BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 2116—2126 (1966)

Sigma-Pi Interaction Accompanied by Stereoselection

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(Received January 7, 1966)

A simple molecular orbital theoretical treatment of the sigma-pi interaction caused by chemical reactions of planar-conjugated systems has been developed. The problem of the streoselection of the two alternative directions of configuration altering due to the hybridization change at the centers of interaction has been considered by means of a simple perturbation treatment. Two theoretical indices, which represent the conjugation stabilization by way of the sigma-pi and reagent-pi interactions, have been introduced for this purpose. The theoretical results are consistent with the results of experience so far accumulated in various organic reactions, such as additions, eliminations, substitutions, and rearrangements, of conjugated molecules.

The electronic wave function for planar-conjugated molecules is divided into the so called sigma and pi parts. The former is composed of the molecular orbitals (MO) which are symmetric with respect to the molecular plane and have the direction of extension on that plane, while the latter consists of the MO's antisymmetric with respect to that plane, to which their direction of maximum extension is perpendicular. The condition of this separability has been thoroughly discussed by Lykos and Parr.1) When such a planar system is exposed to a certain perturbation, say, for instance, to a chemical interaction due to the approach of atoms, molecules, radicals, or ions from definite sides of the plane toward definite positions of the molecule, both the sigma and pi MO's will be affected. The change in MO's as well as in energies is obtainable from the usual perturbation calculation on an assumption of an unchanged molecular configuration.2) However, the actual effect will cause a change in the nuclear distances

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1) P. G. Lykos and R. G. Parr, *J. Chem. Phys.*, **24**, 1166 (1956); **25**, 1301 (1956).

2) Hosoya and Nagakura (H. Hosoya and S. Nagakura, Preprint of Symposium on Molecular Structure, Japan (1962), p. 48 (in Japanese)) calculated the deformation of MO's with the mixing of the 3s orbital with the $2p\pi$ orbitals due to the approach of a point charge to an ethylenic bond.

and valence angles near the center of approach, giving rise to changes in the hybridization of carbon atoms. Such an altering in the molecular configuration is not calculable by a mere perturbation treatment. The most favorable configuration would be obtained as the one which gives the minimum adiabatic potential due to the Born-Oppenheimer approximation adopted for the perturbed system. This procedure is not, however, simple enough to be practical for organic chemists.

This paper will present a simple MO treatment of organic chemical processes in planar-conjugated molecules, thus providing a method by which we can discuss very simply the direction of the configuration-altering of molecules associated with the hybridization change in carbon atoms. This configuration's frequent alterations arise stereospecifically; it is the purpose of the present paper to elucidate the rule which governs this stereoselection.

Simple Perturbation Treatment

Let us consider a planar-conjugated hydrocarbon molecule having several carbon 2pπ atomic orbitals (AO). The carbon atom, t, has one π orbital, ϕ_t, and three sp^2 hybridized σ orbitals, χ_t, $\chi_{t'}$, and $\chi_{t''}$, to combine with neighboring carbon sp^2 orbitals or otherwise with hydrogen 1s orbitals, ζ_p's. The direction of the extension of these real hybridized orbitals conforms to the direction of bonding, so that they have always positive values in the region of their maximum extension (Fig. 1). All 2pπ orbitals are taken as having the same sign on the same side of the molecular plane. The total unperturbed wave function is assumed to be a product of the π part and the σ part, both of which are represented by a mere product of the usual simple Hückel MO's, which are written as:

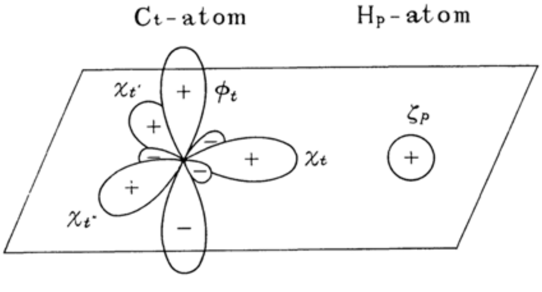

Fig. 1. The atomic orbitals.

$$\psi_i = \sum_t c_t^i \phi_t \qquad \text{for the } \pi \text{ part, and} \qquad (1a)$$

$$\varphi_k = \sum_t b_t^k \chi_t + \sum_p d_p^k \zeta_p \qquad \text{for the } \sigma \text{ part,}^{3)} \qquad (1b)$$

where ψ_i and φ_k are ith π MO and kth σ MO respectively. The first term on the right side of the latter equation signifies the summation with respect to each of three σ hybrids, namely:

$$\sum_t (b_t^k \chi_t + b_{t'}^k \chi_{t'} + b_{t''}^k \chi_{t'})$$

Instead of proceeding with the usual perturbation concept, we may here adopt the "method of perturbed secular determinant."[4],* This method is suitable for calculating the energy difference between two systems for which the secular determinants differ slightly. The characteristic feature of this method is that it makes possible the calculation of the changes in energy, electron density, bond order, and other MO-theoretical quantities without an explicit knowledge of the change in the Hamiltonian operator or in that of wave functions.

The nonperturbed MO's of the π part are orthogonal to those of the σ part. The resonance integral between ϕ_t and χ_t's for the nonperturbed field is, of course, zero. Let us consider the configuration alteration which is indicated in Fig. 2, corresponding to the hybridization change due to chemical interaction with conjugated molecules. Figure 2 illustrates the case of a two-center interaction. Since, in all cases, our interest is limited to the direction of configuration alteration, each carbon atom is assumed to change its hybridized state from sp^2 to sp^x, where x is a definite number between 2 and 3. With this change the Coulomb integrals of a π orbital and a σ hybrid vary by $(\Delta\alpha)_\pi$ and $(\Delta\alpha)_\sigma$ respectively. The changes in the resonance integrals between a varied and the neighboring π AO's, and between a varied and the neighboring σ hybrids, are $(\Delta\beta)_\pi$ and $(\Delta\beta)_\sigma$ respectively, while the change in the resonance integral between the two σ hybrids of the same carbon atom[3] is $(\Delta\beta)_\sigma'$. The resonance integral between the π orbital and a σ hybrid of the same carbon atom, say t, is designated by γ_t^σ. Since the way of taking the sign of basis orbitals is as illustrated in Fig. 1, we have two cases with respect to the value of γ^σ: namely, the one is the case of the carbons t and u of Fig. 2(i) (or the carbon t of ii), and the other is the case of the carbon u of Fig. 2(ii).

