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An MO-Theoretical Illumination for the Principle of Stereoselection

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The principle of the stereoselection in organic chemistry has been discussed from the point of view of the molecular orbital theory. The stereoselectivity in the stereospecific ring-closure of conjugated polyenes and the stereospecific ring-cleavage of unsaturated carbon cycles, *trans*-1,2-noncycloadditions, *cis*-1,2-additions and *cis*-1,3-dipolar additions have been accounted for with a qualitative generalization. In many cases the symmetry relationship of certain particular molecular orbitals ("frontier orbitals") plays a conspicuously significant role in the steric control of stereochemical processes. This may be put in contrast with the role of the frontier electron density in the orientation process in organic reactions.

The purpose of the present paper is to make an attempt to furnish organic stereochemistry with a theoretical strategy. In view of the multifariousness noticed in the accumulation of recent stereochemical studies, it is hoped that a guiding principle to unravel the entanglements involved will appear. In order to be of practical applicability, such a guiding principle must first of all possess generality and simplicity. Therefore, the molecular orbital (MO) theory seems suitable.

The recent experimental information on the stereoselectivity in several cyclic reactions of unsaturated compounds[1] has been an incentive to start an MO-theoretical attack.[2-4] All these papers pointed out the importance of the symmetry of particular MO's in discussing the problem in question. These particular MO's were the highest-occupied MO (HO) and the lowest vacant MO (LV) of the ground state molecule. Oosterhoff[2] has suggested that the difference in stereochemical behavior between thermal and photo-induced reactions may be attributed to the symmetry characteristics of HO and LV. The important role of HO and LV (the frontier orbitals) in the course of the chemical interaction of organic compounds was early well established in the frontier electron theory,[5,6] and the symmetry of the frontier orbitals was also duly employed for the elucidation of Diels-Alder reactivity.[7]

However, it should be noted that the discrimination of the frontier orbitals from the other MO's should be based upon a proper comprehension of the theoretical grounds. Woodward and Hoffmann[3] discussed, in their elegant generalization of the problem of stereoselectivity, the ring-closure of conjugated olefins, and suggested that the steric course should be determined by the symmetry of HO only. However, this is evidently an "over-discrimination" of HO, since the overlap stabilization between two π atomic orbitals in a single conjugated system should be evaluated as the sum of the contributions from all occupied MO's.[4] The mere coincidence of the results does not justify such improper or less authentic neglect of the other MO's.

The basic idea, used throughout the present paper, for discussing the steric course in a consistent manner is to determine, from the MO perturbation calculation of the energy change of interaction, the direction of the overlap stabilization between interacting atomic orbitals; this will lead to the most likely correct steric course. The details will be illustrated by examples.

The Ring-Closure of Conjugated Polyenes.—Consider a linear conjugated polyene with k π electrons. So-called Hückel MO's of the simplest type are given by[8]:

$$\phi_j=\sum_{r=1}^{k} C_r{}^j\phi_r=\left(\frac{2}{k+1}\right)^{1/2}\sum_{r=1}^{k}\phi_r\sin\frac{jr\pi}{k+1}$$

$$(j=1,\ 2,\cdots k)$$

where ϕ_r is rth carbon $2\text{p}\pi$ atomic orbital (AO), and $C_r{}^j$ is the coefficient of ϕ_r in jth MO. These MO's are obtained by solving the usual secular equations, which yield the secular determinant:

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[1] a) E. Havinga, R. J. de Kock and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); b) E. Havinga and J. L. M. A. Schlatmann, ibid., **16**, 146 (1961); c) G. J. Fonken, *Tetrahedron Letters*, **1962**, 549; d) R. E. K. Winter, ibid., No. 17, 1207 (1965).

[2] L. J. Oosterhoff, private suggestion to the authors of the paper cited in Ref. 1(b), a suggestion quoted on p. 151 of that paper.

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

[4] K. Fukui, *Tetrahedron Letters*, No. 24, 2009 (1965).

[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).

[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. Yonezawz, ibid., **34**, 1111 (1961).

