Orbital Interaction in Three Systems

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Abstract: The three-system interaction theory previously developed for giving an orbital interaction rationale for the role of the catalysts is shown to cover various organic chemical reactions of both ground- and excited-state molecules. The mechanisms of thermal and photochemical multicycloadditions of layered compounds with olefins and the effects of protic acids and of substituents on symmetry-disfavored reactions are clarified, especially in connection with orbital phase relation. Bicyclic compounds with π bonds on each bridge are classified into three groups, i.e., electron-delocalizing, semielectron-delocalizing, and electron-localizing systems. The bridge flipping in such bicyclic compounds is also discussed.

Molecular orbital (MO) perturbation methods have played conspicuous roles in developing the theory of chemical reactions.[1-4] Further theoretical foundation and its application and extension have been made on the basis of the concept of configuration interaction.[5-10] Theories of organic chemical reactions thus far developed have been engaged in the two-system interaction, but a few have been engaged in the three-system interaction.[11] Recently the present authors have given a theoretical basis on which one can discuss mechanisms of metal-catalyzed reactions in a unified manner by taking a catalyst as one of the members of three interacting systems.[8] In the present paper the authors refine the procedure of deriving the orbital phase condition for stabilizing three systems, newly apply the theory to photochemical, thermal, and non-metal catalyzed reactions, and discuss the stabilization of bicyclic compounds with π bonds on each bridge.

Theory

Suppose that an eigenfunction of interacting system Ψ_I is approximately given by a linear combination of various configuration functions Φ_K's constructed from the MO's of isolated subsystems, A, B, and C:

$$\Psi_I = \sum_K C_K \Phi_K$$

The eigenvalue E_I of Ψ_I is approximately derived by expanding the secular equation at $E = H_{II}$ where the main configuration in Ψ_I is supposed to be Φ_I.

$$E_I = H_{II} + \sum_K \frac{|H_{IK} - S_{IK}H_{II}|^2}{H_{II} - H_{KK}}$$

$$+ \sum_K \sum_L \frac{(H_{IK} - S_{IK}H_{II})(H_{KL} - S_{KL}H_{II})(H_{LI} - S_{LI}H_{II})}{(H_{II} - H_{KK})(H_{II} - H_{LL})}$$

$$+ \ldots \quad (1)^8$$

The integrals, H_{MN} and S_{MN}, are defined as

$$H_{MN} = \int \Phi_M{}^* H \Phi_N \, d\tau$$

$$S_{MN} = \int \Phi_M{}^* \Phi_N \, d\tau$$

in which H is the total Hamiltonian operator of the whole system. From the condition that the third-order energy term contributes to stabilization, i.e.,

$$S_{IK}S_{KL}S_{LI} > 0 \quad (2)^8$$

the present authors have drawn the orbital-phase relation for energetically favorable modes of three-system interactions.[8]

There are two ways of dividing three systems by their roles. They are two donors and one acceptor in one way (case I), and two acceptors and one donor in the other way (case II). In case I the orbital phase relation for stabilization has been found[8] to be in phase (+) between the HOMO of donor A and the LUMO of acceptor C, in phase between the HOMO of donor B and the LUMO of acceptor C, and out of phase (−) between the (HOMO)$_A$ and (HOMO)$_B$, according to the convention (Figure 1). In case II each relation should be in phase between (LUMO)$_A$ and (HOMO)$_C$, between (LUMO)$_B$ and (HOMO)$_C$, and between (LUMO)$_A$ and (LUMO)$_B$ as depicted in Figure 1.[8] The orbital phase restriction comes out when one takes into consideration the interaction between the important transferred configurations besides the interaction of the initial configuration with them. The transferred configurations are obtained from the initial configuration by shifting an electron from the HOMO of either donor to the LUMO of the acceptor in case I, or from the HOMO of the donor to the LUMO of either acceptor in case II. The direction of the electron shifts is shown by the arrow in the donor-acceptor diagram in Figure 1. The dashed line shows that the interaction between the transferred configurations involves the HOMO-HOMO interaction between the donors in case I or the LUMO-LUMO interaction between the acceptors in case II.

The orbital phase condition in the excited-state interaction
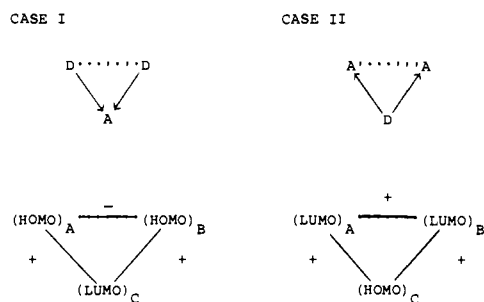
Figure 1. A conventional presentation of orbital-phase conditions for ground-state interactions.
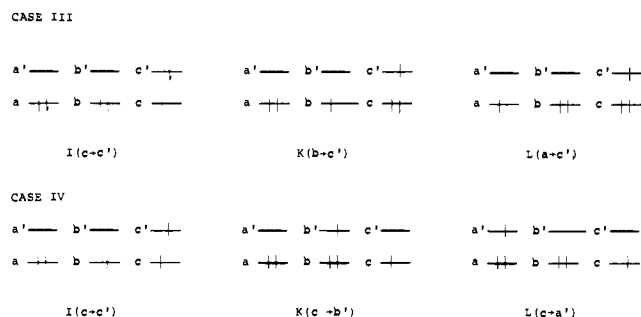
Figure 2. A simplified presentation of important configurations. Case III: excited molecule C is an acceptor. Case IV: excited molecule C is a donor.

Figure 3. A conventional presentation of orbital phase conditions for excited-state interactions.

is obtained similarly. Suppose that molecule C is excited electronically, two singly occupied MO's being denoted by SOMO and SOMO' (lower and higher ones in energy, respectively). The excited system acts as an acceptor through the interaction of the SOMO with the HOMO of the other system (case III), or as a donor through the interaction of the SOMO' with the LUMO of the other system (case IV). The configurations involved in the significant interaction are illustrated in Figure 2. The stabilization conditions in case III and case IV are given by

$$S_{c \rightarrow c', b \rightarrow c'} S_{b \rightarrow c', a \rightarrow c'} S_{a \rightarrow c', c \rightarrow c'} \simeq -s_{ab} s_{bc} s_{ca} > 0 \quad (3a)$$

$$S_{c \rightarrow c', c \rightarrow b'} S_{c \rightarrow b', c \rightarrow a'} S_{c \rightarrow a', c \rightarrow c'} \simeq s_{a'b'} s_{b'c'} s_{c'a'} > 0 \quad (3b)$$
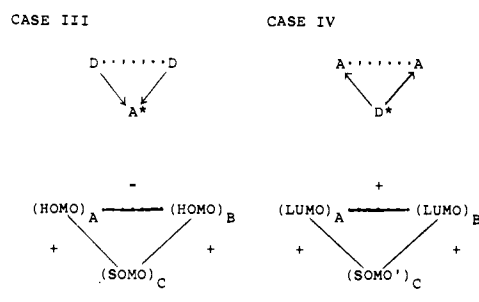
These conditions are visualized in Figure 3.

Summarizing the orbital phase condition for stabilizing three systems in both ground and excited states, one can obtain a rule.

Rule I: (A) The orbitals between which a partial electron is transferred, i.e., HOMO and LUMO, HOMO and SOMO, and LUMO and SOMO', should be combined in phase. (B) The HOMO's from which a partial electron is transferred to the LUMO or the SOMO of the third system should be combined out of phase. (C) The LUMO's to which a partial electron is transferred from the HOMO or the SOMO' of the third system should be combined in phase.

We consider the acyclic interaction among three systems. There are four typical interaction patterns, i.e., D–D–A, A–A–D, D–A–D, and A–D–A. The term "acyclic" is used to mean the absence of the direct MO overlap between the terminal systems.