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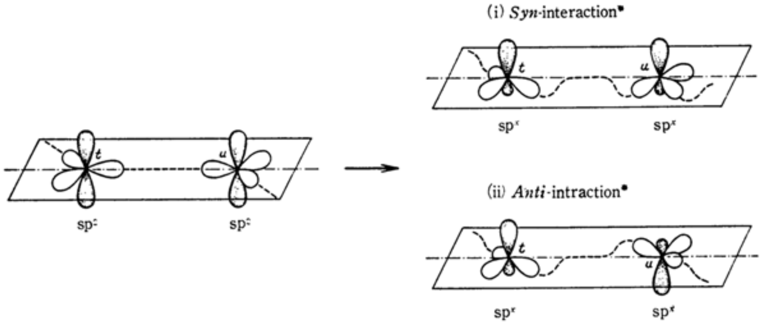
[3] a) K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura and C. Nagata, This Bulletin, **35**, 38 (1962); b) see also K. Fukui, H. Kato and T. Yonezawa, ibid., **34**, 442, 1111 (1961); **35**, 1475 (1962); T. Yonezawa, H. Kato, H. Saito and K. Fukui, ibid., **35**, 1814 (1962); K. Morokuma, K. Fukui, T. Yonezawa and H. Kato, ibid., **36**, 47 (1963); H. Kato, K. Fukui and T. Yonezawa, ibid., **38**, 189 (1965).

[4] K. Fukui, C. Nagata, T. Yonezawa, H. Kato and K. Morokuma, *J. Chem. Phys.*, **31**, 287 (1959); K. Fukui, K. Morokuma, T. Yonezawa and C. Nagata, This Bulletin, **33**, 963 (1960).

* The term "perturbation" is here employed to imply the origin of the change in particular parameters in the secular determinant. The change in any quantum-mechanical quantity derived by solving it can be obtained by a procedure similar to the usual perturbation calculations.



(x: a number between 2 and 3)

Fig. 2. A schematic representation of the mode of two-center σ-π interaction with a conjugated molecule.
* The terms *syn*- and *anti*- are used in order to evade confusion with *cis*- and *trans*-configurations of the remaining double bonds.

In the former case γ^{σ} is clearly negative, while in the latter it is positive. In addition, we have to consider the interaction with the reagent system. The resonance integral for the overlapping at the rth π orbital of the conjugated molecule with the reagent system (mostly one or two independent systems) is denoted by γ_r^{R}.

The increase in the total energy, ΔE, is thus represented by the following equations:[4]

$$\Delta E=(\Delta E)_{\sigma}+(\Delta E)_{\pi}+(\Delta E)_{\mathrm{R}} \\ +(\Delta E)_{\sigma\pi}+(\Delta E)_{\mathrm{R}\pi} \tag{4}$$

$$(\Delta E)_{\sigma}=2\sum_{k}^{\mathrm{occ}}\sum_{t}(b_t^k)^2(\Delta\alpha)_{\sigma} \\ +4\sum_{k}^{\mathrm{occ}}\sum_{t}\left\{\sum_{u}^{nei}b_t^kb_u^k(\Delta\beta)_{\sigma}+\sum_{t'}^{\mathrm{sam}}b_t^kb_{t'}^k(\Delta\beta)_{\sigma}'\right\} \\ +2\sum_{k}^{\mathrm{occ}}\sum_{l}^{\mathrm{uno}}\frac{1}{\eta_k-\eta_l}\left\{\sum_{t}b_t^kb_t^l(\Delta\alpha)_{\sigma}\right. \\ +\sum_{t}\sum_{u}^{\mathrm{nei}}(b_t^kb_u^l+b_u^kb_t^l)(\Delta\beta)_{\sigma} \\ \left.+\sum_{t}\sum_{t'}^{\mathrm{sam}}(b_t^kb_{t'}^l+b_{t'}^kb_t^l)(\Delta\beta)_{\sigma}'\right\}^2 \tag{5}$$

$$(\Delta E)_{\pi}=2\sum_{i}^{\mathrm{occ}}\sum_{t}(c_t^i)^2(\Delta\alpha)_{\pi} \\ +4\sum_{i}^{\mathrm{occ}}\sum_{t}\sum_{u}^{\mathrm{nei}}c_t^ic_u^i(\Delta\beta)_{\pi} \\ +2\sum_{i}^{\mathrm{occ}}\sum_{j}^{\mathrm{uno}}\frac{1}{\varepsilon_i-\varepsilon_j}\left\{\sum_{t}c_t^ic_t^j(\Delta\alpha)_{\pi}\right. \\ \left.+\sum_{t}\sum_{u}^{\mathrm{nei}}(c_t^ic_u^j+c_u^ic_t^j)(\Delta\beta)_{\pi}\right\}^2 \tag{6}$$

$$(\Delta E)_{\sigma\pi}=2\left(\sum_{i}^{\mathrm{occ}}\sum_{k}^{\mathrm{uno}}-\sum_{k}^{\mathrm{occ}}\sum_{i}^{\mathrm{uno}}\right)\frac{1}{\varepsilon_i-\eta_k} \\ \times\left(\sum_{t}c_t^ib_t^k\gamma_t{}^{\sigma}\right)^2 \tag{7}$$

$$(\Delta E)_{\mathrm{R}\pi}=2\left(\sum_{i}^{\mathrm{occ}}\sum_{l}^{\mathrm{uno}}-\sum_{l}^{\mathrm{occ}}\sum_{i}^{\mathrm{uno}}\right)\frac{1}{\varepsilon_i-e_l} \\ \times\left(\sum_{r}c_r^id_{r'}^l\gamma_r{}^{\mathrm{R}}\right)^2+2\left(\sum_{i}^{\mathrm{occ}}\sum_{l'}^{\mathrm{uno}}-\sum_{l'}^{\mathrm{occ}}\sum_{i}^{\mathrm{uno}}\right) \\ \times\frac{1}{\varepsilon_i-e_{l'}}\left(\sum_{s}c_s^id_{s'}^{l'}\gamma_s^{\mathrm{R}'}\right)^2+\cdots \tag{8}$$

In addition to the right-side terms in Eq. 4, there may happen to exist zero-order terms which have no connection with stereochemical problems.

