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Orbital Symmetry Control in the Interaction of Three Systems

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Some perturbation equations for calculating the interaction energy of three independent systems have been derived in the frame of the simple Hückel MO approximation. The results of the numerical calculation of some typical interactions of three conjugated systems are presented in order to show the effect of the orbital symmerty upon the interaction energy. The role of the d orbitals of transition-metal catalysis olefin metathesis is examined.

Some important information on the nature of chemical interactions in unimolecular reactions has been derived by considering the conjugation between two parts of a molecule, using a partitioning technique.[1] To discuss the stability of a molecular system by means of the conjugation stabilization of the interaction of three or four parts of a molecule properly partitioned seems to be promising for the purpose of illuminating the essential features of complicated chemical reactions.[2] Recently, Goldstein and Hoffmann extended the concept of aromaticity to some multi-centric interactions of more than three systems.[3] They discussed the interaction of three systems by regarding it as two successive cyclic interactions of two systems, based upon the concept of orbital interaction between the highest occupied (HO) molecular orbital (MO) of one system and the lowest unoccupied (LU) MO of the other system. The applicability of the theory of the HOMO–LUMO interaction to predicting the favorable reaction paths has been verified in numerous cases.[1,4] Therefore, the generalization of aromaticity by Goldstein and Hoffmann may be accepted. Since such multi-centric interactions of three systems are highly related to the catalytic action of transition-metal complexes, we would like to present some simple formulae for the simultaneous cyclic interactions of three independent systems. These formulae will be useful for a semi-quantitative comparison of various types of interactions of three systems.

Interaction Energy

Longicyclic Interactions. First, let us consider the longicyclic interaction[3] of three systems, A, B,

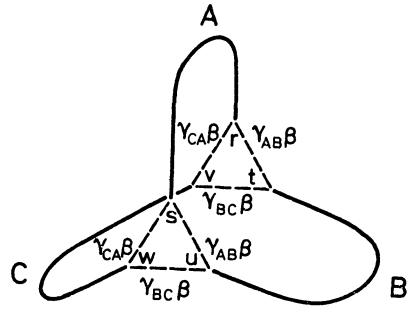


Fig. 1. Longicyclic interaction of three systems A, B and C.

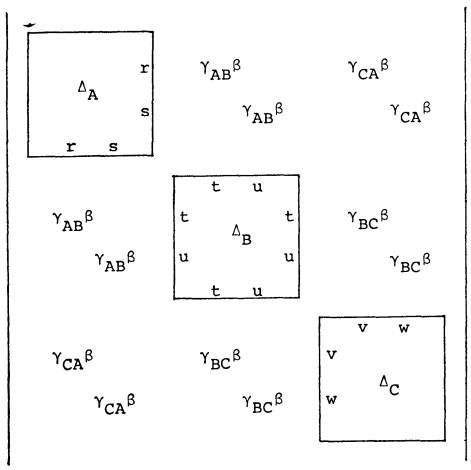
1) a) K. Fukui and H. Fujimoto, "Mechanisms of Molecular Migrations," B. S. Thyagarajan, Ed., Interscience, New York, N. Y. (1969), pp. 117—190. b) K. Fukui, *Accounts Chem. Res.*, **4**, 57 (1971).

2) a) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967). b) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971). c) R. Hoffmann and W. D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971). d) L. A. Paquette, M. R. Short, and J. F. Kelly, *ibid.*, **93**, 7179 (1971).

3) M. J. Goldstein and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 6193 (1971).

4) a) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology," P. -O. Löwdin and B. Pullman, Eds., Academic Press, New York, N. Y. (1964), pp. 513—537. b) K. Fukui, "Modern Quantum Chemistry. Istanbul Lectures, Part I," O. Sinanoğlu, Ed., Academic Press, New York, N. Y. (1965), pp. 49—84. c) K. Fukui, "Sigma Molecular Orbital Theory," O. Sinanoğlu and K. B. Wiberg, Eds., Yale University Press, New Haven, Conn. (1970), pp. 121—129. d) K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970). e) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968). f) L. Salem, *ibid.*, **90**, 543, 553 (1968). g) K. Fukui and H. Fujimoto, This Bulletin, **41**, 1989 (1968). h) K. Fukui and H. Fujimoto, *ibid.*, **42**, 3399 (1969). i) H. Fujimoto, S. Yamabe, and K. Fukui, *ibid.*, **44**, 2936 (1971). j) R. G. Pearson, *Theor. Chim. Acta*, **16**, 107 (1970).