The effect of three-system interaction is less appreciable in the acyclic case. This is shown by estimating the magnitude of the third-order energy in terms of the MO overlap order on the assumption that $H_{MN} - S_{MN}H_{II} \propto S_{MN} = o(s_{AB}{}^\lambda s_{BC}{}^\mu s_{CA}{}^\nu)$·where λ, μ, and ν stand for the minimum numbers of the electron shifts between A and B, between B and C, and between C and A required to obtain the electron configuration M from N.[7a,8,9] The third-order energy is estimated by the magnitude of $S_{IK}S_{KL}S_{LI}$ (see eq 1). In the cyclic in-

teraction $S_{IK}S_{KL}S_{LI} = o(s_{AB}{}^1 s_{BC}{}^1 s_{CA}{}^1)$ where I is the initial configuration, K and L being the important transferred configurations. In the acyclic interaction of the A–B–C system, $S_{IK}S_{KL}S_{LI} = o(s_{AB}{}^2 s_{BC}{}^2)$ since the overlap between a pair of the important configurations, approximated to be s_{CA} in the cyclic interaction, should be replaced by $s_{AB}s_{BC}$ because of $s_{CA} = 0$.[12] Accordingly, the third-order perturbation energy of interest is smaller in the acyclic interaction. As a result it may be said that the acyclic interaction of three systems is usually considered as two sets of the two-system interactions between the neighboring ones. The familiar consequences of the two-system interactions[1,7] can be applied to the acyclic interactions. The HOMO–LUMO interaction between the neighboring systems contributes most to electron delocalization or stabilization. The HOMO–HOMO interaction between them destabilizes the system through exchange repulsion. The LUMO–LUMO interaction has no effect since no electron is involved.

In a special case, however, there is a conspicuous effect peculiar to the three-system interaction even in the acyclic interaction. Suppose that the donor–acceptor relation between a pair of systems is so appreciable that the initial configuration and a transferred configuration (denoted by D) are nearly degenerate ($H_{II} \simeq H_{DD}$). Then one can obtain a new type of perturbation energy term[9]

$$\sum_K \frac{|H_{DK} - S_{DK}H_{DD}|^2}{H_{DD} - H_{KK}} \quad (4)$$

which has the same form as the second-order energy term in the nondegenerate case. This shows that both I and D contribute equivalently in the degenerate case. The perturbation energy term 4 is chemically of great importance.

The D–D–A and the A–A–D systems, in which the donor–acceptor relation between a D–A pair is significant, appreciably gain the additional stabilization (the term 4) through the HOMO–HOMO interaction between D's and the LUMO–LUMO interaction between A's, respectively, while the corresponding D–A–D and A–D–A systems do not. The important configurations, D and K, contained in the energy term 4, are visualized in Figure 4. In the D–D–A interaction pattern they are two transferred configurations where an electron is shifted from the HOMO of either of the D's to the LUMO of A. The configuration interaction involves the HOMO–HOMO interaction between D's. The key orbital interaction is depicted on the right of the important configurations in Figure 4. In the A–A–D interaction pattern the important configurations are the transferred ones where an electron is shifted from the HOMO of D to the LUMO of either of the A's. The configuration interaction involves the LUMO–LUMO interaction between A's. In the above cases the important configuration interactions are both reduced to the key orbital interaction between the neighboring systems. In D–A–D or A–D–A the important configuration interactions are, however, reduced to the orbital interactions between the

terminal systems; the HOMO–HOMO interaction between the terminal D's in D–A–D and the LUMO–LUMO interaction between the terminal A's in A–D–A do not occur efficiently on account of the special separation. As a result, one may say the following with respect to the ground-state interaction:

Rule II: In the acyclic D–D–A or A–A–D systems where the donor–acceptor relation between the neighboring D–A pair is significant, the HOMO–HOMO interaction between D's or the LUMO–LUMO interaction between A's appreciably contributes to the stabilization.

The "abnormal" stabilization through the HOMO–HOMO interaction or through the LUMO–LUMO interaction is attributed to the SOMO-like property of the HOMO having released electrons or the SOMO′-like property of the LUMO having accepted electrons. Such stabilizing HOMO–HOMO and LUMO–LUMO interactions have also been recognized in the bimolecular interactions involving pseudoexcitation.[9,10]

The stabilization of the acyclic three-system interactions does not depend on the sign relation among the particular orbitals involved, although the orbital phase continuity between each pair of the neighboring systems should be satisfied if the cyclic conjugation occurs between the two. This is evident. There are no energy terms relating the signs of three orbitals significantly involved in the acyclic interaction. There is no orbital overlap between the terminal systems.

Rule II is here given in another way. The method rests on the procedure of sequential orbital interactions. In usual cases the HOMO of the D–A system is composed of an out-of-phase combination of the HOMO's of D and A, and the LUMO of the D–A system is composed of an in-phase combination of the LUMO's of D and A. In the D–D–A the interaction between the HOMO of the terminal D and the LUMO of the D–A is important. The interaction involves the HOMO–LUMO interaction between D's. In the A–A–D the interaction between the LUMO of the terminal A and the HOMO of the D–A is important. The interaction also involves the HOMO–LUMO interaction between A's. The HOMO–LUMO interaction between the adjacent systems is similarly found to be important in A–D–A and D–A–D. The situation changes when the donor–acceptor relation is significant between the neighboring D–A pair. In this case the HOMO and the LUMO of D–A are composed of an in-phase and an out-of-phase combination of the HOMO of D and the LUMO of A, respectively. The important interaction between the HOMO of the terminal D and the LUMO of D–A in D–D–A involves the HOMO–HOMO interaction between D's. The important interaction between the LUMO of the terminal A and the HOMO of D–A in A–A–D involves the LUMO–LUMO interaction between A's. The interaction between the HOMO of D and the LUMO of A–D in D–A–D and the interaction between the LUMO of A and the HOMO of D–A in A–D–A involve the HOMO–LUMO interaction between the neighboring D and A.

In the excited-state interactions the donor–acceptor relation between an excited molecule and a ground-state molecule is expected to be significant even in usual cases since the SOMO or an originally doubly occupied orbital demands electrons strongly, and since the SOMO′ or an originally unoccupied orbital readily releases electrons. The excited molecule is relatively strong donor (D*) or acceptor (A*). Therefore, there may also be a similar effect peculiar to the three-system interaction even in the acyclic interaction.

Rule III: In the acyclic D–D–A* or A–A–D* excited-state interactions the HOMO–HOMO(–SOMO) interaction or the LUMO–LUMO(–SOMO′) interaction contributes to stabilization and to bond formation between D's or A's.

Application and Exemplification

(I) Cyclic Interaction. The orbital phase condition derived
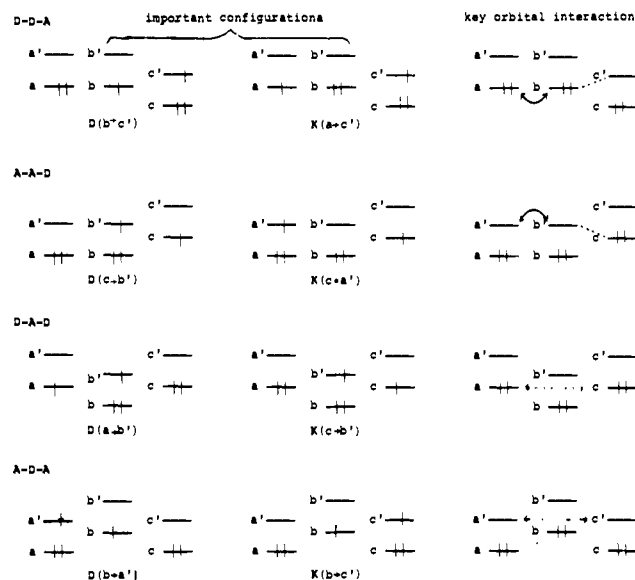
Figure 4. A simplified presentation of important configurations and key orbital interactions peculiar to acyclic three-system interaction with remarkable donor–acceptor relation.

from the third-order perturbation energy is compatible with the Woodward–Hoffmann rule.[13] The merit of the three-system interaction scheme developed here consists in allowing one to consider the interaction on the basis of each functional group, and to take into account the detailed aspect of chemical reactions through the donor–acceptor property of the interacting entities. One can find some suitable examples in the following reactions.