We may proceed further without mentioning the modification well-known to be necessary for the case of any type of degeneracy with respect to MO energies which may yield first-order terms in these equations in lieu of the corresponding second-order terms. The terms $(\Delta E)_{\sigma}$, $(\Delta E)_{\pi}$ and $(\Delta E)_{\mathrm{R}}$ signify the change in energy due to the interaction in the sigma, pi, and reagent parts respectively, while $(\Delta E)_{\sigma\pi}$ and $(\Delta E)_{\mathrm{R}\pi}$ are the conjugation stabilizations through sigma-pi and reagent-pi interactions respectively. In these equations occ and uno mean all the occupied and unoccupied MO's respectively, while nei and sam imply all neighboring orbitals and all hybrids of the same carbon atom respectively. When a radical plays a part, the terms due to the half-occupied orbital must not be doubled. The energy of ith π-MO and kth σ-MO are denoted by ε_i and η_k respectively. The summation with respect to t on the right sides of Eqs. 5 and 7 has the same meaning as in Eq. 1b. For the reagent part, e_l and $d_{r'}^l$ are the energy and the coefficient of r'th AO (at which the overlapping takes place with the rth π orbital of the reactant) of the Reagent System 1 (which is, of course, not limited to a conjugated system). Similarly, $e_{l'}$ and $d_{s'}^{l'}$ are for Reagent System 2, and so forth. The term $(\Delta E)_{\mathrm{R}}$ represents the energy change in the reagent, which may have a form similar to $(\Delta E)_{\sigma}$ and $(\Delta E)_{\pi}$.

The stereoselectivity of this type of reaction is thus governed by the terms of $(\varDelta E)_{\sigma\pi}$ and $(\varDelta E)_{R\pi}$ since, in such a problem, $(\varDelta E)_{\sigma}$, $(\varDelta E)_{\pi}$ and $(\varDelta E)_{R}$ are deemed as common in the two opposite configurations in Fig. 2. In addition, the geometrical circumstances in the interaction of the reagent system with the reactant system, or the interesting effect of neighboring-group participation, should never be left out of account; however, this is obviously a problem to be discussed in a separate paper.

The Parametrization

In order to calculate the value of $\varDelta E$, we need to evaluate the integrals of both σ and π parts on a unified basis. These we have already made available in several of our previous papers,³⁾ and also summarized in a recent paper in which we adopted a slightly different estimation.⁵⁾ In the present paper we will use the latter values, with slight modifications, plus the values of newly-evaluated integrals for aromatic skeletons, as are listed in Table I. These numerical values have been determined with reference to the analytical form of the Slater orbitals and the theoretical evaluation of the overlap integrals in order to be consistent with various empirical data.

TABLE I. THE PARAMETERS EMPLOYED FOR HYDROCARBONS

Coulomb integrals:
  for carbon p orbital: $\alpha-0.15\beta$
    sp³ hybrid: $\alpha-0.10\beta$
    sp² hybrid: α
    sp hybrid: $\alpha+0.10\beta$
  for all hydrogens: $\alpha-0.20\beta$
Resonance integrals:
  for C-C single bonds:
    sp³-sp³: 0.84β sp³-sp²: 0.88β sp³-sp: 0.96β
    sp²-sp²: 0.92β sp²-sp: 0.98β sp-sp: 1.04β
  for C-C double bonds:
    p-p (π): 0.30β
    sp²-sp² (σ): 1.00β sp²-sp (σ): 1.04β
    sp-sp (σ): 1.08β
  for C-C triple bonds:
    p-p (π): 0.35β
    sp-sp (σ): 1.13β
  for aromatic C-C bonds:
    sp²-sp²: 0.96β
  for C-C bonds of polyenyl radicals:
    sp²-sp²: 0.96β
  for two σ hybrids belonging to the same carbon:
    sp³-sp³: 0.30β sp²-sp²: 0.38β sp-sp: 0.60β
  for C-H bond:
    sp³ carbon: 0.90β
    sp² carbon: 0.94β
    sp carbon: 0.96β

(α: the Coulomb integral of a carbon sp² hybrid
β: the resonance integral for two bonding carbon sp² hybrids in the ethylenic double bond.)

(The resonance integrals for C-C single bond other than sp³-sp³ are given for the single bonds of such types as C-C= (sp³-sp²), C-C≡ (sp³-sp); =C-C= (sp²-sp²), and so on. Such a clasification obviously does not possess any essential meaning. The slight difference in these resonance integrals does not affect seriously the result.)