and C, which are joined together at the AO's, r and s of A, t and u of B, and v and w of C. The interaction of these three systems is represented by the $\gamma_{AB}\beta$, $\gamma_{BC}\beta$, and $\gamma_{CA}\beta$, resonance integrals respectively, as is shown in Fig. 1. The simple Hückel secular equation for the system is given by:



(1)

where $\Delta_A(\varepsilon)=0$, $\Delta_B(\varepsilon)=0$, and $\Delta_C(\varepsilon)=0$ are the secular equations for the A, B, and C systems respectively in their isolated states. By expanding Eq. (1) in the power series of the interaction integrals, $\gamma\beta$, we obtain:

$$\begin{aligned}&\Delta_A\Delta_B\Delta_C\\&-(\gamma_{AB}\beta)^2\{\Delta_{Arr}\Delta_{Btt}+\Delta_{Ass}\Delta_{Buu}+2(-1)^{r+s+t+u}\Delta_{Ars}\Delta_{Btu}\}\\&-(\gamma_{BC}\beta)^2\{\Delta_{Btt}\Delta_{Cvv}+\Delta_{Buu}\Delta_{Cww}+2(-1)^{t+u+v+w}\Delta_{Btu}\Delta_{Cvw}\}\\&-(\gamma_{CA}\beta)^2\{\Delta_{Cvv}\Delta_{Arr}+\Delta_{Cww}\Delta_{Ass}+2(-1)^{v+w+r+s}\Delta_{Cvw}\Delta_{Ars}\}\\&+\cdots\cdots\\&=0\end{aligned} \tag{2}$$

where Δ_{Ars}, for instance, is the minor of Δ_A with respect to the (r, s) element of the determinant. Assuming that $|\gamma_{AB}|$, $|\gamma_{BC}|$, $|\gamma_{CA}|$ are small in comparison with unity, we may expand the eigenvalues of the perturbed secular equation in the power series of the interaction integrals.[5] When the ith root, ε_{Ai}, of the secular equation, $\Delta_A(\varepsilon)=0$, is not simultaneously the root of $\Delta_B(\varepsilon)=0$ and $\Delta_C(\varepsilon)=0$, the perturbed eigenavlue of Eq. (1) is given by:

$$\begin{aligned}\varepsilon_{Ai}' = \varepsilon_{Ai} &- \sum_j^{\text{all}} \frac{(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_u^{(j)})^2}{\varepsilon_{Bj}-\varepsilon_{Ai}}(\gamma_{AB}\beta)\\&- \sum_k^{\text{all}} \frac{(c_r^{(i)}c_v^{(k)}+c_s^{(i)}c_w^{(k)})^2}{\varepsilon_{Ck}-\varepsilon_{Ai}}(\gamma_{CA}\beta)^2+\cdots\cdots\end{aligned} \tag{3}$$

where $C_r^{(i)}$, for instance, is the coefficient of the (AO) r atomic orbital in the MO i of A, and where j and k denote the MO's of B and C respectively. Similar equations can be derived for ε_{Bj}', and ε_{Ck}', corresponding to the jth root of $\Delta_B(\varepsilon)=0$ and the kth root of $\Delta_C(\varepsilon)=0$ respectively. When all of the three systems have closed-shell electronic structures, the conjugation stabilization energy due to the interaction is given by:

