparison, γ and $-\gamma$ $(\gamma<0)$ respectively.[17] Thus, we write

$$D^{(N)}(z) = D(z) - a$$

$$D^{(P)}(z) = D(z) + a$$

where

$$D(z) = \Delta^{(0)}(\alpha_0 + z) - \gamma^2 \Delta^{(0)}_{11,nn}(\alpha_0 + z)$$

$$a = 2(-1)^n \gamma \beta_{12}\beta_{23}\cdots\beta_{n-1n} > 0$$

The equation $D(z)=0$ also has m negative and $(n-m)$ positive roots. Twice the sum of the negative roots of $D(z)\mp a=0$ is denoted by $E^{(N)}$ and $E^{(P)}$. This can be expressed by the Coulson and Longuet-Higgins' integral representation.[18] Thus, we get

$$E^{(N)} - E^{(P)}$$

$$= \frac{1}{\pi}\int_{-\infty}^{+\infty} iy\left\{\frac{D'(iy)}{D^{(N)}(iy)} - \frac{D'(iy)}{D^{(P)}(iy)}\right\}\mathrm{d}y$$

If we put

$$D(iy) = R(y) + iyS(y)$$

where $R(y)$ and $S(y)$ are real even functions of y, an integral by parts leads us to the formula

$$E^{(N)} - E^{(P)}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} \log\left\{1 + \frac{4aR}{(R-a)^2 + y^2S^2}\right\}\mathrm{d}y$$

Now, we regard $D(0)$ as a function of α_0, indicating it by $A_0(\alpha_0)$. The equation $A_0(\alpha_0)=0$ possesses n real roots. In order that $D(z)=0$ possesses m negative and $(n-m)$ positive roots, α_0 must be in the interval ranging from the mth to the $(m+1)$th root of $A_0(\alpha_0)=0$. Such an α_0 obviously satisfies the condition

$$(-1)^m A_0(\alpha_0) > 0$$

Further, if we write

$$R(y) = A_0(\alpha_0) - A_2(\alpha_0)y^2 + \cdots \begin{cases} (-1)^{n/2}A_n(\alpha_0)y^n & \text{(for even } n) \\ (-1)^{(n-1)/2}A_{n-1}(\alpha_0)y^{n-1} & \text{(for odd } n) \end{cases}$$

it follows evidently that

$$A_{2q}(\alpha_0) = \frac{1}{(2q)!}\left[\frac{\mathrm{d}^{2q}}{\mathrm{d}z^{2q}}D(z)\right]_{z=0}$$

$$= \frac{1}{(2q)!}\frac{\mathrm{d}^{2q}}{\mathrm{d}\alpha_0^{2q}}A_0(\alpha_0)$$

$$q = 0, 1, 2, \cdots \begin{cases} n/2 & \text{(for even } n) \\ (n-1)/2 & \text{(for odd } n) \end{cases}$$

Now we put

$$R(y) = (-1)^m T(y)$$

where

$$T(y) = f(\alpha_0) - \frac{1}{2!}f''(\alpha_0)y^2 + \frac{1}{4!}f''''(\alpha_0)y^4 \cdots \begin{cases} \dfrac{(-1)^{n/2}}{n!}f^{(n)}(\alpha_0)y^n & \text{(for even } n) \\ \dfrac{(-1)^{(n-1)/2}}{(n-1)!}f^{(n-1)}(\alpha_0)y^{n-1} & \text{(for odd } n) \end{cases}$$

and

$$f(\alpha_0) = (-1)^m A_0(\alpha_0)$$

in which α_0 has been taken so as to satisfy

$$f(\alpha_0) > 0$$

Here we limit the discussion, from both mathematical and practical points of view, to the following most common cases:

$$\left.\begin{array}{ll} \text{i.} & n=\text{even},\ m=n/2 \\ & \text{(mostly a neutral system),} \\ \text{ii.} & n=\text{odd},\ m=(n-1)/2 \\ & \text{(mostly a cationic system),} \\ \text{iii.} & n=\text{odd},\ m=(n+1)/2 \\ & \text{(mostly an anionic system).} \end{array}\right\} \quad (2)$$