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

$$\Delta(\varepsilon)=\begin{vmatrix} -\varepsilon & \beta & \cdots & 0 & 0 \\ \beta & -\varepsilon & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & \cdots & -\varepsilon & \beta \\ 0 & 0 & \cdots & \beta & -\varepsilon \end{vmatrix} = \beta^k \frac{\sin(k+1)\theta}{\sin\theta} \quad (1)$$

$$(\varepsilon = -2\beta\cos\theta)$$

(k rows and k columns)

where the zero point of the energy, ε, is taken as equal to the Coulomb integral of carbon $2\mathrm{p}\pi$ AO, β being the resonance integral between two adjacent $2\mathrm{p}\pi$ AO's.

The change in the π-electronic energy in the case of the overlapping of the first and kth AO's is clearly approximated by:

$$\Delta E = 2\sum_{j=1}^{k} \nu_j C_1{}^j C_k{}^j \gamma = 2P_{1k}\gamma \quad (2)$$

by the first-order perturbation calculation, where ν_j is the number of π electrons occupying the jth MO, while γ is the resonance integral between ϕ_1 and ϕ_k in the case of the σ-like overlapping of these two orbitals in the distorted π electron system. The sign of γ is obvious, as is indicated by the scheme of Fig. 1.

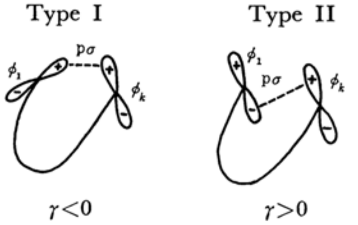

Fig. 1. Two types of overlap stabilization.

The quantity, P_{1k}, has the same form as that defined as the well-known "bond order," but in the present case it serves to determine the stability due to the overlapping of two π orbitals; it may thus appropriately be tentatively named the "overlap stabilization." If this quantity is positive, the overlapping of Type I is preferred, while if it is negative, Type II is more preferable, in the case of cyclization.

For the ground state of linear conjugated polyenes, P_{1k} is known to be easily expressed in an integral representation[9] as:

$$P_{1k} = \frac{\beta^{k-1}}{\pi}\int_{-\infty}^{+\infty}\frac{\mathrm{d}y}{\Delta(iy)} = 4(-1)^{k/2+1}\frac{1}{\pi} \times \int_0^{\infty}\frac{\cosh^2\varphi\,\mathrm{d}\varphi}{\cosh(k+1)\varphi} \quad (3)$$

$$(y = -2\beta\sinh\varphi)$$

which is immediately convertible into the form:

$$P_{1k} = \frac{(-1)^{k/2+1}}{k+1}\left(1+\frac{1}{\cos(\pi/(k+1))}\right) \quad (4)$$

Therefore, it follows clearly that, when $k=4m+2$, P_{1k} is positive, so that the cyclization of Type I occurs, while when $k=4m$, P_{1k} is negative, so that a Type II cyclization results; this is consistent with experimental facts in the case of $k=6$.[1]

This relationship is not limited to the cyclization due to the bonding between two termini. It is likewise very easy to prove mathematically that P_{rs} is positive in the cyclization forming a $(4m+2)$-membered ring, leading to a Type I course, whereas the cyclization forming a $4m$-membered ring would follow a Type II course. The discussion of this sort has already been made by numerical calculations more comprehensively and also more elaborately in connection with the theory of aromaticity by Fukui et al.[10]

A reverse relation holds in the first excited state, in which we assume the jumping of one π electron of HO into LV. In the present simple treatment, both the triplet and the singlet states will be discussed in terms of the same theoretical quantity. The overlap stabilization, which is in this case denoted by $P_{1k}{}^*$, is easily represented by:

$$P_{1k}{}^* = \frac{(-1)^{k/2}}{k+1}\,\frac{\cos(\pi/(k+1))+1}{\cos(\pi/(k+1))} \times \left(2\cos\frac{\pi}{k+1}-1\right) \quad (5)$$

Therefore, it is positive when $k=4m$, and negative when $k=4m+2$, provided $k\geqq 4$. Photo-induced cyclizations are known experimentally to take place by the Type II course when $k=6$.[1]

The steroselection in polyene cyclization, whether Type I or Type II, may thus be understood to be governed by the following rule:

	Thermal reaction	Photo-induced reaction
$k=4m$	Type II	Type I
$k=4m+2$	Type I	Type II

The steric courses, Type I and Type II, were named by Woodward and Hoffmann[3] "disrotatory" and "conrotatory" processes respectively, in their first generalization of this interesting cyclic conversion.