Homo–Diels–Alder Reactions.[13] Diels–Alder reactions have been interpreted as simultaneous bond-forming processes. The interactions between the HOMO of diene and the LUMO of dienophile and between the LUMO of diene and the HOMO of dienophile are favored by the symmetries of the particular orbitals. It seems more appropriate to interpret homo-Diels–Alder reactions in terms of the three-system interaction among two π bonds in diene and a π bond in dienophile since in all homo-dienes the double bonds do not interact with each other so strongly that the two π bonds are taken as a single functional group. In eq 5 is depicted one of the particular orbital sets, the

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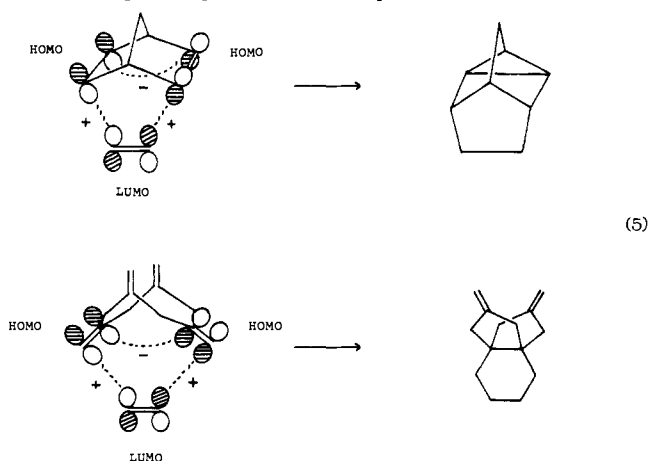
HOMO's of the π bonds in diene and the LUMO of dienophile. The interaction among the HOMO of dienophile and the LUMO's of the π bonds in diene is formally possible. Such "inverse" homo-Diels-Alder reactions have not been reported as yet.

The out-of-phase combination between the HOMO's does not stand for the repulsive force between the π bonds. Although the HOMO–HOMO interaction usually causes only exchange

repulsion in the case of interaction between the two systems, the HOMO-HOMO interaction in the three systems contributes to stabilization under the influence of the third system. The stabilization may be attributed to a SOMO-like property of the original HOMO's resulting from the partial electron release to the LUMO of the third system.

Cope Rearrangements.[14,15] The merit of the three-system interaction theory is unquestionable when the orbital phase aspect of Cope rearrangement is considered in terms of orbital interaction. Two orbital interaction schemes were thus far required to understand the mechanism of Cope rearrangements in detail: one for the orbital interaction weakening the C-C σ bond to yield a pair of allyl fragments and the other for the interaction stabilizing the transition state.[1e] According to the three-system interaction theory, the nature, especially the orbital phase aspect, of Cope rearrangements is simply described by a single scheme of the interaction among the HOMO's of the two π bonds and the LUMO of the σ bond, or among the LUMO's of the π bonds and the HOMO of the σ bond. Only cyclic (HOMO, HOMO, LUMO) interaction is depicted here.


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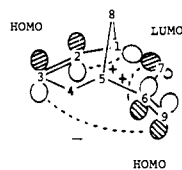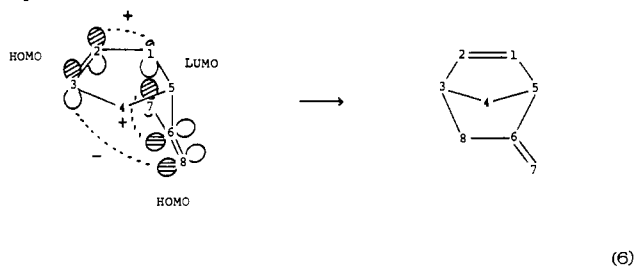
2,3-Sigmatropic Shifts.[13,17,18] The mechanism of 2,3-sigmatropic shifts is also better interpreted as an interaction among three functional groups. The HOMO of the lone pair or something like this, the LUMO of the π bond, and the LUMO of the σ bond may interact most significantly since the ability of the lone pair to donate electrons may be the most prominent. The cyclic (HOMO, LUMO, LUMO) interaction scheme depicted here implies that the rearrangements begin with the simultaneous charge transfers from the HOMO of the lone pair to the LUMO of the π bond (nucleophilic attack) and to the LUMO of the σ bond (weakening of the σ bond), accompanying the interaction between the transferred configurations or the LUMO-LUMO interaction between the π bond and the σ bond (formation of a new π bond) (eq 7).

Ene and Retroene Reactions.[18,19] One feels inclined to draw from the Woodward-Hoffmann rule the concerted property of ene and retroene reactions since both reactions involve six electrons in the cyclic interactions. Indeed, the AO sign relation of the HOMO and the LUMO of alkyl olefins is suitable for simultaneous interaction with unsaturated species at either reacting site. However, the particular orbitals of alkyl olefins have too small an amplitude at the C-H site to cause an effective cyclic interaction. An intermediary mechanism between the concerted and the two-step mechanisms has been proposed; at an initial stage a cyclic three-centered interaction occurs among the p orbitals of the π bond of alkyl olefins and a p orbital of an electrophilic center of the reaction partner, and then the transient three-membered ring collapses with hydrogen transfer and the π bond shift.[20] The mechanism is here reinterpreted in terms of the three-orbital interaction among the


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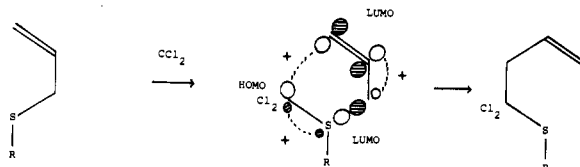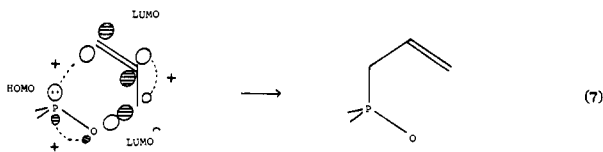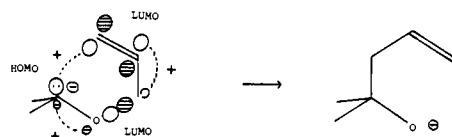
HOMO of the π bond in the alkyl olefin, the LUMO of the π bond of the reaction partner, and the LUMO of the C-H bond of the olefin. The interaction scheme implies that the partial electron transfer from the π HOMO of the alkyl olefin to the LUMO of the attacking species is sequentially followed by "back donation" from the LUMO having accepted electrons to the LUMO of the C-H bond, or that the charge transfers from the HOMO of the π bond of the olefin intermolecularly to the LUMO of the reaction partner and intramolecularly to the LUMO of the C-H bond accompany the interaction between the LUMO's having accepted electrons. The intramolecularly transferred configuration is an excited configuration. The ground-state process where an excited configuration of one or both reactants is involved significantly was previously referred to as pseudoexcitation.[9] The reactions accompanying pseudoexcitation proceed by an intermediary mechanism between typical concerted and two-step mechanisms even if the high stereoselectivity happens to be observed.


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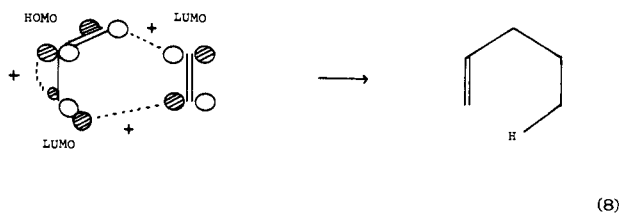
Isomerization of Alkyl-Substituted Three-Membered Ring Dipolar Species.[21] Alkyl derivatives of aziridine N-oxide or episulfoxide rearrange to the allylic compounds through an intramolecular abstraction of an alkyl hydrogen by the oxygen atom (Y) accompanying the C-X bond cleavage. A nucleophilic attack of the negatively charged oxygen atom on the C-H hydrogen is unquestionably one of the important interactions. From the prominent ability of the oxygen lone pair to donate electrons the cleaving C-X bond is expected to act as an acceptor toward the lone pair. The cyclic (HOMO, LUMO, LUMO) interaction is depicted here.

