Mechanism of Delocalization of σ-Electrons from Bonds to Bonds. Conformationally Dependent Delocalization between Geminal Bonds in Antiperiplanar Effects

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A theory is presented for bond-to-bond delocalization of σ-electrons and applied to the antiperiplanar effects including anomeric and gauche effects. The delocalization between geminal bonds is, surprisingly, dependent on the conformation. The geminal delocalization from the intervening bond between donor and acceptor bonds to the latter is proposed to be important as well as the vicinal delocalization from the donor to acceptor bond. Each delocalization is controlled by the orbital phase.

The three-dimensional structures of molecules are retained by σ-bonds oriented in specific directions. The steric courses of chemical reactions are also determined by specific directions of incipient σ-bonds, in which reagents attack on substrates. Accordingly, the behaviors of σ-electrons are important to stereochemistry in both static states and dynamic processes.

σ-Electrons can be treated in entirely the same manner as π-electrons. Most usually, we employ canonical molecular orbitals, which delocalize all over molecules. The feature of the molecular orbitals makes a contrast with a conventional concept of chemical bond. Electrons in molecules have been considered to localize well in the chemical bonds, except for a special example such as π-electrons in aromatic molecules. Chemical bonds have been assumed to have their intrinsic properties, and to exchange electrons with one another. The structures of molecules and the mechanisms of reactions have been explained and predicted on the basis of the concept of the chemical bonds. The approach along this line is still believed to be fundamental in organic chemistry, and to be more suitable especially for the σ-electrons which localize well. The mechanisms of the delocalization of the σ-electrons from bonds to bonds are investigated in this paper.

We will examine the antiperiplanar effect as a simple model, which includes the anomeric effect (Fig. 1),[1] and the gauche effect.[2] The term 'anomeric effect' was introduced by Lemieux in 1958 as a result of a detailed study of the anomerization of acetylated pento- and hexopyranoses. The effect refers to the tendency of an electronegative substituent at C-1 of a pyranoid ring to assume the axial rather than equatorial orientation, in contrast to prediction based solely on steric grounds.

Several explanations have been proposed to account for the origin. The first rationalization attributed the phenomenon to an unfavorable dipole-dipole interaction between the carbon-oxygen bond on the ring and the equatorial polar bond.[3] Another interpretation is based on the suggestion that the n-σ^* interaction of the ring-oxygen lone pairs with the exocyclic polar bond stabilizes the axial orientation due to antiperiplanar relation (Fig. 1). The importance of the special arrangement of the oxygen lone pairs had previously been pointed out by Edwards[4] to explain the difference in stabilities to acid hydrolysis of α- and β-methyl pyranosides. The n-σ^* interaction between the oxygen p-type lone pair and the adjacent carbon-halogen bond was first considered in 1959 by Lucken[5] as a possible explanation of the abnormally low NQR frequencies of α-halo ethers. Later on, Altona[6] showed that the same phenomenon could explain the peculiarities of some bond lengths in similar compounds.

Recently, Dewar[7] explained the anomeric effect in terms of σ-conjugation (Fig. 2). The adjacent hybrid orbitals can interact with each other. The σ-orbital system may be regarded as the four p-orbital system in butadiene. The 1,4 bond order (p_{14}) is negative. Accordingly, the system of positive resonance integral ($h_{14}>0$) is stabilized. The antiperiplanar form is more stable.

Some investigators have studied this aspect of het-

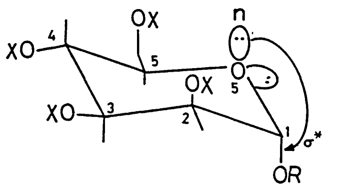

Fig. 1. Anomeric effect.

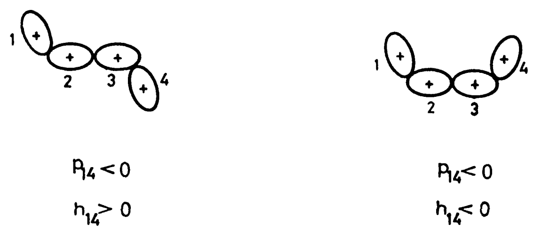

Fig. 2. σ-Conjugation.

eroatom electronic structure in other contexts. The one most generally accepted is the gauche effect, originally prompted by the need to explain the unexpected gauche conformation of fluoromethanol.[2] This refers to a tendency to adopt that structure which has the maximum number of gauche interactions between the adjacent electron pairs and/or polar bonds. The lone pairs (donor bonds) prefer to be in the antiperiplanar relation to the acceptor bonds.