The Ring-Opening of Cyclic Olefins.—The reverse process to the above-mentioned cyclization have also been studied and found to follow the same stereoselection rule;[1] these reactions in two opposite directions were explained *en bloc* by Woodward and Hoffmann by emphasizing the symmetry of HO and LV.[3] This sort of ring-opening reaction is, however, supposed to

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[8] See, for instance, A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961), p. 50.

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

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

be governed essentially by a sigma-pi interaction between a part of the π-electron system and the σ bond to be broken. A more plausible, separate explanation must be given on the basis of the direction of stabilization in this sigma-pi interaction.

The electrons to be taken into account are two σ-bonding electrons in the a—b bond to be broken and (k-2) π electrons in the conjugated part of the ring, r-t-s in Fig. 2.

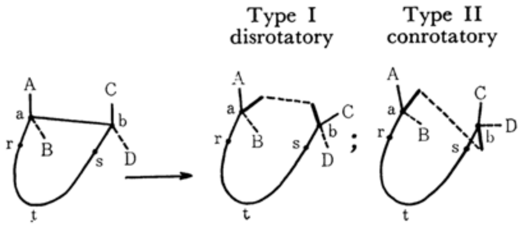


Fig. 2. Two types of interaction in the ring-cleavage.

The open-chain polyene to be produced has k π electrons. At the initial stage, the sigma and pi parts evidently have no appreciable interconjugation. As soon as the ring-cleavage begins to proceed, however, a π-like conjugation will take place between each of the two "incipient" orbitals appearing at the carbon atoms, a and b, and each end of the conjugated part, r-t-s.

The components of the two incipient orbitals perpendicular to the plane of the conjugated part are parallel and antiparallel to each other in the interactions of Type I and Type II respectively.[11]

The change in the energy of the system, ΔE, may be evaluated most simply by a perturbation treatment as a second-order term, if we regard the above-mentioned π-like conjugation as a small perturbation. The result is[12]:

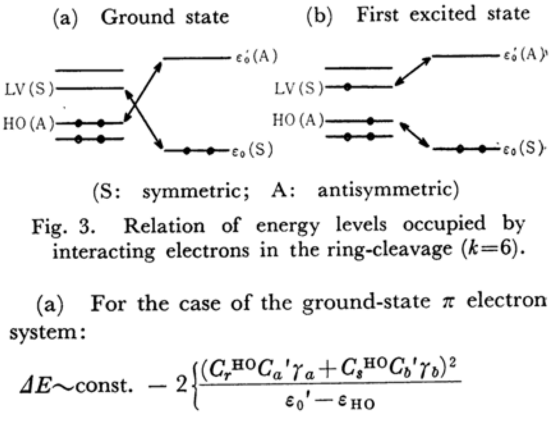
$$\Delta E = \text{const.} + \left\{\sum_j \nu_j \frac{(C_r{}^j C_a{}'\gamma_a + C_s{}^j C_b{}'\gamma_b)^2}{\varepsilon_j - \varepsilon_0{}'} - \sum_j (2-\nu_j) \frac{C_r{}^j C_a\gamma_a + C_s{}^j C_b\gamma_b)^2}{\varepsilon_j - \varepsilon_0}\right\} + 0(\gamma^4) \quad (6)$$

where (1) ε_0 and $\varepsilon_0{}'$ are the energies of a—b bonding and antibonding orbitals, which are denoted by $\chi = C_a\varphi_a + C_b\varphi_b$ and $\chi = C_a{}'\varphi_a + C_b{}'\varphi_b$ respectively, in which φ_a and φ_b are the initially-existing, carbon sp^3 hybridized orbitals of the a—b bond: (2) ε_j is the energy of the jth MO of the $(k-2)$ π electron system, which is written as $\varphi_j = \sum_t C_t{}^j \phi_t$, where ϕ_t is tth atomic orbital; (3) ν_j is the number of electrons occupying the jth MO; (4) γ_a and γ_b are the "resonance" integrals (although this terminology may be inadequate for their positive value) between each of the two incipient orbitals appearing at the carbon atoms, a and b, with the adjacent 2pπ orbital at the carbon atoms, r or s; and (5) the term const. signifies the term which is involved almost always in both Type I and Type II interactions.

As may clearly be understood from the illustration, the sign, γ_a and γ_b which favors the minimization of ΔE will control the direction of the steric course. The same sign of γ_a and γ_b means the interaction of Type I, whereas Type II corresponds to γ_a and γ_b with opposite signs.