Moreover, we make an important proposition that it is possible to choose a value of α_0 so as to make $T(y)$ positive for all real values of y. This proposition is strictly right in the cases $n=2$, $n=3$, and $n=4$ for chains with any set of α's and β's and in the cases of any n for chains with equal α's. In the cases $n\geqq 5$, where all α's are not necessarily equal, this proposition, in a rigorously mathematical sense, not always holds; but anyone can always ascertain for each given case by a very simple numerical calculation along the line mentioned above, in advance to the employment of the subsequent theoretical result giving the selection rule, whether this proposition is actually true or not. From the results of a number of such calculations,

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[17] The present paper is connected with those electrocycles in which the comparison of the two cases, $\beta_{1n}=\gamma$ and $-\gamma$, is effectual: hence, the terminal AO's (1 and n) are usually required to be pπ and the interaction between them is of pσ type (Fig. 1). Thus, the stereoselection rule of the present paper has nothing to do, for instance, with the problem of the stability of an sp$^3\sigma$ chain of cycloparaffin like skeletons, in which the interactions of two sp^3 hybrids with positive and negative β_{1n}'s can never be discussed as having an essentially equal efficiency of orbital overlapping.

[18] C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191**, 39 (1947); **A192**, 16 (1947).

it is known that the exception lies only in the region to which actual chemical systems can hardly belong. Moreover, we can always choose α_0 even for $n \geqq 5$ so as to make

$$T_0(y) = f(\alpha_0) - \frac{1}{2!} f''(\alpha_0) y^2$$

positive for the whole interval of real y. But it is seen from Eq. (3) that only the range of small y contributes to the right-side integral. Therefore, the value of the integral will not appreciably change if we replace $T(y)$ by $T_0(y)$. Such circumstances will not only diminish the error caused by making the general assumption that the proposition applies in almost all practical occasions even in the case of $n \geqq 5$, but also enable us, if necessary, to step outside from the limitation of (2). Numerical calculations can make sure of these circumstances.

In this way, we get, provided the proposition mentioned above holds,

$$E^{(\mathrm{N})} - E^{(\mathrm{P})} = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \log \left\{ 1 + (-1)^m \frac{4aT}{(R-a)^2 + y^2 S^2} \right\} \mathrm{d}y \begin{cases} >0 \text{ for even } m, \\ <0 \text{ for odd } m. \end{cases} \tag{3}$$

This result implies that:

For odd m the interaction with negative β_{1n} will dominate, while for even m the interaction with positive β_{1n} will be prevalent. **[*Theorem A*]**

This theorem describes the function of the "electrocyclic effect" which controls the steric course of cyclic interactions.

It is striking that the essential principle of stereoselection originates not from the number of AO's but from the number of electrons, or the number of doubly occupied MO's, although the number of electrons is not independent of the number of AO's through the assumption of (2). The verification of the theorem will follow with respect to a number of examples. Numerical calculations also assured this theorem.[12]

The Ring-Closure of Linear Conjugated Chains

The general rule governing the stereoselectivity of the thermal ring-closing reaction of linear conjugated chains which was proposed by Woodward and Hoffmann with the correspondence to experimental results is as follows:[19]

The ring formation by connecting both ends of a chain containing $2k\pi$ electrons should occur in the "conrotatory" mode for even k and in the "disrotatory" mode for odd k. **[*Rule 1*]**

Theorem A immediately leads one to *Rule 1* if both n and $2m$ are put equal to $2k$, since the disrotatory interaction evidently corresponds to negative β_{1n} and the conrotatory one to positive β_{1n}.

The Cyclic Interaction between Two Systems

The interaction in the Diels-Alder addition, like the reaction between 1, 2-positions of ethylene derivatives and 1, 4-positions of butadiene derivatives, is a special case of the interaction of the present kind in which $n=6$, $m=3$. The 1, 4-dipolar additions which has recently been reported[20] also belong to the case of $n=6$, $m=3$. The transition states in the Cope rearrangement and, in an approximate sense, also in the Claisen rearrangement, correspond also to the case of $n=6$, $m=3$. These are all known to occur in *cis*-mode. On applying *Theorem A* to this problem, we are able to deduce at once the following rule:

The cyclic reaction between two systems forming a cycle composed of 2k electrons in 2k atomic orbitals in the transition state takes place in the cis-trans or trans-cis fashion when k is even, while in the cis-cis or trans-trans fashion when k is odd. **[*Rule 2*]**

The geometrical situation will determine the selection of each of two modes of occurrence; for instance, the Diels-Alder reaction takes place only in the *cis-cis* mode.