Theory

We employ a simple three-bond system (Fig. 3). The donor bond is denoted by A with an electron-donating orbital (a), which is at one end of the single bond (B) with bonding and antibonding orbitals (b and b*). The acceptor bond at the other end is denoted by C with an electron-accepting orbital (c*). The bond orbitals are linear combinations of appropriate hybrid atomic orbitals.

The electronic structure prior to any interactions between the bonds is represented by the electron configurations where neither electron shift between any pairs of bonds nor electron promotion in any bonds takes place. This is termed the ground configuration, G, which is usually the main component of the wave function after the interactions between bonds are allowed. The interactions accompany electron shifts from bonds to bonds. The electron delocalization is expressed by mixing of the electron-transferred configuration, T(i→j*), where an electron is shifted from a bonding orbital (i) of a bond to an antibonding orbital (j*) of another.

There are three bond-to-bond delocalization modes in the model system (Fig. 3). The delocalization from the donor to the acceptor, believed to be responsible for the antiperiplanar effect, occurs between the vicinal bonds. This is termed vicinal delocalization.[8] The delocalizations from the intervening bond to the acceptor bond and from the donor bond to the intervening bond occur between the geminal bonds. These are termed the geminal delocalizations.[8]

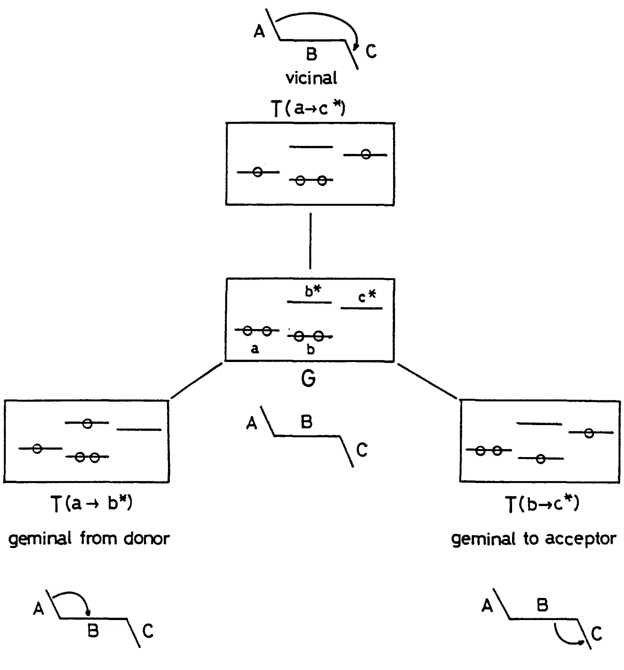

Fig. 3. Three-bond model for the antiperiplanar effect.

Electron delocalization is expressed by the G-T configuration interaction. The interaction is estimated in a perturbational approach[9] to be $H_{GT}-S_{GT}H_{GG}$, where the conventional notation is used. The term can be rewritten in terms of bond orbitals. The G-T(b→c*) interaction for the geminal delocalization to the acceptor bond is approximated as follows:

$$\begin{aligned} &H_{GT(b\to c^*)}-S_{GT(b\to c^*)}H_{GG} \\ &\simeq 2N_GN_T[(h_{bc^*}-h_{bb}s_{bc^*})-(h_{ab}-h_{aa}s_{ab})s_{ac^*} \\ &-(h_{ac^*}-h_{bb}s_{ac^*})s_{ab}] \end{aligned} \tag{1}$$

where N is the normalization factor. In the approximation, the higher-order terms than the second-order ones, e.g., $h_{ij}s_{kl}^2$, $h_{ij}^2s_{kl}$, are neglected on the assumption that h_{ij} and s_{ij} are infinitesimals of the first order, relative to h_{ii} and s_{ii}.