In the light of our knowledge about the parameters used in the MO treatment of σ electron systems developed by Fukui et al.,[13] the chief contributing terms on the right side of Eq. 6 are demonstrated to be those associated with HO and LV. Figure 3 indicates an example for the case of $k=6$. The charge transfer interaction of an HO electron with the a—b antibonding orbital will drive the σ bond into cleavage so as to cause a narrowing of the separation of $\varepsilon_0{}'$ and ε_0, resulting in a stronger and stronger interaction.

If we take into account, for the sake of simplicity, only the most dominant term in each summation of the right side, Eq. 6 may be reduced to the following form:


(a) Ground state (b) First excited state

(S: symmetric; A: antisymmetric)

Fig. 3. Relation of energy levels occupied by interacting electrons in the ring-cleavage (k=6).

(a) For the case of the ground-state π electron system:

$$\Delta E \sim \text{const.} - 2\left\{\frac{(C_r{}^{\mathrm{HO}} C_a{}'\gamma_a + C_s{}^{\mathrm{HO}} C_b{}'\gamma_b)^2}{\varepsilon_0{}' - \varepsilon_{\mathrm{HO}}} + \frac{(C_r{}^{\mathrm{LV}} C_a\gamma_a + C_s{}^{\mathrm{LV}} C_b\gamma_b)^2}{\varepsilon_{\mathrm{LV}} - \varepsilon_0}\right. \quad (7)$$

(b) For the case of the first-excited-state π electron system:

$$\Delta E \sim \text{const.} - \left\{\frac{(C_r{}^{\mathrm{LV}} C_a{}'\gamma_a + C_s{}^{\mathrm{LV}} C_b{}'\gamma_b)^2}{\varepsilon_0{}' - \varepsilon_{\mathrm{LV}}}\right\} + \left.\frac{(C_r{}^{\mathrm{HO}} C_a\gamma_a + C_s{}^{\mathrm{HO}} C_b\gamma_b)^2}{\varepsilon_{\mathrm{HO}} - \varepsilon_0}\right\} \quad (8)$$

where the super- and subscript HO's and LV's signify the highest occupied and the lowest vacant MO's in the ground state.

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[11] The description of line 9, page 3 of Ref. 4 should be reversed with regard to "conrotatory" and "disrotatory" processes.

[12] K. Fukui, C. Nagata, T. Yonezawa, H. Kato and K. Morokuma, *J. Chem. Phys.*, **31**, 287 (1959); also see Ref. 7.

[13] K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **33**, 1198 (1960); also see Ref. 6a).

The orbital symmetry[14] of HO is antisymmetric (A) when $k-2=4m$, and symmetric (S) when $k-2=4m-2$, while LV is S when $k-2=4m$ and A when $k-2=4m-2$. The symmetry of the ε_0 level is, of course, S, and ε_0' is A. Therefore, in order for ΔE to be minimized,

(a) For the ground state: γ_a and γ_b should have opposite signs when $k=4m$, and the same sign when $k=4m+2$;

(b) For the first excited state: γ_a and γ_b should have the same sign when $k=4m$, and opposite signs when $k=4m+2$.

Hence we are led to the following stereoselection rule, which has already been pointed out by Woodward and Hoffmann,[3] in accordance with the experimental results[1,3]:

	Thermal reaction	Photo-induced reaction
$k=4m$	Type II, conrotatory	Type I, disrotatory
$k=4m+2$	Type I, disrotatory	Type II, conrotatory

It should be noted that the orbital symmetry of HO and LV plays an essential role in determining the steric course. The discrimination of the "frontier orbitals" is thus justified in this case. This may be put in contrast with the fact that the "frontier electron density" plays an important role in determining the intramolecular orientation.

The *trans*-1, 2-Noncycloadditions. — The predominance of noncyclic *trans*-1, 2-additions in olefins has been well established in many experimental results in both ionic and radical additions.[15] It therefore appears appropriate to discuss the problem by dividing it into two items:

i) In the case in which the attacking reagent, XY, is used in highly dissociative conditions, the *trans*-selectivity may be attributed to the well-discussed symmetrical adduct of X to the ethylenic bond, which is supposed to be formed in the first stage.[16] No further, new way of explanation seems to be necessary in such a case, except a consideration of the orbital symmetry relation of X and the ethylenic bond which creates the possibility of forming such a symmetrical adduct. This point will be discussed in detail in the next section, on *cis*-1, 2-additions.