The Sigma-pi Interaction

The quantity, $(\varDelta E)_{\sigma\pi}$, which has been introduced above is useful in various problems in which the hybridization change participates. We assume, in this connection, that the arbitrary value of r_t^{σ} in Eq. 7 is to be regarded as equal to $g_t\gamma^{\sigma}$, in which g_t is $+1$ (as in the case of the carbons t and u of Fig. 2(i) and the carbon t of ii) and -1 (in the case of the carbon u of Fig. 2 (ii) and γ^{σ} is a negative constant; thus we may difine a new index, which we tentatively denote by $h_{tu\cdots}$, as:

$$\begin{aligned} h_{tu\cdots} &= (\varDelta E)_{\sigma\pi}\beta/(\gamma^{\sigma})^2 \\ &= 2\left(\sum_{i}^{\text{occ}}\sum_{k}^{\text{uno}} - \sum_{k}^{\text{occ}}\sum_{i}^{\text{uno}}\right)\frac{(-\beta)}{\eta_k-\varepsilon_i} \\ &\quad \times (c_t^i c'^k_t g_t + c_u^i c'^k_u g_u + \cdots\cdots)^2 \end{aligned} \tag{9}$$

where $c'^k_t = b_t^k + b_{t'}^k + b_{t''}^k$, where β is the resonace integral between two bonding carbon sp² hybrids in the ethylene double bond, and where t, u,$\cdots$ imply the carbon atoms at which the hybridization change takes place.* Several of the simplest cases are specified by:

$$h_t = 2\left(\sum_{k}^{\text{occ}}\sum_{i}^{\text{uno}} - \sum_{i}^{\text{occ}}\sum_{k}^{\text{uno}}\right)\frac{(-\beta)}{\varepsilon_i-\eta_k}(c_t^i)^2(c'^k_t)^2 \tag{10a}$$

$$\begin{aligned} h_{tu}^{(syn)} &= 2\left(\sum_{k}^{\text{occ}}\sum_{i}^{\text{uno}} - \sum_{i}^{\text{occ}}\sum_{k}^{\text{uno}}\right)\frac{(-\beta)}{\varepsilon_i-\eta_k} \\ &\quad \times (c_t^i c'^k_t + c_u^i c'^k_u)^2 \end{aligned} \tag{10b}$$

$$\begin{aligned} h_{tu}^{(ant)} &= 2\left(\sum_{k}^{\text{occ}}\sum_{i}^{\text{uno}} - \sum_{i}^{\text{occ}}\sum_{k}^{\text{uno}}\right)\frac{(-\beta)}{\varepsilon_i-\eta_k} \\ &\quad \times (c_t^i c'^k_t - c_u^i c'^k_u)^2 \end{aligned} \tag{10c}$$

For the systems having a half-occupied level, i, the terms due to that level must not be doubled but must be summed over all the k's.

The index h_t represents the ease of hybridization of the tth π orbital, namely, the ease of mixing the s-nature into the p AO; thus we may refer to

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5) K. Fukui in "Modern Quantum Chemistry," Vol. I, Ed. by O. Sinanoglu, Academic Press, New York (1965), p. 49.

* In the two-center interaction at the equivalent positions (t, u) of a molecule with C_{2h}-symmetry, in which we assume that $|g_u| = a|g_t|$ $(a>0)$, it is easy to show that:

$$h_{tu}^{(syn)} - h_{tu}^{(ant)} = a\left[h_{tu}^{(syn)} - h_{tu}^{(ant)}\right]_{a=1}$$

it as the "hybridizability" of the tth pπ atomic orbital. This quantity is closely related to the problem of olefinicity (and, therefore, also to that of aromaticity), which will be discussed elsewhere.

The index h_{tu} is connected with the stability of the activated complex of the two-center reactions of conjugated molecules, a discussion of which will immediately follow.

Acyclic Two-center Interactions

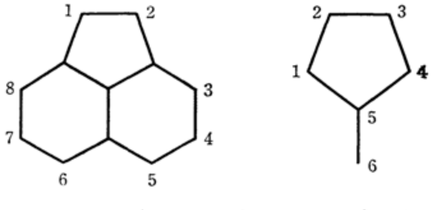
Let us proceed further by dividing the problem into two cases, those of cyclic and of acyclic interactions. Also, let us limit the discussion to the two-center interaction only.

By an "acyclic two-center interaction" we mean a simultaneous or quasi-simultaneous interac-

TABLE II. THE COMPARISON OF $h_{tu}^{(syn)}$ AND $h_{tu}^{(ant)}$ FOR NONCYCLIC TWO-CENTER INTERACTIONS IN SEVERAL CONJUGATED HYDROCARBONS

Conjugated hydrocarbons	Positions of interaction, tu	$h_{tu}^{(syn)}$	$h_{tu}^{(ant)}$	Favorable configurations
(I) α, β-Interaction				
Ethylene	1,2	3.1194	5.5244	*anti*
(excited)		(8.9912)	(5.5180)	(*syn*)
Butadiene	1,2	3.2486	5.4947	*anti*
Hexatriene	1,2	3.2994	5.4671	*anti*
Benzene	1,2	3.4428	5.0468	*anti*
Styrene	α, β	3.2301	5.5457	*anti*
Naphthalene	1,2	3.3883	5.2540	*anti*
Anthracene	1,2	3.3728	5.3021	*anti*
Acenaphthylene*1	1,2	3.4096	5.4107	*anti*
Fulvene*1	1,2	3.4124	5.3581	*anti*
(II) α, γ-Interaction				
Allyl cation	1,3	5.0844	4.7323	*syn*
Pentadienyl cation	1,3	4.7313	4.5092	*syn*
Allyl	1,3	4.7528	5.1758	*anti*
Pentadienyl	1,3	4.5738	4.9189	*anti*
Allyl anion	1,3	4.4212	5.6192	*anti*
Pentadienyl anion	1,3	4.4163	5.3286	*anti*
(III) α, δ-Interaction				
Butadiene	1,4	4.6130	4.4241	*syn*
Hexatriene	1,4	4.5679	4.3888	*syn*
Benzene	1,4	4.3817	4.1079	*syn*
Naphthalene	1,4	4.5559	4.2012	*syn*
Anthracene	1,4	4.5840	4.2128	*syn*
Anthracene	9,10	4.8058	4.3194	*syn*
Fulvene	1,4	4.2373	4.7009	*anti**2
(IV) α, ε-Interaction				
Pentadienyl cation	1,5	4.7367	4.7737	*anti*
Pentadienyl	1,5	4.8185	4.7737	*syn*
Pentadienyl anion	1,5	4.9002	4.7737	*syn*
(V) α, ζ-Interaction				
Hexatriene	1,6	4.5570	4.5775	*anti*

*1 Numbering for acenaphthylene and fulvene:



*2 The prediction of *anti*-predominance of 1,4-interaction in fulvene may be attributed to the odd-membered ring, in which this interaction is regarded also as α, γ-.