Similarly, the following equations are obtained for the vicinal delocalization:

$$\begin{aligned} &H_{GT(a\to c^*)}-S_{GT(a\to c^*)}H_{GG} \\ &\simeq 2N_GN_T[(h_{ac^*}-h_{aa}s_{ac^*})-(h_{bc^*}-h_{aa}s_{bc^*})s_{ab} \\ &-(h_{ab}-h_{bb}s_{ab})s_{bc^*}] \end{aligned} \tag{2}$$

and for the geminal delocalization from the donor:

$$\begin{aligned} &H_{GT(a\to b^*)}-S_{GT(a\to b^*)}H_{GG} \\ &\simeq 2N_GN_T[h_{ab^*}-h_{aa}s_{ab^*}] \end{aligned} \tag{3}$$

In the conventional orbital interaction theroy, the G-T configuration interaction has been approximated to be the interaction between the orbitals donating and accepting an electron. For the geminal delocalization to the acceptor bond, the G-T(b→c*) interaction used to be approximated as the b-c* orbital interaction, which corresponds to the terms, $h_{bc^*}-h_{bb}s_{bc^*}$, in the first parentheses of Eq. 1. The b-c* interaction is independent of the conformation. Accordingly, the geminal delocalization has been considered not to accompany any stereochemical effects.

However, the approximation including higher order terms (in the second and third parentheses) shows that the geminal delocalization to the acceptor bond is under the influence of the orientation of the donor bond or dependent of the conformation. The G-T(b→c*) interaction involves the orbitals of the occupied orbital, a, of the donor bond in addition to b and c*. The G-T(b→c*) interaction depends on the sign relation between the terms in the three paren-

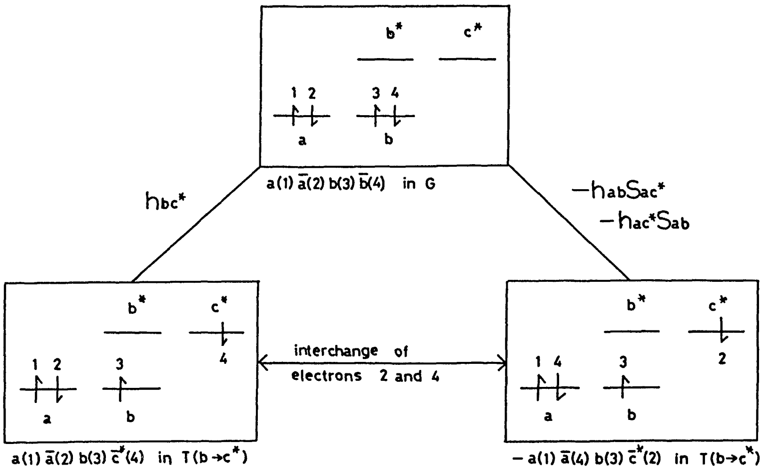

Fig. 4. Cyclic three-orbital interaction in two-configuration interaction.

theses. Assuming as usual that s_{ij} is considered to be small, h_{ij} may be more important than $h_{ii}s_{ij}$ in each pair of parentheses. When we see the sign relation, $h_{ii}s_{ij}$ can be neglected. For greater G-T(b→c*) interaction the sign of h_{bc^*} in the first term is required to be the same as $-h_{ab}s_{ac^*}$ in the second term and $-h_{ac^*}s_{ab}$ in the third term. We obtain:

$$h_{bc^*}h_{ab}s_{ac^*}<0 \text{ and } h_{bc^*}h_{ac^*}s_{ab}<0. \qquad (4)$$

Similarly, the vicinal donor-to-acceptor delocalization or the G-T(a→c*) interaction used to be approximated as the a-c* orbital interaction or $h_{ac^*}-h_{aa}s_{ac^*}$. The orbital interaction is dependent on the conformation. The higher order approximation (Eq. 2) shows that the vicinal delocalization involves the bonding orbital, b, of the intervening bond. Similar inequalities

$$h_{ac^*}h_{bc^*}s_{ab}<0 \text{ and } h_{ac^*}h_{ab}s_{bc^*}<0 \qquad (5)$$

are required for greater G-T(a→c*) interaction.

The sign of h_{ij} is usually opposite to that of s_{ij}. The inequalities (4) and (5) can be rewritten in an identical form:

$$s_{bc^*}s_{ac^*}s_{ab}<0. \qquad (6)$$

This requires an odd number of out-of-phase relation between a, b, and c*. The orbitals, a and b, are electron-donating orbitals, c* being an electron-accepting orbital. The present phase continuity requirements are included in those[10] derived previously: (i) the electron-donating orbitals out of phase; (ii) the accepting orbitals in phase; and (iii) the donating and accepting orbitals in phase.