ii) For the case of almost simultaneous noncyclic additions, however, there seems to be a more plausible explanation than the existing ones if we consider the relationship of the orbital symmetry[14] between the reagent and the olefin. The direction of the approach of the reagent is supposed to be perpendicular to the plane of the ethylenic molecule.[17] The characteristic feature of the noncyclic addition of XY may be specified as the unfavorable square-form interaction of XY with the C-C double bond in the course of approach. For instance, a non-dissociated Br_2 molecule does not have any MO with a symmetry suitable for entering into square-form conjugation with ethylenic π orbitals. Its lowest vacant MO is antisymmetric, so that the interaction with ethylenic π electrons could be facilitated only by orbital overlapping in opposite directions at two terminals, as is illustrated in Fig. 4.[18] The formulation of this relation is in essence identical to the treatment of Eqs. 1—4 (Fig. 4(a)); it is also possible to apply Eq. 7 for the same purpose (Fig. 4(b)). The electron transfer from the π bond to the X-Y antibonding MO will give rise to the dissociation of XY, leading to the stage indicated by (b) in Fig. 4. The explanation mentioned above may lead to a presumption of 1, 2-*cis*-noncycloaddition in the photo-excited state under suitable conditions.

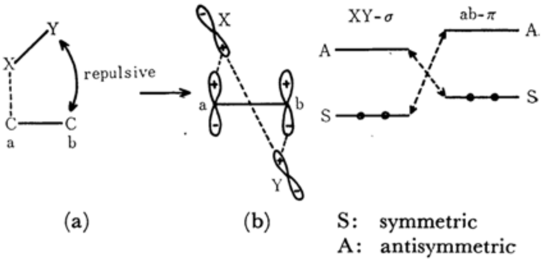

Fig. 4. The mode of initial interaction of the attacking reagent with an ethylenic bond.

No experimental results seem to be available for the stereoselectivity in noncyclic additions more distant than to 1, 2-positions of conjugated

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[14] More generally, it is, of course, not required to be exactly symmetric or antisymmetric. Only the relation between the signs of the coefficients in Eq. 7 is essential.

[15] See, for instance, a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt & Co., New York (1959), p. 514, 733 ff.; b) B. A. Bohm and P. I. Abell, *Chem. Revs.*, **62**, 599 (1962).

[16] Evidence has been given early for the two-step additions (A. W. Francis, *J. Am. Chem. Soc.*, **47**, 2340 (1925)).

[17] The opinion of Bader et al. (A. R. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 5621 (1957)) that the approach of the methyl radical in the additions to olefins was along the double bond axis was later corrected (M. Matsuoka and H. Szwarc, ibid., **83**, (1961)).

[18] The author does not intend to reject the assumption of a bridged intermediate like the cyclic bromonium ion. Depending on conditions, we might have to take into account the interaction of X and C_b in addition to that of X and C_a. The essential point of the present discussion lies in pointing out the possibility of a mechanism with which we need no further, too-far-fetched views.

[19] It should be noted that the terms "1, 4-" or "1, 6-addition" are used here in a purely mechanistic sense. They do not include a reaction composed of a series of successive processes. Hence, it is desirable that the starting conjugated polyene have a specific favorable structure: i. e., the *cis*-butadiene form for 1, 4-addition and the *cis-cis*-hexatriene form for 1, 6-addition. Also, we have to avoid confusion due to the term "*trans*-1, 4-addition," by which e. g., the following reaction is meant:

Butadiene + Cl_2 → *trans*-1, 2-Bischloromethyl ethylene

The term "*cis*-1, 4-addition" employed above signifies an addition of XY by the attack of X and Y from the same side of the molecular plane of conjugation.

olefins. Discussions similar to those for 1, 2-additions are possible if we make a consideration analogous to that of Fig. 4. The conclusion is that 1, 4-noncycloaddition should be *cis*, 1, 6-, *trans*, and so forth.[19]