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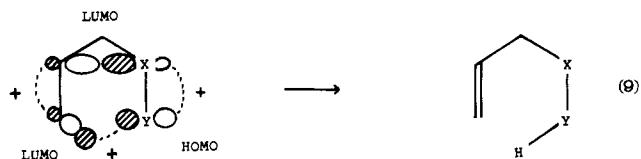
Degenerate Isomerization of Snoutene.[22] This is also a typical reaction of three bonds. The orbital interaction scheme is better described as a three-system interaction rather than any two-system interactions. Here the HOMO of the π bond and the LUMO's of the σ bonds are used in the illustration, although the quantitative evidence is not available for the preference over the cyclic interaction among the HOMO's of the σ bonds and the LUMO of the π bond.

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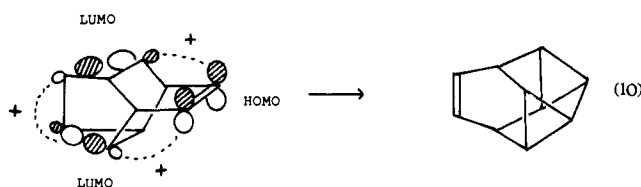
Intramolecular Nucleophilic Substitution.[23] This process is almost unique in that it sometimes results in retention of configuration about the α carbon atom. The simultaneity of the bond interchange is not so complete as that of typical concerted reactions, for example, Diels-Alder reactions. However, the reaction is considered to take place through a four-centered transition state. Here an orbital interaction scheme is depicted for the transition state. The C–O bond and the S–Cl bond are weakened. The slightly negatively charged chlorine is bound to the positively charged carbon. The key orbitals should be the HOMO of chloride ion, and the LUMO's of the carbonium cation and the SO_2 part. The intramolecular nucleophilic substitution reaction of chroloformate is explained similarly.


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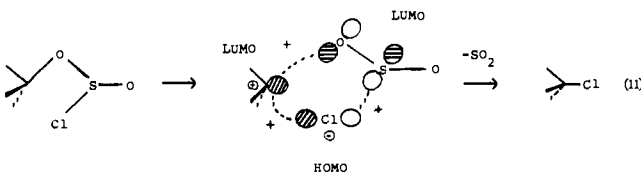
Insertion of Sulfur Dioxide into a Metal–Carbon Bond.[24] Interestingly, the insertion of SO_2 into the Fe–R bond of $(\eta^5$-ring)Fe(CO)$_2$R results in inverting the configuration at the α carbon of alkyl R. The observed rate dependence on the nature of R suggests that the cleavage of the Fe–R bond is a heterolytic process caused by the back-side attack of SO_2 on the α carbon of R and that a contact ion pair forms. One reasonably imagines the process as follows; at first the interaction between the bonding orbital of the Fe–R bond and the LUMO of sulfur dioxide (with the largest amplitude at sulfur) weakens and lengthens the Fe–R bond with the charge separation between the iron and the carbon, and a sequential interaction among the HOMO of the anionic carbon, the LUMO of the cationic iron, and the LUMO of sulfur dioxide stabilizes the transition state. It is interesting that the orbital interaction scheme is quite similar to that of the intramolecular nucleophilic substitution.


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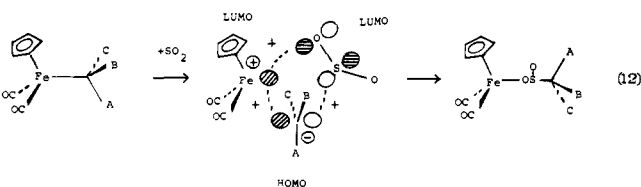
Di-π-methane Rearrangement.[25] The photochemical conversion of 1,4-dienes to vinylcyclopropanes, known as di-

π-methane rearrangement, proceeds with stereospecificity. The configuration integrity about the π bond in the migrating moiety (C_4=C_5) is maintained; the substituents at C_5 cis and trans to the C_3–C_4 bond in the reactant are ones cis and trans to the C_2–C_4 bond in the product, respectively.[25b] With respect to ring closure between C_1 and C_3 there exists a strong preference for occurring at the side anti to the migrating π bond,[25c,d] with inversion of configuration at the methane carbon (C_3).[25e]

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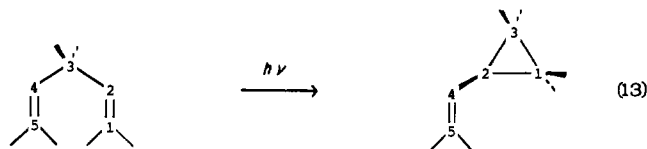
The observed stereochemistry of the products of the di-π-methane rearrangements is compatible with the two-system interaction scheme (1). The key parts are the π bond and the σ bond that are broken during the reaction. However, an inevitable question comes into our minds. Why does the C_4=C_5 π bond remain intact through the process? We believe that the π orbital seemingly not involved plays a significant role, as Zimmerman has noted. In fact, it has been demonstrated that neither the singlet nor the triplet of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene (monoene) rearranged in the di-π-methane-like fashion.[26]
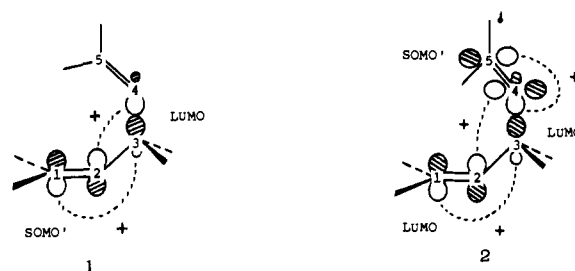
The interaction involving the C_4=C_5 π bond is best described by the three-system interaction scheme (2). An electron in the SOMO' of a π bond first delocalizes to the other π bond through the interaction with the LUMO between C_2 and C_4. The interaction causes folding of the structure of the di-π-methane. The geometrical change necessarily involves the bending of one or both of the C_2–C_3 and the C_3–C_4 σ bonds out of the incipient three-membered ring. The direction of the bending is both geometrically and from the viewpoint of orbital phase continuity suitable for the cyclic (SOMO', LUMO, LUMO) interaction involving the LUMO of the C_3–C_4 σ bond or the LUMO of the C_2–C_3 σ bond (the former case is depicted in 2). The C_4 front-side lobe of the σ LUMO interacts with the C_5 exo lobe of the π SOMO' to accept electrons. The C_3 back-side lobe of the σ LUMO interacts with the C_1 exo lobe of the π LUMO.

As a result the three-orbital phase condition is completely compatible with the smooth change of the geometry required to account for the stereochemistry of the di-π-methane rearrangement. This conclusion is also obtained from the cyclic (HOMO, HOMO, SOMO) interaction.

In the above discussion the interaction between the π SOMO' and the π LUMO has been described as preceding the others. The separate discussion on the orbital interactions comes mainly from the convenience. It is likely that the di-π-methane rearrangement may occur through the sequential interactions, and that one interaction between a subsystem pair never begins after another is completed. Otherwise, one should have concluded a randomization of the stereochemistry.