The conclusion disclosed above also includes, as a special case, that of Hoffmann and Woodward (for thermal reactions)[8] which gives a theoretical explanation for the stereoselection in cycloadditions by an orbital symmetry consideration. *Rule 2* is applied *in statu quo* also to the cyclic interactions of more than two systems, provided appropriate examples are encountered.

An interesting example of application of *Theorem A* is to the hydrogen migration. The transition state of the $(1, 2k+1)$ hydrogen radical migration of the type

$$\mathrm{H_3C{-}(CH{=}CH{-})_{\mathit{k}-1}CH{=}CH_2} \rightarrow \mathrm{H_2C{=}CH{-}(CH{=}CH{-})_{\mathit{k}-1}CH_3}$$

belongs to the case of $n=2k+2$, $m=k+1$. So, we obtain the following rule:

The $(1, 2k+1)$ hydrogen radical migration takes place by way of "suprafacial" fashion[21] if k is even, while by way of "antarafacial" fashion[21] if k is odd. **[*Rule 3*]**

This conclusion includes the stereoselection rule for the hydrogen-migration (thermal) given by Woodward and Hoffmann.[10]

The cycle of odd number AO's also supplies an interesting example. The $(1, 2k)$ proton migration of the type

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19) Woodward and Hoffmann discussed the excited-state reaction as well as the ground-state reaction. But by the mathematical reason the present authors limit the problem to the ground-state reaction only.

20) R. Huisgen and K. Herbig, *Ann.*, **688**, 98 (1965).

21) This was named by Woodward and Hoffmann (Ref. 10).

$$H_3C\text{-}(CH{=}CH\text{-})_{k-1}CH_2^+ \rightarrow H_2C^+\text{-}(CH{=}CH\text{-})_{k-1}CH_3$$

or the protonation of conjugated olefins belongs to the case of $n=2k+1$, $m=k$. For instance, the 1, 2-migration of α-proton in ethyl cation is known to be allowed ($n=3$, $m=1$). *Theorem A* at once derives the following conclusion:

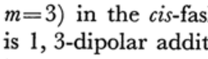
The (1, 2k) proton migration or protonation can actually take place by way of "suprafacial" fashion if k is odd. **[*Rule 4*]**

The interaction of 1, 3-positions of allyl cation with 1, 4-positions of butadiene ($n=7$, $m=3$) will be in the *cis*-mode. Similarly, allyl anion will interact with ethylene derivatives ($n=5$, $m=3$) in the *cis*-fashion. An example of this type is 1, 3-dipolar additions, which are known to occur in the *cis*-mode. The other examples of an odd-membered cycle with even number electrons are: the phenonium cation, the transition state of the singlet addition of carbenes to olefins, the transition state in hydroboration of olefins, and so on. All of these examples belong essentially to the case $n=3$, $m=1$, and are known to occur actually.

To the contrary, the 1, 4-interaction of two butadiene ($n=8$, $m=4$) will take place in "antarafacial" mode.

The Ring-Opening of Cyclic Olefins and the Deamination of Cyclic Unsaturated Imines.

Here it is thought desirable to add to what has been described above that *Theorem A* is also applicable to the cyclic transition states of the ring-opening of cyclic olefins②



$$\begin{matrix}\text{-}(CH{=}CH\text{-})_k\text{-} \\ \text{-}CH_2 - CH_2\text{-}\end{matrix} \rightarrow H_2C{=}CH\text{-}(CH{=}CH\text{-})_{k-1}CH{=}CH_2$$

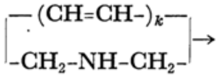
TABLE 1. THE SELECTION RULE FOR SOME RING-CLEAVAGE REACTIONS

	even k	odd k
The ring-opening of cyclic olefins[a] ($n=2k+2$, $m=k+1$)	Disrotatory opening	Conrotatory opening
The deamination of cyclic imines[b] ($n=2k+4$, $m=k+2$)	Axisymmetric fragmentation	Sigmasymmetric fragmentation

a) The AO's constituting the electrocycle are $2k$ carbon pπ AO's and two incipient orbitals appearing in the transition state on each carbon forming the sigma bond to be broken.

b) The AO's of the electrocycle are $2k\pi$ AO's and four incipient orbitals, one each for the two carbons and two for the nitrogen atom of the two N-C bonds to be broken.

and the deamination of unsaturated cyclic imines.[22]



$$\begin{matrix}-(CH{=}CH\text{-})_k- \\ \text{-}CH_2\text{-}NH\text{-}CH_2\text{-}\end{matrix} \rightarrow H_2C{=}CH\text{-}(CH{=}CH\text{-})_{k-1}CH{=}CH_2$$

The rule will be what is illustrated in Table 1, in conformity with the previous explanations based on the orbital symmetry[3,22] consideration.