The *cis*-1,2-Additions.—The *cis*-1,2-addition to an ethylenic bond can take place when the reagent has a vacant MO (of course, preferably LV, for the reason understood through Eq. 6), of a symmetry that is advantageous for interaction with the occupied MO of the ethylenic π bond. For this reason the reagents which have the LV orbital symmetrical with respect to the middle of their two reaction centers are qualified as having a possibility of *cis*-addition. The formation of the intermediates considered in the two-step mechanism of stereospecific *trans*-additions, such as the bridged cation of protonated ethylene, may clearly be understood by the fact that the reagent ion has a symmetrical LV orbital. The other reagents which can satisfy this symmetry requirement are the phenyl cation in the phenonium ion,[20] the oxygen atom in epoxidation, carbenes in their singlet-state adducts to olefins,[21] the permanganate ion,[22] osmium tetroxide,[23] dienes in the Diels-Alder addition, and so on. Among these the symmetry of LV in various dienes has already been investigated by numerical calculations.[7] With respect to the other species, it is also easy to show by an appropriate MO treatment that their LV satisfies the symmetry conditions mentioned above.

The *cis*-1, 2-addition in hydroboration is well known. The result of an extended Hückel calculation by Kato et al. for boron compounds[24] may be useful in comprehending how borane can add to the *cis* positions. The LV of the BH_3 molecule is completely localized at the central boron $2p\pi$ AO, so that a strong charge-transfer interaction is possible with bonding π electrons of the C–C double bond (Fig. 5). As the $p\sigma$-overlapping proceeds, the bond populations of B–H sigma as well as of C_a–C_b pi are seriously reduced, so as to repel the hydrogen atom and force it to combine with the C_b carbon. Thus, a square-form interaction[25] is performed to give rise to *cis*-addition. From this explanation it is easy to realize that the hydroboration is a reaction of an electrophilic nature.

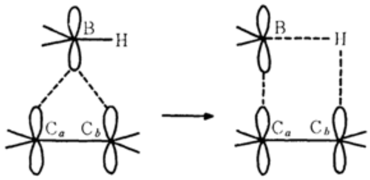

Fig. 5. The square-form interaction of BH_3 with C–C double bond.

Under these circumstances it is interesting that the easiness of the photo-induced cyclodimerization of olefins[26] in comparison with thermal reactions is also intimately connected with the symmetry relationship of HO and LV orbitals. In such cases, the *cis*-addition is geometrically desirable in order for the cyclodimerization to take place. Consequently, the orbital symmetry must be favorable for the square form interaction. As may easily be understood from the illustration in Fig. 6, in which acenaphthylene is chosen as an example, Eqs. 7 and 8 show that the square form interaction is thus facilitated in *excited-state* reactions.[27] The relation of the opposite symmetries of HO and LV in the ground state also holds as a general rule in alternant hydrocarbons, such as anthracene and pentacene, whose photodimerization has been well studied.

We have to remember that these circumstances must be similar in the case of the strong charge-transfer interaction in which one electron jumps from the olefin into the reagent orbital. The orbital symmetry requirement for a square-form

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20) S. Winstein, E. Grunwald and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948); D. J. Cram, ibid., **71**, 3863 (1949); as regards the MO-theory, see Ref. 8, p. 382; the LV orbital of the phenyl cation is localized at the sp^2-like sigma orbital on the attached carbon atom (K. Fukui, H. Kato and T. Yonezawa, This Bulletin, **35**, 1475 (1962); K. Morokuma, S. Ohnishi, T. Masuda and K. Fukui, ibid., **36**, 1228 (1963)), which is, therefore, symmetrical with respect to the bisecting plane of the C-C double bond in the phenonium cation.

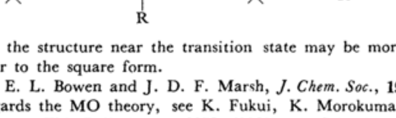
21) P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 3409, 5430 (1956).

22) J. Boeseken, *Rec. Trav. Chim.*, **40**, 553 (1921); **47**, 683 (1928); K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957); concerning the $MnO_4{}^{2-}$ cis-addition, see J. S. F. Pode and W. A. Waters, *J. Chem. Soc.*, **1956**, 717.

23) R. Criegee, B. Marchand and H. Wannowius, *Ann.*, **522**, 75 (1936); **550**, 99 (1938).

24) H. Kato, T. Yonezawa and K. Fukui, Summary, 18th Annual Meeting of the Chemical Society of Japan (1965) (in Japanese), p. 440; H. Kato, K. Yamaguchi, T. Yonezawa and K. Fukui, This Bulletin, (in press).

25) Some alkyl borane compounds are known to react as a dimeric form. In such cases, the mode of interaction would resemble that of the S_N2 reaction of the halogen anion with alkyl halide.