The present derivation of the orbital phase continuity conditions is different from the previous one.[10] The conditions were previously derived from the interactions of at least three electron configurations. One is the ground configuration G, the others being electron transferred configurations T_1 and T_2. The configurations interact in a cyclic manner ($\overline{\text{G-T}_1\text{-T}_2}$). The interaction of each pair of configurations is approximated as the corresponding orbital interaction. Therefore, the cyclic configuration interaction is reduced to cyclic orbital interaction. The phase conditions are then derived.

In the present work, the phase conditions have been derived from the interaction between the two configurations, G and T (Fig. 4). For the geminal delocalization to the acceptor bond or the G-T(b→c*) interaction (Eq. 1), the predominant orbital interaction takes place between the orbitals, b and c*, which donate and accept an electron. The b-c* interaction comes from the term $a(1)\bar{a}(2)b(3)\bar{b}(4)$ in G and $a(1)\bar{a}(2)b(3)\bar{c}^*(4)$ in T. When the higher order terms of the orbital interactions are neglected, no orbital phase restriction arises for the geminal delocalization. However, the interchange of electron space and spin coordinates should be taken into account. Figure 4 illustrates the term, $-a(1)\bar{a}(4)b(3)\bar{c}^*(2)$, for 2⇆4 electron interchange in T. This gives rise to the higher order terms, $-h_{ab}s_{ac^*}$ and $-h_{ac^*}s_{ab}$, with $a(1)\bar{a}(2)b(3)\bar{b}(4)$ in G, or the a-b and a-c* orbital interactions, respectively. As a result, the G-T(b→c*) interaction contains the cyclic $\overline{\text{a-b-c}^*}$ interaction.

Applying to the orbital interactions of the present interest, the requirements were found to be simultaneously satisfied for the antiperiplanar arrangement: a-b out of phase, b-c* and a-c* in phase (Fig. 5).

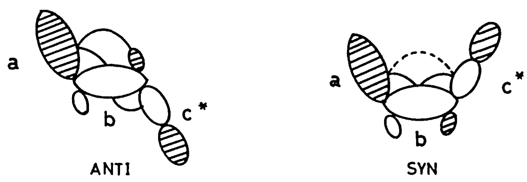

Fig. 5. Geminal and vicinal electron delocalizations controlled by orbital phase.

The synperiplanar arrangement cannot meet at least one of the requirements. The delocalization, whether geminal or vicinal, is enhanced in the antiperiplanar arrangement, while depressed in the synperiplanar arrangement.

The prediction[13] is surprising that the geminal delocalization has stereochemical effects. The deloalization from the intervening bond to the acceptor bond is more or less responsible for the antiperiplanar effect. The G-T(b→c*) interaction used to be approximated to the b-c* interaction in the conventional orbital interaction theory. The b-c* orbital interaction is independent of the conformation. The present theory shows that the geminal delocalization is under the influence of the orientation of the donor bond.

The G-T(a→c*) interaction involved in the vicinal delocalization from the donor to the acceptor is conventionally approximated to the a-c* interaction. The orbital interaction has been believed to prefer the antiperiplanar arrangement. However, the present theory suggests that the intervening bond is significantly involved. In this sense, a sort of the through-bond[14] interaction plays an important role in the vicinal delocalization.

Model Calculation and Discussion

Bond Orbital On-Off Calculation. In the present work, we investigate the bond-to-bond delocalization of σ-electrons. The effects of the bonding and antibonding orbitals need to be numerically estimated in a separate manner. The extended Hückel theory only enables us to calculate readily the electronic structure with or without bond orbitals. The bond orbital on-off calculations were carried out for the three-bond model system (Fig. 3). The canonical molecular orbital of the whole system and the bond orbitals are obtained as linear combinations of sp^3 hybrid orbitals. The single Slater determinant wavefunctions for the ground state of the whole system were then subjected to the electron configuration analysis for many-system interaction[15] based on the bond orbitals. The standard bond lengths and angles[16] were used.

Although the simple theory and model were employed, the relative energies of the anti- vs. synperiplanar arrangements (Table 1) reproduced the antiperiplanar effect as the minus signs in the column (a,b,b*,c*) show. The results encourage us to analyze the electronic structure by the bond orbital on-off calculation and to examine the preceding qualitative theory. Without the intervening bond, B, all models (ac*) did not exhibit the antiperiplanar effect. These results support the preceding conclusion that the geminal delocalization from the intervening bond and the involvement of the intervening bond in the vicinal delocalization are important for the antiperiplanar effect.