The Noncyclic Two-Center Interaction in Linear Conjugated Systems

The problem of the stereoselection in the addition to unsaturated bonds was generally and comprehensively discussed already by the present authors by the frontier electron method[11] and by a perturbation treatment.[12] It was shown to be the σ-π interaction that might possess an essential meaning for the stereoselection of this sort.[23] The theoretical results indicated that 1, 2- and 1, 6-additions should take place through the "*anti*"-interaction, whereas 1, 4-addition through the "*syn*"-interaction.[24] Here, we expect a more general, non-perturbation treatment for demonstrating this theorem.

The energy change is compared with respect to the "*syn*" and "*anti*" two-center σ-π interactions, which are schematically illustrated in Figs. 2 and 3. The change of hybridization is taken into account only at the terminal carbons.

It is recommended[25] to adopt sp^2 (or sp) hybrids as the basis AO's composing the σ chain since the chain thus made up will most sensibly transmit the effect of the stereoselection. The deformed π AO at the sites of interaction may be represented by a sp^x($x>3$) hybrid. The treatment of σ electron

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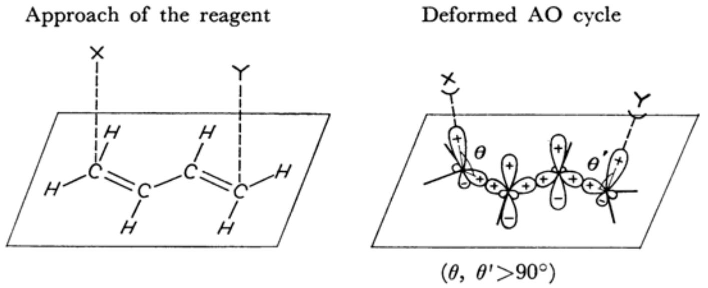
[22] D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, **88**, 1335 (1966).

[23] The importance of the σ-π interaction in the stereospecificity of some ring-opening reactions was also pointed out by Fukui (see Ref. 9). Also see the paper of Longuet-Higgins and Abrahamson (Ref. 3).

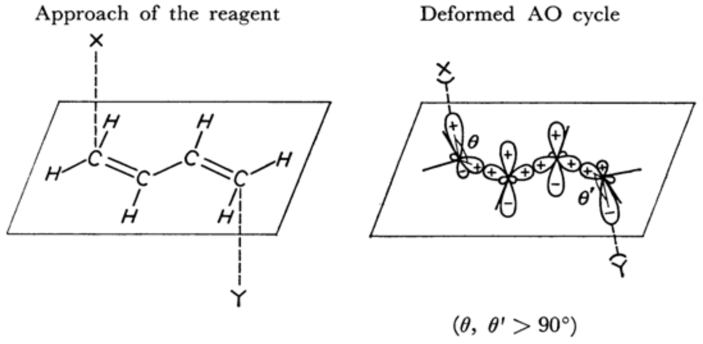
[24] The terminology "*syn*" and "*anti*" is employed, in place of "*cis*" and "*trans*" respectively, in order to avoid confusion in the case of additions to polyenic olefins.

[25] Those who are not accustomed to the σ AO treatment are advised to proceed along the following way of consideration. At first, the LCAO MO's based upon the valence AO's taken in the fixed direction (*e. g.* 2s, 2p$_x$, 2p$_y$, and 2p$_z$ of all carbon atoms assigned to the spatially fixed coordinates) are obtained by any appropriate method (*e. g.* R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963) and subsequent papers, or J. A. Pople, D. P. Santry and G. A. Segal, *ibid.*, **43**, S129 (1965); J. A. Pople and G. A. Segal, *ibid.*, **43**, S136 (1965)). The set of MO's thus obtained is then converted by the Lennard-Jones orthogonal transformation to another set of MO's which are substantially localized in one atom making a hybrid like orbital which extends in the direction of bonding (*cf.* J. Lennard-Jones, *Proc. Roy. Soc. (London)*, **A198**, 1, 14 (1949)). The value of β's and γ's may be evaluated by using these newly obtained MO's and Hamiltonian operator.