The orbital interaction scheme for the di-π-methane rearrangement is applicable to similar rearrangements of dienones and bicyclo[3.2.1]octa-2,6-diene (eq 14).[27]

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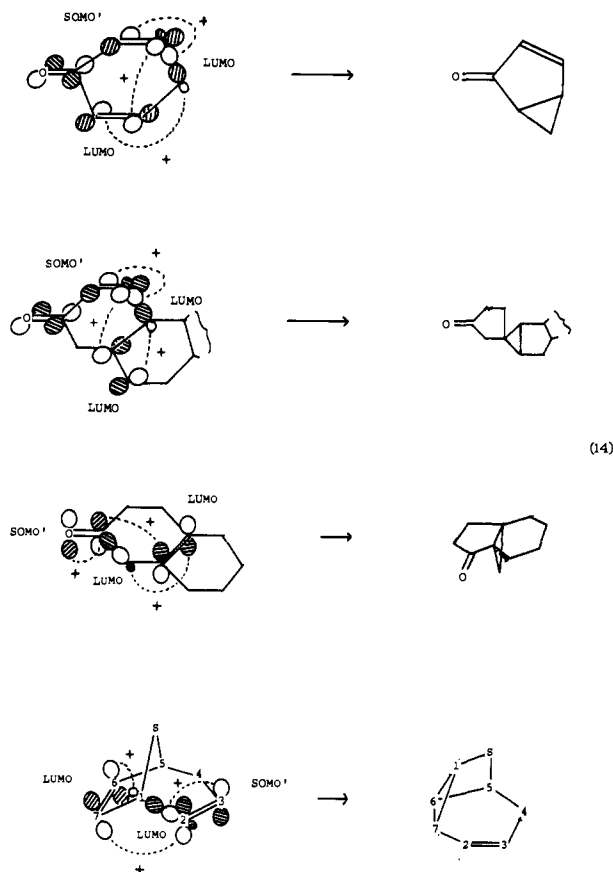
Stabilization of Bicyclic π-Conjugate Molecules. The interaction of π bonds in bicyclic compounds (3) is suitably treated on the basis of the three-system interaction theory. It will be shown that such bicyclic compounds may be classified into the three groups electron-localizing (4), semielectron-delocalizing (5), and electron-delocalizing (6) systems. They
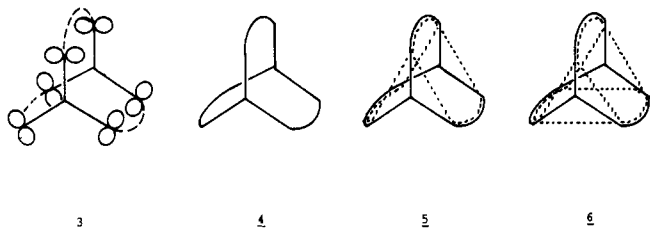
have been divided into the two classes, stabilized or destabilized systems, in the pioneering work of Goldstein and Hoffmann.[11a,b] A rationale for the bridge flipping will also be given by the present theory.

The bicyclic compounds in which each HOMO-LUMO interaction is symmetry disfavored between any π-system pair are classified as electron localizing (4). The systems in which the HOMO-LUMO interaction is symmetry favored between two pairs of π systems yield the other two classes. The compounds dissatisfying and satisfying the three-orbital phase condition (rule I) are referred to as semielectron-delocalizing (5) and electron-delocalizing (6) systems, respectively.

An important corollary, closely related to the bridge flipping, follows from rule II. Some semielectron-delocalizing and electron-delocalizing molecules can be distorted in favor of the HOMO-LUMO interaction at the expense of the other. Such geometrical change implies a shift of the interaction pattern from the cyclic (D, D, A) or (A, A, D) to the acyclic D–D–A or A–A–D. The HOMO-LUMO interactions between D's and between A's are disfavored by the orbital symmetry in 5 or 6. Accordingly, no additional stabilization is usually expected to come from the interaction between D's or A's. The

HOMO-HOMO interaction between D's and the LUMO-LUMO interaction between A's are favored by the symmetry property. If these interactions contribute to stabilization, the acyclic D–D–A and A–A–D are more likely to be stable relatively. This is the case with the bicyclic compounds where the donor–acceptor relation is significant between a D–A pair.

Corollary: The HOMO-HOMO(-LUMO) interaction between D's and the LUMO-LUMO(-HOMO) interaction between A's contribute, at least in part, to transforming the symmetrical structure of electron-delocalizing and semielectron-delocalizing compounds with a significant D–A pair into the distorted structure.

The electron-delocalizing 7-norbornadienyl cation 7 is known to adopt an unsymmetrical structure[28-31] represented by 8.[32] This is explained in the corollary. The introduction of a second double bond in the norbornane framework causes a further rate enhancement for ionization at C_7 of 10^3 relative to the already anchimerically accelerated *anti*-7-norbornenyl derivative.[29,30] The degree of rate enhancement is smaller than that of the effect of the introduction of the first π bond (10^{11}),[29,33] The additional rate enhancement is here interpreted to come from the HOMO-HOMO interaction between the π bonds. If the HOMO-HOMO interaction does not contribute to stabilization, the solvolysis rate of 7-norbornadienyl derivatives must be comparable to that of *anti*-7-norbornenyl derivatives since in the distorted 7-norbornadienyl cation there is no significant interaction but one between the HOMO of a π bond and the LUMO of the ionizing center, common to *anti*-7-norbornenyl cation.
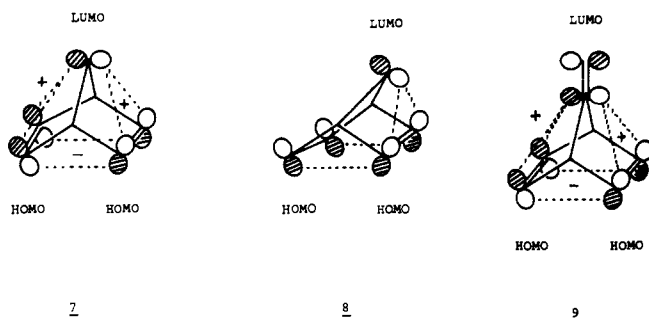
7-Methylenenorbornadiene (9) is also an electron-delocalizing system. Comparable interactions between the vinylene bridges and the C_7 p orbital are expected from the experimental results.[34] The donor–acceptor relation between any pairs of subsystems is too ambiguous to cause bridge flipping.[35] The observed dipolar (negative terminus at C_8)[34] supports the orbital interaction scheme.

A typical semielectron-delocalizing system is 4-bicyclo[3.2.2]nonatrienyl anion 10. Although the two-system interactions between the HOMO of the allyl anion moiety with the LUMO's of the double bonds are favored by the symmetry property, 10 is not favored by the three-orbital phase condition.
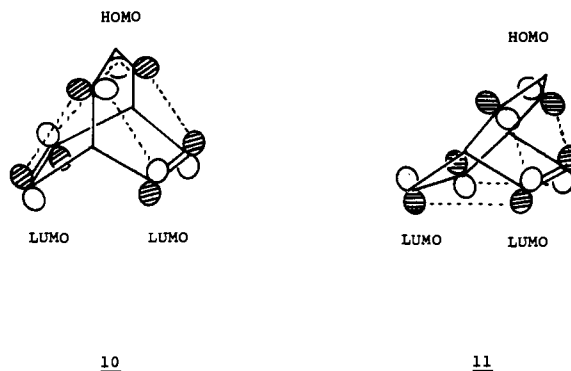
There is a possibility that the anion **10** undergoes such bridge flipping (**11**) as **7** since the donor–acceptor relation is significant between the allyl anion and the π bonds. If there are some factors preventing the bridge flipping, an important one may be an exchange repulsion between the symmetrical lowest lying π orbital of the allyl fragment and the HOMO of the double bond. Electron delocalization has been shown to occur to an appreciable degree.[36] No convincing evidence for a symmetrical or unsymmetrical equilibrium geometry is available now.