$$\begin{aligned}\Delta E \cong 2\Big(\sum_i^{\text{occ}}\sum_j^{\text{uno}} - \sum_i^{\text{uno}}\sum_j^{\text{occ}}\Big)&\frac{(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_u^{(j)})^2}{\varepsilon_{Ai}-\varepsilon_{Bj}}(\gamma_{AB}\beta)^2\\+2\Big(\sum_j^{\text{occ}}\sum_k^{\text{uno}} - \sum_j^{\text{uno}}\sum_k^{\text{occ}}\Big)&\frac{(c_t^{(j)}c_v^{(k)}+c_u^{(j)}c_w^{(k)})^2}{\varepsilon_{Bj}-\varepsilon_{Ck}}(\gamma_{BC}\beta)^2\\+2\Big(\sum_k^{\text{occ}}\sum_i^{\text{uno}} - \sum_k^{\text{uno}}\sum_i^{\text{occ}}\Big)&\frac{(c_v^{(k)}c_r^{(i)}+c_w^{(k)}c_s^{(i)})^2}{\varepsilon_{Ck}-\varepsilon_{Ai}}(\gamma_{CA}\beta)^2\end{aligned} \tag{4}$$

where the $\sum^{\text{occ}}$ and $\sum^{\text{uno}}$ symbols imply the summation over all the doubly-occupied and unoccupied MO's respectively. Equation (4) indicates that, as to the second-order perturbation energy, the conjugation stabilization due to the interaction of three systems is simply given by the sum of those of the interaction between two systems. By the use of the results of calculations for cyclic interaction between two systems presented in our previous paper,[6] we obtain the results shown in Table 1. The conjugation stabilization of the cyclic syn-interaction[6] of two systems is large when the number of electrons forming a cycle is $4n+2$, while the stabilization is not large when the number of electrons is $4n$.[1,6] When A is a 4n-electron system, both B and C should be $(4n+2)$-electron systems in order to make the conjugation stabilization due to the interaction between A and B and that between A and C large. When the A system is a $(4n+2)$-electron system, the case in which both B and C are 4n-electron systems leads to a large stabilization.

Table 1. The conjugation stabilization energy in longicyclic interaction of three conjugated systems

A[a]	B[a]	C[a]	$\Delta E/\gamma^2\beta$[b]
2	2	2	0.0
4	4	4	2.147
6	6	6	2.987
2	4	4	4.293
2	2	6	1.244
2	6	6	2.239
6	4	4	4.200
4	2	2	3.578
4	2	6	4.153
4	6	6	4.480

a) 2; ethylenic, 4; butadienic, 6; hexatrienic: by the term ethylenic, for instance, is meant the employment of the π MO's of ethylene.

b) $|\gamma_{AB}|=|\gamma_{BC}|=|\gamma_{CA}|=\gamma$: hereafter β is taken always negative.

In both the cases, however, the interaction between B and C does not produce a large stabilization. In this sense, the interaction can be classified into doubly-stabilized and unstabilized cases, following the notations introduced by Goldstein and Hoffmann.[3] Equation (4) supplies us with a simpler and even more quantitative means than the step-by-step method of Goldstein and Hoffmann to discuss the cyclic interactions of three independent systems.

5) a) K. Fukui, C. Nagata, T. Yonezawa, H. Kato, and K. Morokuma, *J. Chem. Phys.*, **31**, 287 (1959). b) K. Fukui, K. Morokuma, T. Yonezawa, and C. Nagata, This Bulletin, **33**, 963 (1960),

6) K. Fukui and H. Fujimoto, *ibid.*, **39**, 2166 (1966),

When one of the three systems, say A, has a singly-occupied MO, 0, the following additional term appears:

$$+\left(\sum_{j}^{\text{uno}}-\sum_{j}^{\text{occ}}\right)\frac{(c_r^{(0)}c_t^{(j)}+c_s^{(0)}c_u^{(j)})^2}{\varepsilon_{A0}-\varepsilon_{Bj}}(\gamma_{AB}\beta)^2$$
$$+\left(\sum_{k}^{\text{uno}}-\sum_{k}^{\text{occ}}\right)\frac{(c_r^{(0)}c_v^{(k)}+c_s^{(0)}c_w^{(k)})^2}{\varepsilon_{A0}-\varepsilon_{Ck}}(\gamma_{CA}\beta)^2$$

Laticyclic Interactions. The equation representing the conjugation stabilization energy of the laticyclic interaction[3] of A, B, and C is immediately derived from Eq. (4) by putting one of the three integrals, say $\gamma_{CA}\beta$, equal to zero. When B is interposed between A and C, as is shown in Fig. 2, we obtain:

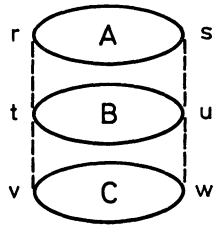


Fig. 2. Laticyclic interaction of three systems A, B and C.

$$\Delta E\cong 2\left(\sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}}-\sum_{i}^{\text{uno}}\sum_{j}^{\text{occ}}\right)\frac{(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_u^{(j)})^2}{\varepsilon_{Ai}-\varepsilon_{Bj}}(\gamma_{AB}\beta)^2$$
$$+2\left(\sum_{j}^{\text{occ}}\sum_{k}^{\text{uno}}-\sum_{j}^{\text{uno}}\sum_{k}^{\text{occ}}\right)\frac{(c_t^{(j)}c_v^{(k)}+c_u^{(j)}c_w^{(k)})^2}{\varepsilon_{Bj}-\varepsilon_{Ck}}(\gamma_{AB}\beta)^2 \quad (5)$$

The results of the calculation for several laticyclic interactions of three conjugated systems are given in Table 2. We can see that the conjugation stabilization is large in the following two cases: (i) when A and C are (4n+2)-electron systems and B is a 4n-electron system, and (ii) when A and C are 4n-electron systems and B is a (4n+2)-electron system.

TABLE 2. THE CONJUGATION STABILIZATION ENERGY IN LATICYCLIC INTERACTION OF THREE CONJUGATED SYSTEMS

A[a]	B[a]	C[a]	$\Delta E/\gamma^2\beta^{b}$
2	2	2	0.0
2	2	4	1.789
2	4	2	3.578
2	4	4	2.504
4	2	4	3.578
2	2	6	0.622
2	6	2	1.244
4	4	4	1.431
2	4	6	3.531
2	6	4	2.364
6	2	4	2.411
2	6	6	1.617
6	2	6	1.244
4	4	6	2.458
4	6	4	3.483
4	6	6	2.738
6	4	6	3.484
6	6	6	1.991

a) 2; ethylenic, 4; butadienic, 6; hexatrienic.
b) $|\gamma_{AB}|=|\gamma_{BC}|=\gamma$

Pericyclic Interactions. Next, let us consider the pericyclic interaction[3] of the three systems, A, B, and C, as is shown in Fig. 3. The perturbed secular equation is:

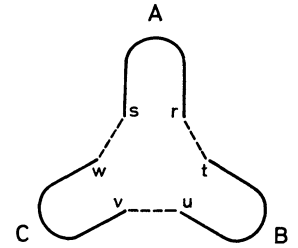
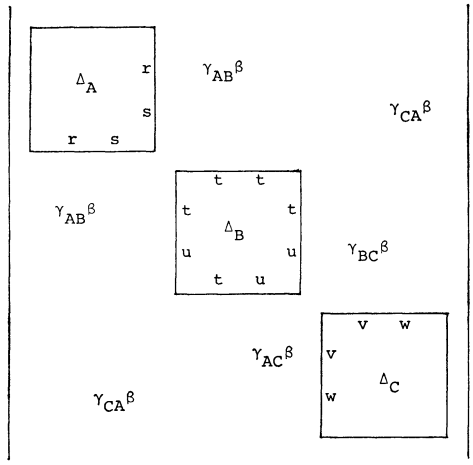


Fig. 3. Pericyclic interaction of three systems A, B and C.



(6)

Expanding the perturbed MO energies in the power series of $\gamma\beta$, the second-order perturbation energy is given by:

$$\Delta E=2\left(\sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}}-\sum_{i}^{\text{uno}}\sum_{j}^{\text{occ}}\right)\frac{(c_r^{(i)}c_t^{(j)})^2}{\varepsilon_{Ai}-\varepsilon_{Bj}}(\gamma_{AB}\beta)^2$$
$$+2\left(\sum_{j}^{\text{occ}}\sum_{k}^{\text{uno}}-\sum_{j}^{\text{uno}}\sum_{k}^{\text{occ}}\right)\frac{(c_u^{(j)}c_v^{(k)})^2}{\varepsilon_{Bj}-\varepsilon_{Ai}}(\gamma_{BC}\beta)^2$$
$$+2\left(\sum_{k}^{\text{occ}}\sum_{i}^{\text{uno}}-\sum_{k}^{\text{uno}}\sum_{i}^{\text{occ}}\right)\frac{(c_w^{(k)}c_s^{(i)})^2}{\varepsilon_{Ck}-\varepsilon_{Ai}}(\gamma_{CA}\beta)^2 \quad (7)$$