Approach of the reagent

Deformed AO cycle

Fig. 2. A schematic representation of the "*syn*"-interaction of σ and π chains of AO's. Butadiene is taken as an example of the conjugated system. The approaching reagent is represented by XY (or X and Y in their "concerted" or "quasi-concerted" approach).


Approach of the reagent

Deformed AO cycle

Fig. 3. A schematic representation of the "*anti*"-interaction of σ and π chains of AO's. Butadiene is taken as an example of the conjugated system. The approaching reagent is represented by XY (or X and Y in their "concerted" or "quasi-concerted" approach).

systems by employing these hybrids as the basis AO's has been developed by many authors.26) The secular determinant with the σ-π interaction is represented by

$$\Delta^{(\sigma,\pi)}(\varepsilon)=\left|\begin{array}{ccc|ccc}
\alpha_1^{(\pi)}-\varepsilon & \beta_{12}^{(\pi)} & \cdots\cdots & \gamma & \cdots\cdots & \cdots\cdots \\
\beta_{12}^{(\pi)} & \alpha_2^{(\pi)}-\varepsilon & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\
\cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\
\cdots\cdots & \cdots\cdots & \alpha_k^{(\pi)}-\varepsilon & \cdots\cdots & \cdots\cdots & \gamma' \\
\hline
\gamma & \cdots\cdots & \cdots\cdots & \alpha_1^{(\sigma)}-\varepsilon & \beta_{12}^{(\sigma)} & \cdots\cdots \\
\cdots\cdots & \cdots\cdots & \cdots\cdots & \beta_{12}^{(\sigma)} & \alpha_2^{(\sigma)}-\varepsilon & \cdots\cdots \\
\cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots & \cdots\cdots \\
\cdots\cdots & \cdots\cdots & \gamma' & \cdots\cdots & \cdots\cdots & \alpha_{2k-2}^{(\sigma)}-\varepsilon
\end{array}\right| \tag{4}$$

in which superscript (π) and (σ) denote the originally pi and the sigma parts respectively, γ and γ' being the "resonance" integrals of σ-π interaction at carbon 1 and carbon k respectively. If we take a negative value for γ, the "*syn*"- and "*anti*"-interactions correspond to a negative and a positive γ' respectively. A glance at Eq. (4) makes us to learn that this is nothing but a special case of Eq. (1-b). Accordingly, by putting $k=2\nu$, one is immediately led to a rule which says:

In the $(1, 2\nu)$ interaction of a cycle of $(6\nu-2)$ electrons the "syn"-mode is predominant for even ν, while for odd ν "anti"-mode prevails, [***Rule 5***]

in accordance with experience. Namely, the *trans*-1, 2-addition belongs to the case of $\nu=1$, 1, 4-addition $(\nu=2)$ *syn*, and 1, 6-addition $(\nu=3)$ *anti*.

The *trans*-mode stereoselection in the elimination to produce an unsaturated bond also seems to have a concern with the relation discussed above $(\nu=1)$, although it has been known that for this sort of stereoselection the orienting effect of the nucleophilic group to be repelled is important.13a)

The nucleophilic replacement with the allylic rearrangement (the S_N2' reaction) is one of

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26) a) For the σ MO of conjugated systems, see K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, This Bulletin, **35**, 38 (1962); J. A. Pople and D. P. Santry, *Mol. Phys.*, **9**, 301 (1965); b) also refer to the following papers for saturated systems: C. Sandorfy, *Can. J. Chem.*, **33**, 1337 (1955); H. Yoshizumi, *Trans. Faraday Soc.*, **53**, 125 (1957); Ref. 6; K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **35**, 1475 (1962); T. Yonezawa, H. Kato, H. Saito and K. Fukui, *ibid.*, **35**, 1814 (1962); K. Morokuma, K. Fukui, T. Yonezawa and H. Kato, *ibid.*, **36**, 47 (1963); H. Kato, K. Fukui and T. Yonezawa, *ibid.*, **38**, 189 (1965); J. A. Pople and D. P. Santry, *Mol. Phys.*, **7**, 269 (1964); **9**, 311 (1965).