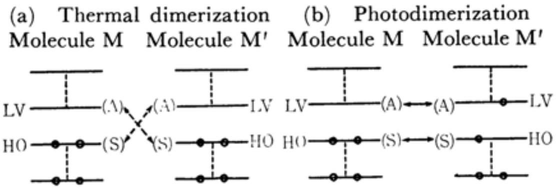
Thus, the structure near the transition state may be more or less similar to the square form.

26) E. L. Bowen and J. D. F. Marsh, *J. Chem. Soc.*, **1947**, 109; as regards the MO theory, see K. Fukui, K. Morokuma and T. Yonezawa, This Bulletin, **34**, 1178 (1960); A Schönberg and A. Mustafa, *J. Chem. Soc.*, **1948**, 2126; A. Mustafa, *Chem. Revs.*, **51**, 1 (1952); O_2 *cis*-addition is also described in G. O. Schenck and K. Ziegler, *Naturwissenschaften*, **32**, 157 (1944).

27) The perturbation theory is modified in case b where the second-order term in Eq. 8 should be replaced by the first-order term,

$$\{|C_r^{\mathrm{LV}}C_{r'}^{\mathrm{LV}}\gamma_a+C_s^{\mathrm{LV}}C_{s'}^{\mathrm{LV}}\gamma_b|^2 \\ +|C_r^{\mathrm{HO}}C_{r'}^{\mathrm{HO}}\gamma_a+C_s^{\mathrm{HO}}C_{s'}^{\mathrm{HO}}\gamma_b|^2\}^{1/2}$$

where rs and $r's'$ are the two pairs of the reaction centers of the M and M′ molecules respectively.



(S and A mean respectively symmetric and anti-symmetric with respect to the symmetry plane.)

Fig. 6. The symmetry relationship of OH and LV of acenaphthylene in connection with dimerization reactivity.

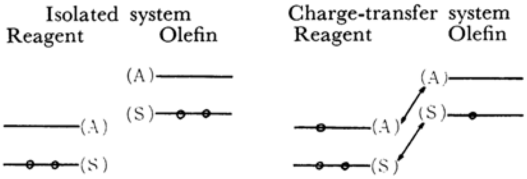


Fig. 7. The relation of orbital symmetry with charge-transfer interaction.

interaction, which the isolated systems are unable to fulfil, will then be satisfied. An instance for such a case is indicated in Fig. 7.

Here we should make reference to the recent finding in the field of polymerization chemistry that several stereospecific ionic polymerizations are thought to occur through successive *cis*-openings of the monomer double bond.[28] An interpretation of this fact has been given from a purely sterical point of view.[29] However, in view of the reasons above set forth it seems likely that the orbital symmetry of the system, including the growing chain end and the counter ion or catalyst part, should be examined after reliable information on the catalyst structure has been obtained. Also, whether or not circumstances like those in Fig. 7 might be realized in these cases is a matter of deep interest. We hope to re-examine the working mechanism of stereomodifiers in stereospecific vinyl polymerizations from the point of view of orbital symmetry. In addition, we may have to consider the participation of the neighboring group in the activated complex influencing the orbital symmetry when the monomer has any conspicuously influential group in the molecule. On this point, we shall present a report in the near future.

The 1, 3-Dipolar Additions.—The addition of 1, 3-dipoles to olefins occurs at positions *cis* with respect to both reactants.[30] Although various species of 1, 3-dipoles are known, the essential structure under reactive conditions may be characterized by the conjugated system which is indicated in Fig. 8.

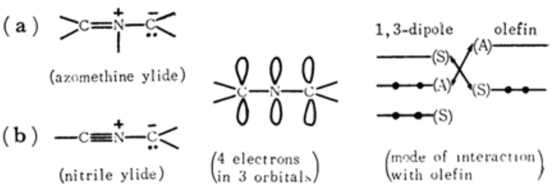


Fig. 8. The schematic representation of 1, 3-dipoles.

The LV orbital of 1, 3-dipoles is symmetric with respect to the two side AO's, so *cis*-interaction with olefin may be made favorable.

Other interesting problems, like the *trans*-1, 2-additions and the *endo*- and *exo*-additions in Diels-Alder reactions, as well as the stable conformations of organic molecular skeletons and the problem of *trans*-β-elimination, are left untouched in the present paper; they will be considered in several separate papers later.

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