The results of the calculations are given in Table 3. Unfortunately, as to the second-order perturbation terms, we can not distinguish the 4n and (4n+2)-electron cycles. For example, the pericyclic interaction of the ethylenic, butadienic, and allyl cationic systems gives the same conjugation stabilization energy as the interaction of the ethylenic, butadienic, and allyl anionic system, 2+4+(3−1). The interaction energy of the third-order with respect to γ is given by:

$$\Delta E=8\left\{\sum_{i}^{\text{occ}}\sum_{j}^{\text{all}}\sum_{k}^{\text{all}}\frac{c_r^{(i)}c_s^{(i)}c_t^{(j)}c_u^{(j)}c_v^{(k)}c_w^{(k)}}{(\varepsilon_{Bj}-\varepsilon_{Ai})(\varepsilon_{Ck}-\varepsilon_{Ai})}\right.$$
$$+\sum_{j}^{\text{occ}}\sum_{k}^{\text{all}}\sum_{i}^{\text{all}}\frac{c_t^{(j)}c_u^{(j)}c_v^{(k)}c_w^{(k)}c_r^{(i)}c_s^{(i)}}{(\varepsilon_{Ck}-\varepsilon_{Bj})(\varepsilon_{Ai}-\varepsilon_{Bj})}$$
$$\left.+\sum_{k}^{\text{occ}}\sum_{i}^{\text{all}}\sum_{j}^{\text{all}}\frac{c_v^{(k)}c_w^{(k)}c_r^{(i)}c_s^{(i)}c_t^{(j)}c_u^{(j)}}{(\varepsilon_{Ai}-\varepsilon_{Ck})(\varepsilon_{Bj}-\varepsilon_{Ck})}\right\}\gamma_{AB}\gamma_{BC}\gamma_{CA}\beta^3 \quad (8)$$

Table 3. The conjugation stabilization energy in pericyclic interaction of three conjugated systems (second-order)

A[a]	B[a]	C[a]	$\Delta E/\gamma^2\beta$[b]
2	2	2	1.500
2	2	4	1.606
2	4	4	1.732
4	4	4	1.878
2	2	1−1	2.500
2	2	1+1	2.500
2	4	1−1	2.894
2	4	1+1	2.894
2	2	3−1	1.914
2	2	3+1	1.914
2	4	3−1	2.154
2	4	3+1	2.154

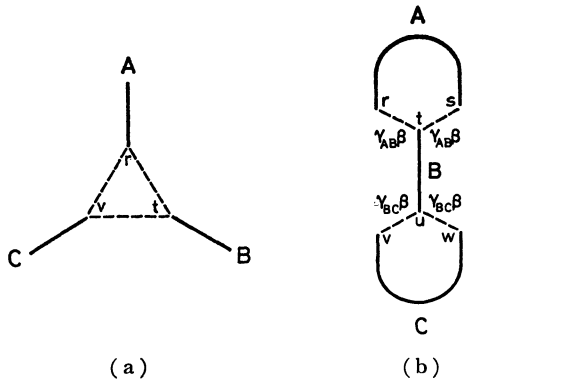
a) 2; ethylenic, 4; butadienic, 1−1; cation with single p AO, 1+1; anion with single p AO, 3−1; allyl cationic, 3+1; allyl anionic.
b) $|\gamma_{AB}|=|\gamma_{BC}|=|\gamma_{CA}|=\gamma$

Table 4. The conjugation stabilization energy in pericyclic interaction of three conjugated systems (third-order)

A	B	C	$\Delta E/\gamma^3\beta$[a]
2	2	1−1	−2.000
2	2	1+1	6.000
2	4	1−1	4.000
2	4	1+1	−4.000
2	2	3−1	4.000
2	2	3+1	0.000
2	4	3−1	−2.000
2	4	3+1	2.000

a) Degeneracy was removed by the method reported in Ref. 5 b).