1, 3-noncyclointeractions, known to proceed stereospecifically in the *cis* fashion.[27] This belongs to the case $k=3$ ($n=3k-2=7$, $m=3$) in Eq. (4). If we put $k=2\mu+1$ in Eq. (4), we obtain from *Theorem A* the following general rule:

In the (1, 2μ+1) interaction of a cycle of 6μ electrons the "syn"-mode is predominant for odd μ and the "anti"-mode is preferable for even μ; and in the cycle containing (6μ+2) electrons vice versa. [***Rule 6***]

These selection rules will supply means to the prediction of favorable steric courses only under the supposition that any other factors do not play a more determinative part. The cyclic intermediate formation in "noncyclic" addition is no doubt one of such influencing factors, although such cyclic intermediates themselves are the system governed by the selection rules mentioned in the preceding sections. In the cases where more than two electrocycles participate, the most determinative one will control the steric course of the reaction.

Aromaticity and the Hückel's 4*n*+2 Rule

Aromatic sextet has long been a subject in organic chemistry. A satisfying explanation to this problem was presented by Hückel, leading to a rule, referred to as the $4n+2$ rule.[28] A quantum mechanical approach to this rule was made by applying the perturbation theory.[29] Heilbronner proposed an interesting idea concerning on the conformations of annulenes that the higher members of them with $4n$ electrons might be twisted once to give a Möbius ring.[30] *Theorem A* is intimately connected to the theory of aromaticity and may supply, in rather qualitative sense, a physical basis of the $4n+2$ rule. The rule obtained is as follows:

The monocyclic conjugated system which contains 2mπ electrons prefers the Hückel perimeter (with negative β_{1n}) if m is odd, (while the Möbius perimeter (with positive β_{1n}) prevails if m is even). [***Rule 7***]

The effect of the steric repulsion as well as the change in β's due to the twist[30] should be also taken into consideration in discussing the possibility of Möbius-type conformations, especially in case of the small ring-conjugated polyenes.[13d]

The Relation to the Perturbation Treatment

It is well known that the energy change due to the introduction of a small change of resonance integrals into the secular determinant in the Hückel MO treatment of conjugated systems is represented in terms of the bond order. The essential feature is not altered also in the treatment of σ electron systems. The one-electron energies and the one-electron wave functions for $\Delta^{(0)}(\varepsilon)$ are designated as $\varepsilon_i^{(0)}$ and $\psi_i^{(0)}$ respectively. The MO's are represented by the linear combination of AO's, ϕ_1, $\phi_2, \dots, \phi_n$, such that

$$\psi_i^{(0)} = \sum_r C_{ir}\phi_r$$

The introduction of β_{1n} into $\Delta^{(0)}(\varepsilon)$ makes the energy increase as much as

$$\Delta E = 4\sum_{i=1}^{m} C_{i1}C_{in}\beta_{1n} = 2P_{1n}\beta_{1n}$$

where the quantity P_{1n} is the "bond order" of the virtual bond considered between carbons 1 and n by way of ϕ_1 and ϕ_n. When it is positive, a negative β_{1n} is favorable, while a positive β_{1n} is advantageous for negative P_{1n}. This quantity was called by the present authors the "overlap stabilization" and was applied to the stereoselectivity in the ring-closure of polyenes.[4,9,12] A similar treatment was made to discuss the transition state configuration in some electrocyclic interactions.[13c]

The present paper includes the perturbation treatment as a special case of small β_{1n}'s and therefore falls on an extension of the perturbation treatment to the region of appreciably large interactions, exhibiting a wider availability in discussing similar problems.

The Relation to the Orbital Symmetry

The symmetry property of MO's for linear polyenes is well established. The $(2k+1)$th MO is symmetric (S) and the $2k$th MO is antisymmetric (A) with respect to the center of the molecule both in even and in odd pπ AO systems. In an S-MO the AO coefficients of two termini have the same sign, while in an A-MO they have different signs.