7-Norbornadienyl anion (**12**),[37] barrelene (**13**),[38] and bicyclo[3.2.2]nonatrienyl cation (**14**)[39] are electron-localizing
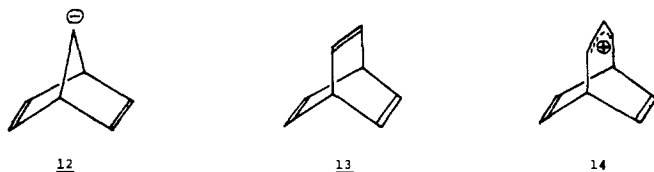
systems. These molecules have been classified by Goldstein and Hoffmann[11b] as the systems that are not stabilized.

Unfortunately, no evidence for or against the practical significance of the classification into the electron-delocalizing and the semielectron-delocalizing systems is available now. Experimental efforts on this problem are to be expected.

It would be meaningful to refer to an essential difference between such an aromatic compound as benzene and the electron-delocalizing bicyclic compounds. Electron delocalization in **6** occurs through the interaction among a set of three particular orbitals as depicted. On the other hand, there are many sets of electron-delocalizing orbital interactions in the aromatic hydrocarbons. For example, in a hypothetical compound, cyclohexatriene, there are six sets of three-orbital interactions.


(15)
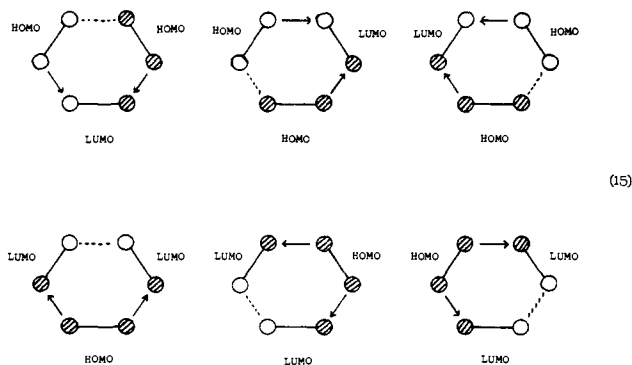
Thus, the degree of electron delocalization is remarkably different between the electron-delocalizing systems **6** and the aromatic compounds.

The present method is different from the Goldstein and Hoffmann's method[1a,b] of treating bicyclics in the procedure and in the conclusion. Their procedure begins by first permitting two of the systems to interact. The resulting composite orbitals are then allowed to interact further with orbitals of the third system. According to our findings one can draw the stabilization condition directly from the donor–acceptor property of each system and the symmetry property of the particular orbitals. In conclusion, the discrimination of the electron-delocalizing **5** from the semielectron-delocalizing **6** system is neglected and both are classified as the stabilized systems. It is in question whether the 7-norbornadienyl cation (**7**) and bicyclo[3.2.2]anion (**10**) are both stabilized (0,2,2) systems. In **7** the HOMO of the combined system of the two π bonds is favored by the orbital phase to interact with the LUMO of the cationic center at the 7 position, while in **10** the LUMO of the combined system of the two π bonds is not favored by the or-

bital phase to interact with the HOMO of the allyl anion fragment.

Quadricyclyl Ions. Quadricyclyl cation and anion are taken as being composed of three functional groups, two cyclopropane rings, and an ionic center. The important orbitals in the cation are obviously the HOMO's of the cyclopropane parts and the LUMO of the cation (**15**). Those orbitals in the anion
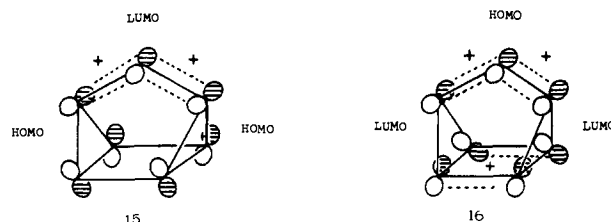

are the LUMO's of the cyclopropane parts and the HOMO of the anionic center (**16**). Both ions are stabilized by the HOMO–LUMO interactions between the ionic center and each cyclopropane ring. However, the cyclic (HOMO, HOMO, LUMO) three-system interaction in the cation does not meet the orbital phase requirement while the cyclic (HOMO, LUMO, LUMO) interaction in the anion is favored by the orbital phase requirement (rule 1). These properties suggest that quadricyclyl cation (with two cyclopropane rings) may be more stabilized than nortricyclyl cation (with one cyclopropane ring) owing to the HOMO–LUMO interaction between each cyclopropane ring and the cation center, but that the destabilization from the cyclic three-system interaction partially diminishes the stabilization.

Loew and Wilcox[40] considered the orbital interaction between the two parts, cyclopropane and cyclopropylcarbinyl cation, and answered the problem that the second cyclopropane provides a mere 20-fold solvolysis rate increase whereas the strict additivity of stabilization energies would dictate 6×10^8-fold enhancement relative to the nortricyclyl system. Although no experimental data are now available for showing the relative stabilities of 7-norbornanyl, nortricyclyl, and quadricyclyl anion, one may say the stabilization by the second cyclopropane ring exceeds the stabilization by the first cyclopropane ring since the cyclic (HOMO, LUMO, LUMO) interaction is stabilizing in contrast to the cyclic (HOMO, HOMO, LUMO) interaction in the cation.

(II) Acyclic Interaction. The interaction in the A–B–C system where A and B, and B and C interact but A and C do not interact is approximately taken as the two independent A–B and B–C interactions in usual cases (see the theoretical section). The stabilization of such systems can be roughly discussed in terms of the HOMO–LUMO interactions between the neighboring systems. The HOMO–HOMO interaction between the D's in the D–D–A system and the LUMO–LUMO interaction between A's in the A–A–D system contribute to stabilization, appreciable as the donor–acceptor relation is significant between the D–A pair (rule II). This "abnormal" effect has been proposed to be an important electronic factor of bridge flipping of the bicyclic compound **3**. The stereochemical courses of some catalyzed "symmetry-forbidden" reactions such as Ag+-catalyzed electrocyclic reactions and valence isomerization of strained cage compounds and 1,3-sigmatropic rearrangements were also elucidated similarly.[8] Here the important role of the HOMO–HOMO or the LUMO–LUMO interaction in the presence of the third entity interacting with one of them will be exemplified by the thermal and the photochemical reactions and by the nonmetal-catalyzed reactions.

Multicycloaddition Reactions. Interesting cycloaddition reactions have recently been observed in the thermal reactions of paracyclophadiynes with an electron-demanding olefin,

tetracyanoethylene (TCNE),[41] and in the photochemical reactions of [10][9.10]anthracenopha-4,6-diyne with furan (X = O) or cyclopentadiene (X = CH$_2$).[42] The thermal reaction is understood in terms of the interaction among the HOMO of the benzene ring, the HOMO of the diyne part, and the LUMO of TCNE.[32] It should be noted that the bond formation between the benzene ring and the diyne part is not favored by the HOMO-LUMO symmetry properties. A highly electron-deficient TCNE attacking the diyne allows the HOMO-HOMO interaction between the diyne part and the benzene ring to contribute to the stabilization and the bond formation between them (rule II). The photochemical multicycloaddition reactions are also understood along the line of rule III in a similar manner. The key orbital interaction is one among the SOMO' of the anthracene part, the LUMO of the diyne, and the LUMO of cyclopentadiene, or among the SOMO of the anthracene, the HOMO of the diyne, and the HOMO of cyclopentadiene.[32]
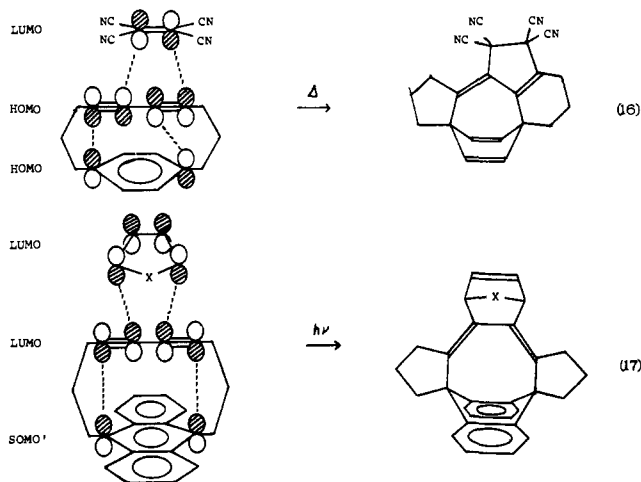
Anchimeric Assistance in Solvolysis. A remarkable additional anchimeric assistance by a remote double bond through conjugation with the double bond directly interacting with the ionizing center has been observed in the solvolysis of **17**.[43] The remote double bond makes **17** ca. 10^3 times more reactive than related *anti*-7-norbornenyl systems. This may also be ascribed to the stabilizing HOMO-HOMO interaction between the double bonds (rule II).[32]
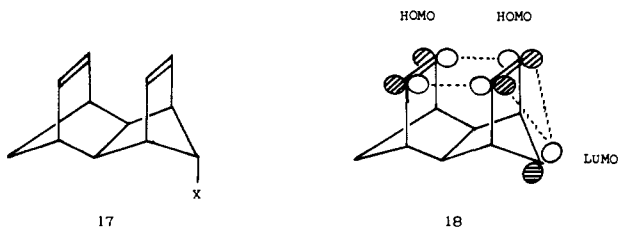