The results of the calculations for several examples are given in Table 4. For instance, the third-order perturbation energy of the cycle composed of the ethylenic, butadienic, and allyl cationic systems is calculated to be $-2.000\,\gamma_{AB}\gamma_{BC}\gamma_{CA}\beta$, while that of the cycle composed of the ethylenic, butadienic and allyl anionic systems is $2.000\,\gamma_{AB}\gamma_{BC}\gamma_{CA}\beta$. Therefore, in order to make the stabilization large, $\gamma_{AB}\gamma_{BC}\gamma_{CA}$ should be negative in the former case, while it should be positive in the latter case. The cyclic conjugation of the three systems in which $\gamma_{AB}\gamma_{BC}\gamma_{CA}$ is positive obviously corresponds to the usual Hückel-type conjugation, while that in which $\gamma_{AB}\gamma_{BC}\gamma_{CA}$ is negative corresponds to the anti-Hückel or Möbius-strip-type conjugation.[7] The conclusions thus derived from the third-order perturbation energy, that the 2+4+(3−1) system favors the anti-Hückel interaction and that the 2+4+(3+1) system favors the Hückel interaction, are in agreement with the results obtained by Goldstein and Hoffmann.[3] However, it should



(a) (b)

Fig. 4. Other types of interactions of three systems A, B and C.

be noted here that whether or not a pericyclic interaction of three independent systems takes place preferentially in the Hückel-type or in the anti-Hückel-type interaction depends not on the symmetry properties of the MO's of the three independent systems, but on the number of electrons forming a cycle. This conclusion is completely consistent with that given in our previous paper,[8] and also with the theory of aromaticity.[9]

Other Kinds of Interactions. Let us now discuss some other kinds of interactions of three independent systems. The first case is the interaction of three systems at the r, t, and v termini, as is shown in Fig. 4(a). The interaction energy is given by:

$$\Delta E \cong 2\left(\sum_{i}^{occ}\sum_{j}^{uno}-\sum_{i}^{uno}\sum_{j}^{occ}\right)\frac{(c_r^{(i)}c_t^{(j)})^2}{\varepsilon_{Ai}-\varepsilon_{Bj}}(\gamma_{AB}\beta)^2 + 2\left(\sum_{j}^{occ}\sum_{k}^{uno}-\sum_{j}^{uno}\sum_{k}^{occ}\right)\frac{(c_t^{(j)}c_v^{(k)})^2}{\varepsilon_{Bj}-\varepsilon_{Ck}}(\gamma_{BC}\beta)^2 + 2\left(\sum_{k}^{occ}\sum_{i}^{uno}-\sum_{k}^{uno}\sum_{i}^{occ}\right)\frac{(c_v^{(k)}c_r^{(i)})^2}{\varepsilon_{Ck}-\varepsilon_{Ai}}(\gamma_{CA}\beta)^2 \quad (9)$$

The next case is the interaction of three systems, A, B, and C, in which the AO's r and s of A conjugate with the AO t of B and the AO's v and w of C conjugate with the AO u of B, as is shown in Fig. 4 (b). The conjugation stabilization energy is then given by:

$$\Delta E \cong 2\left(\sum_{i}^{occ}\sum_{j}^{unc}-\sum_{i}^{uno}\sum_{j}^{occ}\right)\frac{(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_t^{(k)})^2}{\varepsilon_{Ai}-\varepsilon_{Bj}}(\gamma_{AB}\beta)^2 + 2\left(\sum_{k}^{occ}\sum_{j}^{uno}-\sum_{k}^{uno}\sum_{j}^{occ}\right)\frac{(c_t^{(j)}c_v^{(k)}+c_t^{(j)}c_w^{(k)})^2}{\varepsilon_{Ck}-\varepsilon_{Bj}}(\gamma_{BC}\beta)^2 \quad (10)$$

The results of the calculations are given in Table 5. We can see that the number of electrons of the bridge, B, has little influence upon the interaction energy in the interaction of type (b). In addition, when B is neutral, as in the cases of ethylenic, butadienic, *etc.*, the conjugation stabilization does not depend on the number of electrons, *i. e.*, 4n or 4n+2, of A and of C. When B is cationic, the stabilization is large when both A and C have 4n+2 electrons. On the other hand, when B is anionic, when both A and C are

7) a) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964). b) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966). c) M. J. S. Dewar, *Tetrahedron Suppl.* **8**, Part I, 75 (1966).