TABLE III. THE FAVORABLE MODE OF CYCLIC INTERACTIONS AS BASED UPON $(\Delta E)_{R\pi}$ (1)

Conjugated systems	Positions of interaction rs	$(\Delta E)_{R\pi}(\beta'/(\gamma^{R})^2)$*1		Favorable configuration
		syn	*anti*	
Case Ia. The reagent is a vacant single orbital.				
Ethylene	1,2	3.4286	0.0000	*syn*
Butadiene	1,2	3.4757	0.1937	*syn*
	1,4	0.6195	3.6886	*anti*
Hexatriene	1,2	3.5307	0.3237	*syn*
	1,4	0.6599	3.5654	*anti*
	1,6	3.7701	0.9883	*syn*
Benzene*2	1,2	2.3297	0.5714	*syn*
	1,4	0.6154	2.2857	*anti*
Styrene	α, β	3.4606	0.1480	*syn*
Naphthalene	1,2	2.6992	0.4561	*syn*
	1,4	0.6024	2.7136	*anti*
Anthracene	1,2	2.8563	0.4232	*syn*
	1,4	0.5941	2.8733	*anti*
	9,10	0.5729	3.4608	*anti*
Acenaphthylene	1,2	3.4126	0.4886	*syn*
Fulvene	1,2	3.4243	0.5648	*syn*
Case Ib. The reagent is a half-occupied single orbital.*4				
Allyl	1,3	1.2651	16.9705	*anti*
Pentadienyl	1,3	1.2186	16.5163	*anti*
	1,5	16.3511	1.7143	*syn**3
Heptatrienyl	1,3	1.2134	12.9885	*anti*
	1,5	12.5808	1.6210	*syn*
	1,7	1.9770	12.6326	*anti*
Cyclopropenyl	1,2	1.6000	4.8000	*anti*
Cyclopentadienyl	1,2	3.4075	1.4089	*syn**3
	1,3	1.1279	3.6886	*anti*
Cycloheptatrienyl	1,2	3.2612	6.3476	*anti*
	1,3	1.5412	8.0676	*anti*
	1,4	7.2086	2.4002	*syn*
Indenyl	1,2	3.6098	1.7058	*syn*
	1,3	1.1597	5.6332	*anti*
Case Ic. The reagent is a doubly-occupied single orbital.				
Ethylene	1,2	0.0000	4.8000	*anti*
Butadiene	1,2	0.3066	5.5024	*anti*
	1,4	6.4126	0.7618	*syn*
Hexatriene	1,2	0.6629	6.2231	*anti*
	1,4	7.2193	0.8341	*syn*
	1,6	1.2933	8.0676	*anti*

*1 The value of $(\Delta E)_{R\pi}$ depends on the reagent orbital. The values presented here are tentatively calculated for the case of hydrogen migration.
The quantity β' corresponds to the resonance integral of an ethylenic p-p(π) bond. ($=0.3\beta$)

*2 This case corresponds to the 5,6-proton migration of cyclohexa-1,3-dienyl cation. Other cases are also to be interpreted similarly.

*3 The cyclic and acyclic cases were not distinguished in the theory of Woodward and Hoffmann (Ref. 16); namely e. g. the cases of 1,5-migrations of cyclopentadiene and all-*cis*-pentadiene. The former corresponds to the case of 1,2-interaction of cyclopentadienyl and the latter to that of 1,5-interaction of pentadienyl in this table.

*4 The values in case Ib are given for the systems each of which is composed of a vacant single orbital and the anion corresponding to the original reactant except the cases of cyclopropenyl and cycloheptatrienyl. In these two cases, the values are for a doubly-occupied single orbital with cyclopropenyl cation or cycloheptatrienyl cation. The zero-order terms due to electron transfer interaction are deemed as common both in *syn*- and *anti*-interactions.

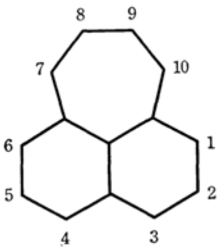
TABLE IV. THE FAVORABLE MODE OF CYCLIC INTERACTIONS AS BASED UPON $(\Delta E)_{R\pi}$ (2)

Conjugated systems	Positions of interaction rs	$(\Delta E)_{R\pi}(\beta'/(\gamma^R)^2)$[*1] *syn*	*anti*	Favorable configuration
Case II. The reagent is ethylenic.				
Ethylene	1,2	0.0000	2.0000	*anti*
Allyl anion[*2]	1,3	2.4142	0.4142	*syn*
Butadiene	1,2	0.1056	1.8945	*anti*
	1,4	1.7889	0.4223	*syn*
Hexatriene	1,2	0.1500	1.8711	*anti*
	1,4	1.6560	0.4503	*syn*
	1,6	0.6218	1.6570	*anti*
Benzene	1,2	0.3333	1.4444	*anti*
	1,4	1.3333	0.4444	*syn*
Naphthalene	1,2	0.7668	2.0701	*anti*
	1,4	1.4491	0.4300	*syn*
Anthracene	1,2	0.2500	1.6036	*anti*
	1,4	1.4748	0.4243	*syn*
	9,10	1.6163	0.4041	*syn*
Pleiadiene[*3]	7,10	1.5269	0.4715	*syn*
Pleiadylene[*3]	5,8	1.4291	0.5330	*syn*

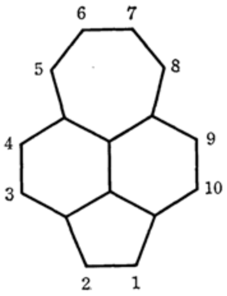
[*1] The values are calculated for the case of reagent of ethylene. $\beta'=0.3\beta$.

[*2] This case presents a model for the 1,3-dipolar additions (R. Huisgen, *Proc. Chem. Soc.*, **1961**, 357).