Acid-Catalyzed Cycloreversion Reaction. In a cage compound, a cyclobutane ring with an adjacent carbonyl group has been reported to undergo 2 + 2 cycloreversion in the presence of trifluoroacetic acid.[44] This symmetry-disfavored transformation can be completely explained by rule II. In this case, a protonated carbonyl group works as a strong acceptor[45] to
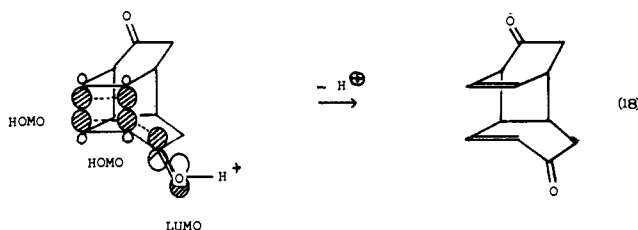
allow the HOMO-HOMO interaction to be bonding between the σ bonds.[32]

A Substituent Effect on Symmetry-Disfavored Reaction. Another interesting symmetry-disfavored reaction has been observed. The thermal 1,3-sigmatropic shift in an olefin with electron-demanding cyano groups takes place with 90% retention of configuration at the migrating carbon center.[46] Usual thermal 1,3-sigmatropic shifts are interpreted in terms of the cyclic HOMO-LUMO interaction between the double bond and the σ bond. The cyano substituents, although they do not take part in the cyclic interaction directly may have influence through the interaction with a member of the cycle. One may expect according to rule II that the HOMO-HOMO interaction between the double bond and the σ bond is appreciably stabilizing under the influence of the interaction between the HOMO of the σ bond and the LUMO of the cyano groups.[32,47]
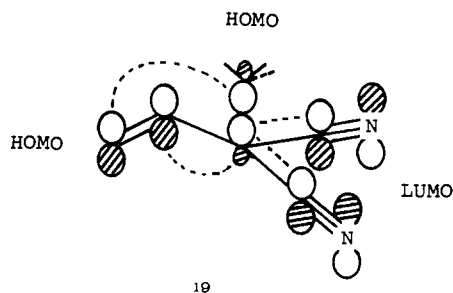
References and Notes

(1) (a) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology", P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, p 513, and references cited therein; (b) K. Fukui, "Modern Quantum Chemistry", O. Sinanoglu, Ed., Vol. 1, Academic Press, New York, N.Y., 1965, p 49; (c) K. Fukui and H. Fujimoto, "Mechanisms of Molecular Migrations", Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1969, p 118; (d) K. Fukui, "Theory of Orientation and Stereoselection", Springer-Verlag, Heidelberg, 1975; (e) K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971).
(2) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
(3) L. Salem, *J. Am. Chem. Soc.*, **90**, 543, 553 (1968).
(4) (a) W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972); (b) R. F. Hudson, *Angew. Chem.*, **85**, 63 (1973); (c) J. D. Bradley and G. C. Gerrans, *J. Chem. Educ.*, **50**, 463 (1973); (d) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).
(5) (a) J. N. Murrell, M. Randić, and D. R. Williams, *Proc. R. Soc. London, Ser. A*, **284**, 566 (1965); (b) J. N. Murrell and G. Shaw, *J. Chem. Phys.*, **46**, 1768 (1967).
(6) R. Rein and M. Pollak, *J. Chem. Phys.*, **47**, 2039 (1967).
(7) (a) K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jpn.*, **41**, 1989 (1968); (b) K. Fukui, *Int. Congr. Pure Appl. Chem. 23rd*, **1**, 65 (1971); (c) H. Fujimoto and K. Fukui, *Adv. Quantum Chem.*, **6**, 177 (1972).
(8) K. Fukui and S. Inagaki, *J. Am. Chem. Soc.*, **97**, 4445 (1975).
(9) S. Inagaki, H. Fujimoto, and K. Fukui, *J. Am. Chem. Soc.*, **97**, 6108 (1975).
(10) N. D. Epiotis, *Angew. Chem., Int. Ed. Engl.*, **13**, 751 (1974), and his preceding papers. Some models employed in his discussion are unlikely.[9,20]
(11) (a) M. J. Goldstein, *J. Am. Chem. Soc.*, **89**, 6357 (1967); (b) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971); (c) H. Fujimoto, S. Kato, S. Yamabe, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **46**, 1071 (1973); (d) F. Bernardi, N. D. Epiotis, and R. L. Yates, *J. Am. Chem. Soc.*, **97**, 1334 (1975).
(12) In the D-D-A system the overlap integral between the initial configuration and the transferred configuration where an electron is shifted from the terminal D to A should be reduced to the overlap integral between the HOMO of the terminal D and the LUMO of A. In the A-A-D system the overlap between the initial configuration and the transferred configuration where an electron is shifted from D to the terminal A should be reduced to the overlap between the HOMO of D and the LUMO of the terminal A. In the D-A-D system the overlap between the transferred configurations where an electron is shifted from each D to A should be reduced to the overlap between the HOMO's of D's. In the A-D-A system the overlap between the transferred configurations where an electron is shifted from D to each A should be reduced to the overlap integral between the LUMO's of A's. These MO overlaps between the nonadjacent systems are assumed to be zero in the acyclic interaction. Accordingly, the above overlap integrals between the configurations are approximated as the products of the two MO overlaps involving the MO of the intermediary system.
(13) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969), and references cited therein.
(14) D. Hasselmann, *Tetrahedron Lett.*, 3465 (1972); 3739 (1973).
(15) J. A. Berson and J. M. Janusz, *J. Am. Chem. Soc.*, **96**, 5939 (1974).
(16) V. Mark, "Mechanisms of Molecular Migrations", Vol. 2, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1969, p 320.
(17) G. A. Russell and G. J. Mikol, "Mechanisms of Molecular Migrations", Vol. 1, B. S. Thyagarajan, Ed., Interscience, New York, N.Y., 1968, p 157.