8) K. Fukui and H. Fujimoto, This Bulletin, **40**, 2018 (1967).

9) See, for instance, A. Strietwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York, N. Y. (1961), p. 256.

Table 5. The conjugation stabilization energy in the interaction of three conjugated systems shown in Fig. 4

	A[a]	B[a]	C[a]	$\Delta E/\gamma^2\beta$[b]
Type (a)	2	2	2	1.500
	2	2	4	1.606
	2	4	4	1.732
	4	4	4	1.878
Type (b)	2	2	2	2.000
	2	2	4	2.106
	2	4	2	2.211
	2	4	4	2.358
	4	2	4	2.211
	4	4	4	2.504
	2	3−1	2	4.828
	2	3+1	2	0.828
	2	3−1	4	3.203
	2	3+1	4	3.203
	4	3−1	4	1.578
	4	3+1	4	5.578

a) 2; ethylenic, 4; butadienic, 6; hexatrienic, 3−1; allyl cationic, 3+1; allyl anionic.
b) $|\gamma_{AB}|=|\gamma_{BC}|=|\gamma_{CA}|=\gamma$

4n-electron systems there will be a large conjugation stabilization. The results in Table 5 correspond to the case in which A, B and C interact through the π-like overlapping of terminal p AO's.

Interaction with d Orbitals

Numerous chemical reactions take place simultaneously with catalysis. In bimolecular reactions of two reactants, A and B, under the influence of a catalysis, C, we must consider the interaction of three independent systems, A, B, and C. Therefore, a theoretical means of handling three systems simultaneously is necessary in order to investigate the role of catalysis in chemical reactions. Recently, the important role of the d orbitals of transition-metal complexes in olefin metathesis was clearly recognized.[4d,10] Some theoretical papers have been published concerning this reaction.[10] However, these consider the process as an interaction between the orbitals of the transition metal and two weakly-coupled olefin molecules or tetramethylene. By the use of Eq. (4), we can examine the role of the d orbitals at the begining of the reaction. The modes of the orbital-overlap interactions are schematically illustrated in Fig. 5. We can see that the HOMO of olefin can interact with $d_{x^2-y^2}$ and that the LUMO can overlap with d_{xy}. Accordingly, the interaction between the d orbitals and π MO's of olefins will result in a net stabilization, although the interaction between two olefins is symmetry-unfavorable and does not lead to stabilization.[6,11] The donation of electrons from the occupied MO's of olefins to the unoccupied d orbital, and that from the occupied d orbital to the unoccupied MO's of olefins, will bring about a loosening of the π bonds of olefins. Consequently, the mixing of the chemically-induced excited state of olefins through the charge-transfer interaction with d orbitals will activate olefins and lessen the symmetry constraint. As the reaction proceeds, it is reasonable to regard the process as an interaction between the d orbitals and two weakly-coupled olefin molecules or a tetramethylene system.[10]

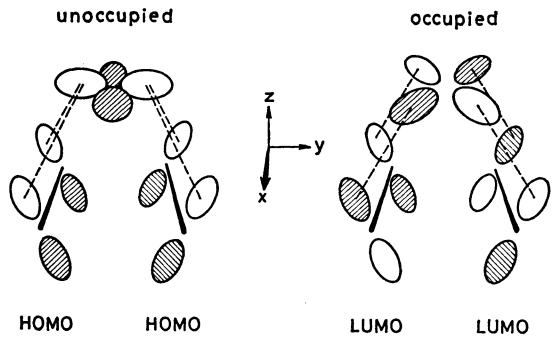


Fig. 5. A schematic representation of orbital overlap interactions in olefin metathesis.