[*3] The numbering is:



Pleiadiene



Pleiadylene

TABLE V. THE FAVORABLE MODE OF CYCLIC INTERACTIONS AS BASED UPON $(\Delta E)_{R\pi}$ (3)

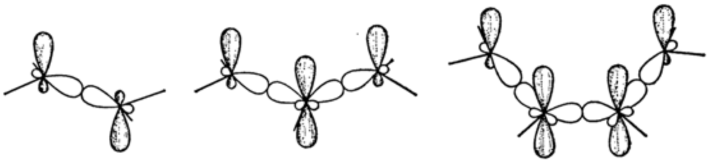
Conjugated systems	Positions of interaction rs	$(\Delta E)_{R\pi}(\beta'/(\gamma^R)^2)$[*1] *syn*	*anti*	Favorable configuration
Case IIIa. The reagent is an allyl cation.				
Ethylene	1,2	0.4142	2.4142	*anti*
Butadiene	1,4	2.7889	0.7889	*syn*
Case IIIb. The reagent is an allyl.				
Allyl	1,3	2.0000[*3]	0.0000[*3]	*syn*[*2]
Case IIIc. The reagent is an allyl anion.				
Ethylene	1,2	2.4142	0.4142	*syn*
Butadiene	1,4	0.7889	2.7889	*anti*
Naphthalene	1,4	0.7175	2.0508	*anti*
Anthracene	9,10	0.7245	2.7245	*anti*
Acenaphthylene	1,2	2.6915	0.4818	*syn*

[*1] $\beta'=0.3\beta$

[*2] This case corresponds to Cope rearrangements. The intramolecular rearrangements like that of *cis*-1,2-divinyl cyclobutane to cycloöcta-1,5-diene (cf. E. Vogel, *Ann.*, **615**, 1 (1958)) are also essentially a Cope rearrangement.

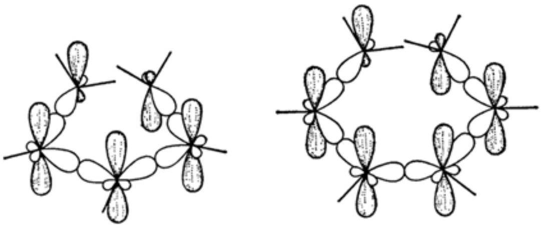
[*3] These values correspond to the first order terms, $2|c_r c_r' \pm c_s c_s'|$ between two half-occupied orbitals in γ^R.

(a) α, β-Interaction (b) α, γ-Interaction [allyl cation type] (c) α, δ-Interaction



(*trans*-noncycloaddition, *trans*-elimination) (S_N2' reaction) (noncyclic 1,4-addition)

(d) α, ε-Interaction [pentadienyl cation type] (e) α, ζ-Interaction



(S_N2' reaction) (noncyclic 1,6-addition)

Fig. 3. A schematic representation of favorable configurations in noncyclic two-center interactions of conjugated molecules.

tion of two independent reagents with each of two positions of the reactant conjugated system. To this group may belong additions, eliminations, substitutions, rearrangements, and so forth. In such a case, if we concentrate our attention on the qualitative direction of the configuration alteration, *syn-* or *anti-* in Fig. 2, it is evident that we need to compare the magnitudes of the term $(\Delta E)_{\sigma\pi}$ only, since $(\Delta E)_{R\pi}$ is as an approximation common in these two configurations. A qualitative determination of the preferable configuration may be possible by a comparison of $h_{tu}^{(syn)}$ and $h_{tu}^{(ant)}$ of Eq. 10.

α, β-Interaction.—The two carbon atoms under consideration, neighboring each other in a conjugated system, are designated as α and β. Let us take the ethylene molecule as an example. The values of $h_{12}^{(syn)}$ and $h_{12}^{(ant)}$ are 3.1194 and 5.5244 respectively; thus, they exhibit the predominance of *anti*-interaction.⁶⁾ This is consistent with a number of well-known experimental results of *trans*-noncycloadditions⁷⁾ and *trans*-eliminations.⁸⁾ The results for the α, β-interactions in other conjugated systems are listed in Table II (I); all of them demonstrate the *anti*-interaction to be favorable.⁹⁾

α, γ-Interaction.—Similarly, we can discuss the α, γ-interactions. The essential feature of S_N2' reactions is regarded as 1, 3-noncyclointeraction of the allyl cation type, because the leaving group takes off two electrons.* These reactions are known to proceed by means of a *syn*-configuration;¹⁰⁾ this is in accordance with the theoretical results obtained in Table II (II).

α, δ-, α, ε-, and α, ζ-Interactions. — These cases seem not yet to have been experimentally established. The theoretical results, however, predict the dominant configurations indicated in Fig. 3, a configuration which corresponds to the calculations of Table II (III, IV, V).

It may be noteworthy that, as is shown in Table II, the differences in the values of $h_{tu}^{(syn)}$ and $h_{tu}^{(ant)}$ become smaller as the two reaction centers become farther apart. Thus, in noncyclic 1, 6-additions, high stereospecificity is not to be expected.

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6) With respect to the MO-theory of the stereoselectivity of additions, see also K. Fukui, This Bulletin, **39**, 498 (1966).

7) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt & Co., New York (1959), p. 514, 732 ff.; B. A. Bohm and P. I. Abell, *Chem. Revs.*, **62**, 599 (1962).

8) E. Frankland, *J. Chem. Soc.*, **1912**, 654; D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953); see also many examples indicated by Gould Ref. 7.

9) The predominance of *trans*-addition has also been discussed as an orientation problem. See K. Fukui, *Tetrahedron Letters*, No. 28, 2427 (1965); see also a paper of the present authors to be published in the near future.

10) 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.) is grateful to Professor Stork for his private communication.

* The hybridized state of β-carbon is assumed to stay unchanged during the course of this reaction. A similar assumption is made in the discussion of other, more distant two-center interactions, and in cyclic cases.