The bonding orbital (b) is essential for the antiperiplanar effects while the effect of the b*-orbital is negligible. The inclusion of b (abc*) almost reproduced the results of the (abb*c*) models. The relative stabilities of the (ab*c) models are close to those of the (a,c*) models. These results support our theory. The vicinal delocalization from a to c* does not involve b* but b. The geminal delocalization occurs from b.

While the significant involvement of the bonding orbital of the intervening bond has also been suggested by the preceding calculation, no numerical information is available to discuss the effects of the geminal and vicinal delocalizations separately. We calculate the G-T interaction energies,

$$E_{\mathrm{int}}(\mathrm{G,T}) = 2C_{\mathrm{G}}C_{\mathrm{T}}(H_{\mathrm{GT}} - S_{\mathrm{GT}}H_{\mathrm{GG}})$$

where C denotes the coefficient of the configuration obtained from the configuration analysis.[15] The geminal delocalization prefers the anti conformation

Table 1. Relative Energies[a] (kcal mol^{-1}) of Syn- and Antiperiplanar Arrangements

Bonds			Bond orbitals involved[b]			
A	B	C	abb*c*	abc*	ab*c*	ac*
H-C	C-C	C-F	−3.457	−3.441	−0.520	−0.483
H-C	C-C	C-Cl	−1.683	−1.610	−0.468	−0.371
n_{C}[c]	C-C	C-F	−3.762	−3.420	1.865	2.063
n_{C}[c]	C-C	C-Cl	−1.916	−1.674	0.156	0.271

a) Energy difference. The minus sign indicates that the antiperiplanar arrangement is more stable. b) For the notation, see the three bond model (Fig. 3). c) A lone pair of electrons on C.

Table 2. Geminal and Vicinal Delocalization Energies (kcal mol^{-1}) of Syn- and Antiperiplanar Arrangements

Bond[a]		Geminal[a]			Vicinal[a]		
A	C	Syn	Anti	Diff.[b]	Syn	Anti	Diff.[b]
H-C	C-F	−5.698	−12.237	−6.539	−0.103	−0.346	−0.243
H-C	C-Cl	−2.690	−5.394	−2.704	−0.003	−0.679	−0.676
n_{C}[c]	C-F	−4.766	−13.657	−8.891	−2.505	−0.244	2.261
n_{C}[c]	C-Cl	−2.027	−6.244	−4.217	−0.713	−0.023	0.690

a) For the notation, see Fig. 3. The bond B is a C-C bond. b) Energy difference. The minus sign indicates that the antiperiplanar arrangement is more stabilizing. c) A lone pair on C.

Table 3. Increase[a] in the Geminal and Vicinal Delocalizations with the Conformational Change

Conformational change[b]	Delocalization	**1**	**2**	**3**	**4**
Syn to anti	Vicinal	0.0402	0.0228	0.0454	0.0389
	Geminal	0.0598	0.0389	0.0556	0.0197
Gauche to anti	Vicinal	0.1237	0.0719	0.1275	0.0656
	Geminal	0.0517	0.0323	0.0453	0.0167

a) Estimated by the coefficient of the electron-transferred configurations (C_T). b) Terminology refers to the spatial arrangements of the donor and acceptor bonds.

in all models examined (Table 2). This is again consistent with the preceding qualitative theory. The preference of the vicinal delocalization to the syn- or antiperiplanar arrangement is dependent on the models.

Ab Initio Calculation. We undertook ab initio calculations to examine the preceding qualitative theory and calculations. Since the geometry optimization of the model compounds, $^-CH_2CH_2F$ (**1**), NH_2CH_2F (**2**), NH_2CH_2Cl (**3**), and PH_2CH_2F (**4**), with the STO-3G basis set reproduced the antiperiplanar effects, the SCF molecular orbitals were used for the configuration analysis to see the bond-to-bond delocalization.[8] The conformational dependence of the geminal and vicinal delocalizations is shown in Figs. 6 and 7. The conformation is defined by the dihedral angle θ. The synperiplanar conformation, where the donor and acceptor bonds are eclipsed, is denoted by $\theta=0°$. The antiperiplanar conformation is denoted by $\theta=180°$. The extent of delocalization is indicated by the configuration coefficients of the electron transferred configurations.

The preference of both geminal and vicinal delocalizations to the anti- rather than synperiplanar arrangement was confirmed by the ab initio configuration analysis for all models examined (Figs. 6 and 7). The first row atom models are represented by NH_2CH_2F since the characteristic features of $^-CH_2CH_2F$ and NH_2CH_2Cl were found to be similar.