Equation (4) suggests that the two reactants should have the same MO symmetry properties in order for both of them to be activated by the same pair of occupied and unoccupied d orbitals. Olefins metathesis is such a case. Polyenes with an even number of electrons can be classified into two classes; one possessing 4n electrons, and the other, 4n+2 electrons. The HOMO of a 4n-electron system is antisymmetric (A) and the LUMO is symmetric (S). The HOMO of a (4n+2)-electron system is S and the LUMO is A. Therefore, when one reactant is a 4n-electron system and the other is a (4n+2)-electron system, only one of them can be activated by one occupied d orbital and one unocupied d orbital of the central metal of catalysis. In order to activate both, more than two occupied and two unoccupied d orbitals should participate in the reaction. Thus, the important role of the d orbitals of transition-metal complex catalysis can be most clearly observed in the interactions of two conjugated systems belonging to the same class, such as the cases of (2+2), (4+4), (2+6), (6+6), ……, which are thermally unfavored without catalysis.[1,6,11,12]

Some concenient equations have been derived for the purpose of calculating the stabilization energy of the simultaneous interaction of three independent systems. The stabilization energy for some types of interactions of three systems has been given in the second-order perturbation forms, using the energies and AO coefficients of the MO's of the isolated reactants. These equations can be used for the semi-

10) a) F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, **89**, 2484 (1967); **91**, 1030 (1969); **93**, 1123 (1971). b) F. D. Mango, *Tetrahedron Lett.*, **1971**, 505. c) W. Th. A. M. van der Lugt, *ibid.*, **1970**, 2281. d) G. S. Lewandos and R. Pettit, *ibid.*, **1971**, 789. e) See also, R. H. Grubbs and T. K. Brunck, *J. Amer. Chem. Soc.*, **94**, 2538 (1972).
11) a) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965). b) R. B. Woodward and R. Hoffman, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969).
12) K. Fukui, This Bulletin, **39**, 498 (1966).

quantitative estimation of the conjugation stabilization at the initial stage of three bodies interactions, regardless of whether or not some particular symmetry exists. The method presented here will be helpful for understanding the important role of the d orbitals of transition metals in complex formations and in the activation of organic molecules in chemical reactions. When the HOMO of one system happens to be degenerate with the LUMO of another, the HOMO-LUMO interaction can be expressed by a first-order perturbation term and comes to play a discriminatively important role.[12]

Appendix

In the case of longicyclie interaction, the third-order interaction energy with respect to $\gamma_{AB}\gamma_{BC}\gamma_{CA}$ is given by

$$\Delta E = 8\left\{\sum_{i}^{occ}\sum_{j}^{all}\sum_{k}^{all}\frac{(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_u^{(j)})(c_t^{(j)}c_v^{(k)}+c_u^{(j)}c_w^{(k)})(c_v^{(k)}c_r^{(i)}+c_w^{(k)}c_s^{(i)})}{(\varepsilon_{Bj}-\varepsilon_{Ai})(\varepsilon_{Ck}-\varepsilon_{Ai})}\right.$$
$$+\sum_{j}^{occ}\sum_{k}^{all}\sum_{i}^{all}\frac{(c_t^{(j)}c_v^{(k)}+c_u^{(j)}c_w^{(k)})(c_v^{(k)}c_r^{(i)}+c_w^{(k)}c_s^{(i)})(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_u^{(j)})}{(\varepsilon_{Ck}-\varepsilon_{Bj})(\varepsilon_{Ai}-\varepsilon_{Bj})}$$
$$\left.+\sum_{k}^{occ}\sum_{i}^{all}\sum_{j}^{all}\frac{(c_v^{(k)}c_r^{(i)}+c_w^{(k)}c_s^{(i)})(c_r^{(i)}c_t^{(j)}+c_s^{(i)}c_u^{(j)})(c_t^{(j)}c_v^{(k)}+c_u^{(j)}c_w^{(k)})}{(\varepsilon_{Ai}-\varepsilon_{Ck})(\varepsilon_{Bj}-\varepsilon_{Ck})}\right\}\gamma_{AB}\gamma_{BC}\gamma_{CA}\beta^3$$

In the case of laticyclic interaction, the third-order interaction energy does not appear.