Cyclic Two-center Interactions

The term "cyclic two-center interaction" signifies a chemical interaction corresponding to the transition state in which a conjugated reactant system interacts simultaneously at two positions with one "connected" reagent system. Thus, for instance, if we regard a diene in the Diels-Alder reaction as a conjugated reactant system, the associated dienophile is a reagent, while if we regard a dienophile as a conjugated reactant system, the associated diene is a reagent. The reagent is, of course, not necessarily a conjugated system; it may be any other system which is capable of interacting simultaneously with two positions of a conjugated system. It may be a proton in a protonated ethylene molecule, a phenyl cation in a phenonium ion, osmium tetroxide in an adduct to conjugated hydrocarbons, and so forth.[11]

MO-theoretical treatments for interactions of such a kind are not new.[12] To such treatments may belong the theoretical studies of the well-known Diels-Alder reaction, the Claisen and the Cope rearrangements, the 1, 3-dipolar cycloadditions, and so on. The significance of the symmetry of the highest-occupied (HO) MO and the lowest-vacant (LV) MO in the problem of selection rule for the Diels-Alder reaction was first pointed out by one of the present authors.[13] Hoffmann and Woodward discussed a similar selection rule for the occurrence of cycloadditions more generally, from the point of view of the MO symmetry conservation.[14]

The problem of the stereoselectivity of these reactions is presented in terms of $(\Delta E)_{\mathrm{R}\pi}$ and $(\Delta E)_{\sigma\pi}$ in Eq. 4. However, it seems likely that, in this cyclic case, $(\Delta E)_{\mathrm{R}\pi}$ is in general more determinative than $(\Delta E)_{\sigma\pi}$. The term $(\Delta E)_{\mathrm{R}\pi}$ in Eq. 8 is reduced to the following form:

$$(\Delta E)_{\mathrm{R}\pi}=\sum_{i}\sum_{l}\frac{\nu_i-\nu_l}{\varepsilon_i-e_l}\Bigl(\sum_{r}c_r^i d_{r'}^l\gamma_r^{\mathrm{R}}\Bigr)^2 \tag{11}$$

where ν_i and ν_l are the numbers of electrons occupying the ith and the lth MO in the reactant and the reagent systems respectively. The sigma-type overlap stabilization of this type has already been discussed in several papers.[13,15] Several important cases will now be treated.

Case I. The reagent orbital is a single s orbital:

(Ia) When the reagent orbital is vacant:

$$(\Delta E)_{\mathrm{R}\pi}=\sum_{i}\frac{\nu_i}{\varepsilon_i-e}(c_r^i\pm c_s^i)^2(\gamma^{\mathrm{R}})^2 \tag{12a}$$

(Ib) When the reagent orbital is half-occupied:

$$(\Delta E)_{\mathrm{R}\pi}=\frac{1}{2}\left\{\sum_{i}\frac{\nu_i}{\varepsilon_i-e}-\sum_{i}\frac{(2-\nu_i)}{\varepsilon_i-e}\right\}\times(c_r^i\pm c_s^i)^2(\gamma^{\mathrm{R}})^2 \tag{12b}$$

(Ic) When the reagent orbital is doubly-occupied:

$$(\Delta E)_{\mathrm{R}\pi}=-\sum_{i}\frac{2-\nu_i}{\varepsilon_i-e}(c_r^i\pm c_s^i)^2(\gamma^{\mathrm{R}})^2 \tag{12c}$$

where ν_i is the number of π electrons occupying the ith MO of the reactant system, and where r and s are the centers of interaction. It is assumed that the absolute values of γ_r^{R} and γ_s^{R} are equal in the transition state, so that the upper and lower signs in parentheses are for *syn*- and *anti*-interactions respectively.

Case I, in particular the hydrogen migration belonging to Case Ib, was very recently discussed theoretically by Woodward and Hoffmann from a different point of view.[16] By Eqs. 12a—c, the results listed in Table III are obtained for the favorable mode of interaction in the ground-state reactions. The stabilization in some "nonclassical" carbonium ions, and also such reactions as the proton or carbonium cation migration in protonated conjugated hydrocarbons or carbonium cations, are covered by Case Ia; similarly, anion migrations belong to Case Ic. The well-known experimental results so far available are consistent with the theoretical results.

The reagent orbital is frequently a single p orbital. Similar arguments can easily show that such an orbital, when it is vacant, is allowed to enter into interaction simultaneously with two π orbitals of the reactant, for which the most favorable configuration is demonstrated to be "*syn*" in Table III, Case Ia. The well-known

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[11] For the discussion of such cases, see also the description of *cis*-1, 2-addition in Ref. 6.

[12] See the many examples given, for example, in A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, New York (1961).

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

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

[15] K. Fukui, *Tetrahedron Letters,* No. 24, 2009 (1965); cf. also Refs. 4 and 6.

[16] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.,* **87**, 2511 (1965): These innovators have, no doubt, brought the first streaks of dawn into the field of theoretical stereochemistry through their elegant generalization (see Ref. 14 and also R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.,* **87**, 395 (1965)). However, from the quantum-chemical point of view, their papers seem to leave a few points open to criticism. One of the present authors has recently made a comment (Ref. 15). In their discussion of "sigmatropic" reactions (*J. Am. Chem. Soc.,* **87**, 2511 (1965)), to take another instance, they determined the expected steric course by considering only the highest-occupied orbital (HO) symmetry, even in excited states. As was pointed out in Ref. 15, such a discrimination of HO would require proper grounds. Thus, the results of the prediction of excited-state reactions would probably be unreliable. Excited-state radical reactions are mostly too complicated to be treated by simple MO theories. In the ground-state reactions, the prediction by HO symmetry only almost coincides with that which is made by Eq. 12b.