In the more general systems presented above which are composed of a chain of any sort of AO's, similar relations are shown to exist. Namely, it follows from the relation of AO coefficients and the secular determinant that[31]

$$C_{i1}C_{in} = (-1)^n \beta_{12}\beta_{23}\cdots\beta_{n-1n}/\Delta'(\varepsilon_i) \begin{cases} >0 & \text{(for odd } i\text{)} \\ <0 & \text{(for even } i\text{)} \end{cases}$$

since β's are all negative and the sign of $\Delta'(\varepsilon_i)$ agrees with that of $(-1)^i$. Therefore the $(2k+1)$th MO is quasi-symmetric (qS) and the $2k$th MO is quasi-antisymmetric (qA). The HO ($i=m$) is qS

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27) H. L. Goering, T. D. Nevitt and E. F. Silversmith, *J. Am. Chem. Soc.*, **77**, 4042 (1955); G. Stork and W. N. White, *ibid.*, **78**, 4609 (1956). One of the present authors (K. F.) thanks to Professor Stork for his private communication on this reaction.

28) E. Hückel, *Z. Physik*, **70**, 204 (1931); **76**, 628 (1932).

29) K. Fukui, A. Imamura, T. Yonezawa and C. Nagata, This Bulletin, **33**, 1591 (1960).

30) E. Heilbronner, *Tetrahedron Letters*, **1964**, 1923.

31) K. Fukui, C. Nagata, T. Yonezawa, H. Kato and K. Morokuma, *J. Chem. Phys.*, **31**, 287 (1959).

if m is odd, and qA if m is even. Hence, even though the following description might be adopted in place of *Theorem A,* the result of prediction would never change:

"If the highest occupied molecular orbital is symmetric (or quasi-symmetric) the interaction with negative β_{1n} will dominate, while if it is antisymmetric (or quasi-antisymmetric) the interaction with positive β_{1n} will be prevalent."

This might be nothing but the reason why Woodward-Hoffmann's discussion[2] by means of the symmetry consideration of HO MO only was able to succeed. The physical basis underlying their interpretation is thus given by *Theorem A.*

The Odd-Electron Systems and Excited-State Reactions

Mainly by the mathematical reason the discussion disclosed above was limited to the ground-state reaction of even-electron systems. However, the principle to discuss the selection of steric courses in odd-electron systems or for excited-state reactions is completely the same as the former cases, if we employ numerical computations. Namely, we are always able to compare $E^{(N)}$ and $E^{(P)}$ by solving numerically the secular determinant, or to calculate P_{1n} to determine the favorable sign of β_{1n} by way of the perturbation procedure. Numerical computations along the former line was made by Zimmerman on the problem of ring-closure of linear olefins[32] and both numerical calculations and, in some special cases, analytical treatments were made for discussing the stereoselection of excited-state reactions along the latter line by the present authors.[4,9,12] The well-known relation that the virtual bond order between two AO's which belong to the same group (starred or unstarred) of an alternant hydrocarbon system is zero suggests that the formation of an odd-membered electrocycle from a chain composed of AO's of equal Coulomb integrals gives the same values to $E^{(N)}$ and $E^{(P)}$. This can be also shown from the secular equations similar to Eq. (1-b) corresponding to $\Delta^{(N)}(\varepsilon)$ and $\Delta^{(P)}(\varepsilon)$. Although changes in the Coulomb integrals may cause the distinction between the energies of the two steric courses, the difference may be rather small in comparison with the one obtained for even-membered electrocycles.

In general, the prediction of the favorable steric courses in a similar fashion may be possible for any kind of reactions accompanied with stereoselection by solving the secular equations corresponding to the two steric courses, provided the comparison of the two cases (γ and $-\gamma$) is effectual.

$$\Delta(\varepsilon) = \begin{vmatrix} \boxed{\Delta_1(\varepsilon)} & \gamma_{12} & & & \pm\gamma_{1n} \\ \gamma_{12} & \boxed{\Delta_2(\varepsilon)} & \gamma_{23} & & \\ & \gamma_{23} & \ddots & & \\ & & & \ddots & \gamma_{n-1\,n} \\ \pm\gamma_{1n} & & & \gamma_{n-1} & \boxed{\Delta_n(\varepsilon)} \end{vmatrix}$$

The selection rules disclosed above may present the method more simple and with more physical foundation, in comparison with the former ones, to predict the favorable steric course of a given reaction. Anyhow, we do not need the solution of secular equation or any MO properties, *e. g.* HO symmetry to discuss the steric course of a ring-closure reaction, or MO energies of the initial and the final systems to draw a correlation diagram, even when we employ the rules most rigorously ascertaining the proposition leading to the *Theorem A.*

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32) H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564, 1566 (1966).