(18) For example, see: H. M. R. Hoffmann, *Angew. Chem.*, **81**, 597 (1969).
(19) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Am. Chem. Soc.*, **89**, 1404 (1967), and references cited therein.
(20) S. Inagaki, S. Yamabe, H. Fujimoto, and K. Fukui, *Bull. Chem. Soc. Jpn.*, **45**, 3510 (1972); S. Inagaki, T. Minato, S. Yamabe, H. Fujimoto, and K. Fukui, *Tetrahedron*, **30**, 2165 (1974); S. Inagaki and K. Fukui, *J. Am. Chem. Soc.*, **97**, 7480 (1975).
(21) J. E. Baldwin, G. Höfle, and S. C. Choi, *J. Am. Chem. Soc.*, **93**, 2810 (1971); J. E. Baldwin, A. K. Bhatnager, S. C. Choi, and T. J. Shortridge, *ibid.*, **93**, 4082 (1971).
(22) L. A. Paquette and J. C. Stowell, *J. Am. Chem. Soc.*, **93**, 2459 (1971).
(23) E. S. Gould, "Mechanism and Structure in Organic Chemistry", Henry Holt, New York, N.Y., 1960, p 295.
(24) (a) G. M. Whitesides and D. J. Boschetto, *J. Am. Chem. Soc.*, **93**, 1529 (1971); (b) S. E. Jacobson and A. Wojcicki, ibid., **95**, 6962 (1973).
(25) (a) H. E. Zimmerman and G. L. Grunewald, *J. Am. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman and A. C. Pratt, *ibid.*, **92**, 6267 (1970); (c) H. E. Zimmerman and G. E. Samuelson, *ibid.*, **89**, 5971 (1967); **91**, 5307 (1969); H. E. Zimmerman, P. Hackett, D. F. Juers, and B. Schroder, *ibid.*, **89**, 5973 (1967); **93**, 3653 (1971); (d) P. S. Mariano and J. K. Ko, *ibid.*, **94**, 1766 (1972); (e) H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *ibid.*, **96**, 4630 (1974). (f) For a review of much of the di-π-methane rearrangement literature, see S. S. Hixon, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(26) H. E. Zimmerman and R. D. Little, *J. Am. Chem. Soc.*, **94**, 8256 (1972); **96**, 5143 (1974).
(27) Reference cited in ref 13 where the two-part $\pi_a + \pi_a$ interaction scheme is adopted.
(28) (a) P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962); (b) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352, 6354 (1967); R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **90**, 7364 (1968).
(29) S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 141 (1969).
(30) S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).
(31) The barrier to the bridge flipping in 7-norbornadienyl cation is greater than 19.6 kcal/mol at 45 °C. According to the corollary the displacement of the vinylene hydrogens by electron-donating substituents such as alkoxy or amino groups, and of the C_7 hydrogen by an electron-accepting substituent such as carbonyl or cyano groups, is expected to make the equilibrium geometry more distorted and to make the barrier higher.
(32) Either sign of the particular MO's can be chosen in principle without changing the physical meaning, as described in the theoretical section.
(33) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

(34) (a) R. W. Hoffmann, R. Schüttler, W. Schäfer, and A. Schweig, *Angew. Chem.*, **84**, 533 (1972); (b) L. A. Paquette and M. J. Broadhurst, *J. Org. Chem.*, **38**, 1893 (1973).
(35) It would be interesting to examine experimentally the bridge flipping in **9** with highly electron-demanding substituents such as cyano or carbonyl groups at the methylene carbon and with highly electron-releasing substituents such as amino or alkoxy groups at the vinylene carbons.
(36) (a) S. W. Staley and D. W. Reichard, *J. Am. Chem. Soc.*, **91**, 3998 (1969); (b) M. V. Moncur and J. B. Grutzner, *ibid.*, **95**, 6449 (1973); (c) M. J. Goldstein and S. Natowsky, *ibid.*, **95**, 6451 (1973).
(37) (a) G. Wittig and E. Hahn, *Angew. Chem.*, **72**, 781 (1960); (b) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964); (c) A. Streitwieser, Jr., and R. A. Caldwell, *ibid.*, **27**, 3360 (1962); (d) G. Wittig and J. Otten, *Tetrahedron Lett.*, 601 (1963); G. Wittig and G. Klumpp, *ibid.*, 607 (1963).
(38) R. B. Turner, *J. Am. Chem. Soc.*, **86**, 3586 (1964); cf. R. B. Turner, P. Goebel, B. J. Mallon, W. E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *ibid.*, **90**, 4315 (1968).
(39) (a) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Am. Chem. Soc.*, **92**, 4454 (1970); (b) J. C. Barborak, J. Daub, D. M. Follweiler, and P. v. R. Schleyer, *ibid.*, **91**, 7760 (1969); J. C. Barborak and P. v. R. Schleyer, *ibid.*, **92**, 3184 (1970); (c) J. B. Grutzner and S. Winstein, *ibid.*, **92**, 3186 (1970).
(40) L. M. Loew and C. F. Wilcox, *J. Am. Chem. Soc.*, **97**, 2296 (1975), and references cited therein.
(41) T. Kaneda, T. Ogawa, and S. Misumi, *Tetrahedron Lett.*, 3373 (1973).
(42) T. Inoue, T. Kaneda, and S. Misumi, *Tetrahedron Lett.*, 2969 (1974).
(43) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 1293 (1968).
(44) (a) T. Iwakuma, O. Yonemitsu, N. Kanamaru, K. Kimura, and B. Witkop, *Angew. Chem.*, **85**, 85 (1973); (b) T. Iwakuma, K. Hirao, and O. Yonemitsu, *J. Am. Chem. Soc.*, **96**, 2570 (1974). (c) The transannular 2 + 2 cycloaddition reaction between a C=C bond and one of the C–C σ bonds of cyclopropane ring has been observed to occur presumably via acylation on the carbonyl oxygen attached to the cyclopropane ring [E. J. Corey and R. D. Balanson, *Tetrahedron Lett.*, 3153 (1973)]. This reaction is taken as being "catalyzed" by acyl cation instead of proton.
(45) π LUMO of a carbonyl compound, acrolein, has been shown by a SCF calculation to be appreciably (~5 eV) lowered through the protonation on a lone pair of the carbonyl oxygen [K. Fukui and H. Fujimoto, *Nippon Kagakuseni Koen-shu*, **29**, 27 (1972)].
(46) R. C. Cookson and J. E. Kemp, *Chem. Commun.*, 385 (1971).
(47) Another electronic cause of symmetry-disfavored 1,3-sigmatropic shift in antibisallylic systems has recently been proposed [S. Inagaki, T. Minato, H. Fujimoto, and K. Fukui, *Chem. Lett.*, 89 (1976)]. The multicyclic interaction effect should be essentially distinguished both from the Berson–Salem's "subjacent orbital" effect and from the three-system interaction substituent effect described here.

Theory and Calculation of Carbon–Nitrogen Spin–Spin Coupling Constants

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Abstract: Nuclear spin–spin coupling constants for ^{13}C and ^{15}N are treated theoretically in a framework of coupled Hartree–Fock theory using localized and delocalized molecular orbitals. Calculations implemented in the INDO integral approximation in this model have been performed for one-, two-, and three-bond couplings in some simple nitrogen-containing organic molecules. It is demonstrated that orbital and dipolar contributions are important in cyanides and nitriles, and furthermore that molecules can be divided into two classes depending on the presence or absence of lone pairs which may contribute to $^1J_{CN}$.

I. Introduction

As is well known,[2a] indirect isotropic nuclear spin–spin coupling constants result from three types of electron coupling mechanisms: (1) Fermi contact interaction between the electron and nuclear spins, J^{Fc}, (2) interaction between the magnetic field arising from the orbital motion of the electron and the nuclear magnetic dipole, J^o, and (3) interaction between the nuclear and electron spin dipoles, J^{sd}. Recently self-consistent field calculations including the effect of the "noncontact" terms, (2) and (3), for first row atoms have been made by Blizzard and Santry,[2b] Towl and Schaumburg,[3] and Schulman and Newton.[4] The latter study of CC one-bond

coupling constants found that the Fermi contact term is usually dominant and is related to the product of the hybrids in the bonding orbitals. However, the orbital and spin–dipolar terms are not necessarily negligible and in a few cases, most notably bicyclobutane (C_1C_3) bonds, they are actually more important than the contact term. This led to the unusual prediction of a negative value for $^1J_{C_1C_3}$[5] which has been recently confirmed by an elegant experiment.[6] For CF coupling constants the orbital terms have been found to be comparable to the contact term.[2b,3]

The present study deals with the case of $C^{13}N^{15}$ coupling constants which has not been systematically studied previously and for which there are a wide variety of bonding situations,