TABLE VI. THE FAVORABLE MODE OF CYCLIC INTERACTIONS AS BASED UPON $(\Delta E)_{R\pi}$ (4)

Conjugated systems	Positions of interaction rs	$(\Delta E)_{R\pi}(\beta'/\gamma^R)^2)^{*1}$		Favorable configuration
		syn	*anti*	
Case IV. The reagent is butadienic.				
Ethylene	1,2	1.7889	0.4223	*syn*
Butadiene	1,2	1.7441	0.4919	*syn*
	1,4	0.7155	1.7888	*anti*[*2]
Benzene	1,2	1.3333	0.6111	*syn*
Naphthalene	1,2	1.4540	0.5731	*syn*
	1,4	0.6577	1.4266	*anti*
Anthracene	1,2	1.4913	0.5627	*syn*
	1,4	0.6565	1.4599	*anti*

[*1] $\beta'=0.3\beta$

[*2] After E. Vogel (*Ann.*, **615**, 1 (1958)), cycloöcta-1,5-diene from catalytic dimerization of butadiene is not likely to come through the direct 1,4-1′,4′-interaction.

TABLE VII. THE FAVORABLE MODE OF CYCLIC INTERACTIONS AS BASED UPON $(\Delta E)_{R\pi}$ (5)

Conjugated systems	Positions of interaction rs	$(\Delta E)_{R\pi}(\beta'/(\gamma^R)^2)^{*1}$		Favorable configuration
		syn	*anti*	
Case V. The reagent is of the osmium tetroxide[*2,*3] type (including permanganate and manganate anions, MnO_4^- [*4] and MnO_4^{2-} [*5]).				
Ethylene	1,2	0.6317	0	*syn*
Butadiene	1,2	0.6095	0.0340	*syn*
	(1,4)	(0.1256)	(0.6025)	(*anti*)
Benzene	1,2	0.4449	0.1053	*syn*
Naphthalene	1,2	0.4934	0.0840	*syn*
Anthracene	1,2	0.5083	0.0784	*syn*
Phenanthrene	9,10	0.5318	0.0642	*syn*

[*1] $\beta'=0.3\beta$

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

[*3] These values are for the case of interaction with MnO_4^- (cf. C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York (1964), p. 126). In these cases, only the z-components of the two adjacent oxygen atomic orbitals of the degenerate highest occupied orbitals are tentatively taken for the simplicity of calculation. The lowest vacant orbitals which belong to E are in favor of *syn* interaction except the case of butadiene 1,4.

[*4] 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).

[*5] J. S. F. Pode and W. A. Waters, *J. Chem. Soc.*, **1956**, 717.

formation of phenonium ions and the singlet-state addition of carbenes, as well as the addition of atomic carbon to olefins,[17] which has recently been found, may involve this type of interaction.

When the reagent p orbital is half-occupied, too, the *syn* addition takes place if the symmetry relation is favorable. The formation of some epoxides, or the reaction with ozone may belong to this case.

Case II. The reagent orbitals are two bonding orbitals, which are equivalent to each other and which can enter into interaction with two orbitals of the reactant. Therefore, we have:

$$(\Delta E)_{R\pi} = \frac{1}{2}\left\{\sum_i \frac{\nu_i}{\varepsilon_i - e'}(c_r^i \mp c_s^i)^2 - \sum_i \frac{2-\nu_i}{\varepsilon_i - e}(c_r^i \pm c_s^i)^2\right\}(\gamma^R)^2 \qquad (13)$$

for the case of a reagent composed of two ethylenic π orbitals, where e and e' are the energies of bonding and antibonding orbitals respectively. The upper and lower signs stand for the *syn*- and *anti*-configurations respectively.

A comparison of the $(\Delta E)_{R\pi}$ values for two configurations of several conjugated systems indicates the dominant direction of change listed in Table IV; this is in agreement with our experience in dienes in Diels-Alder reactions, which belong to this case and which have already been treated by one of the present authors.[13] Excited-state reactions, in which the electron configuration of the reactant is assumed, can also be easily discussed in terms of Eq. 13.

Case III. The reagent orbitals are three

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[17] P. S. Skell and A. Y. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956); P. S. Skell and R. R. Engel, ibid., **87**, 1135, 2493 (1965).

allylic π orbitals, two terminal orbitals of which interact with two reactant π orbitals. The well-known Claisen[18a)] and Cope rearrangements[18b)] are examples of this case. The $(\Delta E)_{R\pi}$ values in Table V demonstrate that, in experimentally-known cases, the theoretically-favorable configuration is *syn*. The 1, 3-dipolar addition occurs at *cis*- with respect dipolarophiles.

Case IV. The reagent orbitals are butadiene-type π orbitals, two terminal orbitals of which interact with two reactant π orbitals. The theoretical results are listed in Table VI. The Diels-Alder reaction is known to take place at *cis* positions in dienophiles.

Case V. The reagent is of another type. The additions of osmium tetroxide, manganate and permanganate anions, and so forth involve transition states in which the reagent system is considered to belong to none of cases, I to IV. The values of $(\Delta E)_{R\pi}$ are calculable separately by Eq. 11, leading to the conclusions indicated in Table VII, which are consistent with experience.

Through all these cases of cyclic interactions, the spatial circumstances of the transition state evidently require *syn* interaction in order for the reaction actually to take place. Therefore, the conclusion obtained in Tables III—VII affords a stereoselection rule: *syn* stands for the "sterically-allowed" case, and *anti*, the "streically-forbidden."

The explanation as to why the dimerization of butadiene yields 1, 2-divinyl cyclobutane compounds only, and not 1, 3-divinyl compounds,[19)] is also an interesting example of Eq. 11, which gives a far larger $(\Delta E)_{R\pi}$ value for the formation of 1, 2- than 1, 3-divinyl compounds.

In all the cases mentioned above, we can easily see that the theoretical conclusion obtained from Eq. 11 for the ground-state reactions is in excellent agreement with that from the consideration of HO and LV only.[6)] These orbitals are nothing but the frontier MO's, which are known to play a significant role in various reactions of organic molecules.

Thus, Eq. 11 has a wide applicability to various other problems of reactivity in conjugated systems, problems which are too manifold to systematize in a single paper. Considerations of them are to be published henceforth in sequence.

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18) a) P. de Mayo, "Molecular Rearrangements," Interscience Publishers, New York (1963); b) E. N. Marvell, J. L. Stephenson and J. Ong, *J. Am. Chem. Soc.*, **87**, 1267 (1965).

19) E. Vogel, *Ann.*, **615**, 1 (1958).