The enhancement of the geminal delocalization by the syn to anti conformational change is more remarkable than that of vicinal one in **1**—**3** (see Table 3). This confirms the result of the extended Hückel calculations that the geminal delocalization is predominant in stabilizing the anti- relative synperiplanar conformations.

The synperiplanar conformation is an eclipsed form, which is not realistic for the equilibrium structure of rotatomers. The gauche arrangement ($\theta=60°$) is to be compared with the antiperiplanar conformation ($\theta=180°$). The vicinal delocalization increases with the gauche to anti conformational change to a greater extent, relative to the geminal delocalization (Table 3). The results of the ab intio calculations imply that the vicinal delocalization is more sensitive to the gauche-to-antiperiplanar conformational change.

In **4** containing a lone pair on phosphorus, a second

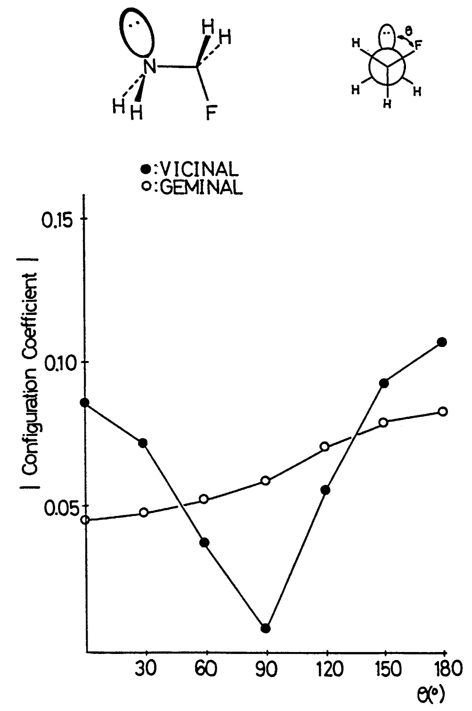

Fig. 6. Conformational dependence of geminal and vicinal delocalizations in NH_2CH_2F.

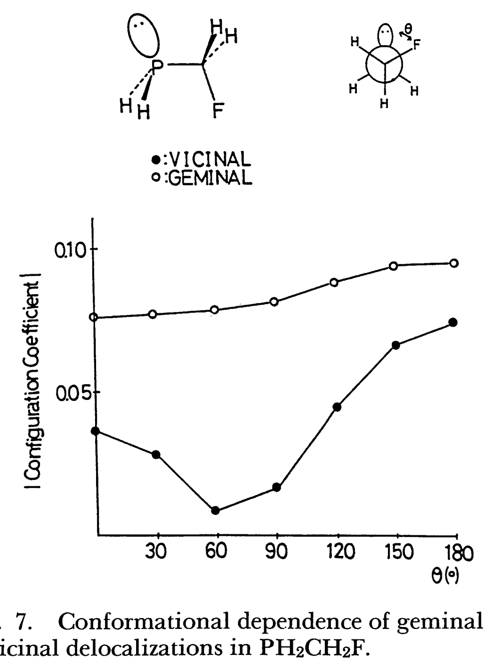

Fig. 7. Conformational dependence of geminal and vicinal delocalizations in PH_2CH_2F.

row atom, both geminal and vicinal delocalizations are less dependent on the conformation (Fig. 7). This is consistent with the conclusion by Schleyer et al.[17] that anomeric effects involving second-row substituents are greatly attenuated relative to their first-row counterparts. They suggested that the attenuated effect could be attributed to the poorer π-donating property and the lower electronegativity of the second-row groups. However, the diffuse extension of the n-orbital on the second-row atoms or its reduced directionality should also be taken into consideration.

Conclusions

A theory has been presented for scrutinizing the mechanism of delocalization of σ(n)-electrons from one bond to another. The bond-to-bond delocalization has been shown to be significantly influenced by the surrounding bonds through the orbital phase.

Most interestingly, the delocalization between the geminal bonds is dependent on the conformation. The delocalization from a bond B to a geminal bond C (Fig. 3) is dependent on the orientation of another bond or a lone pair A on the other end of B. The geminal delocalization is controlled by the orbital phase (Fig. 5) which prefers the antiperiplanar arrangement of A and C.

The delocalization between the vicinal bonds (A and C in Fig. 3) has been believed to be responsible for the antiperiplanar effects including the anomeric effect,[1] the gauche effect,[2] and so on. The vicinal delocalization significantly involves the intervening bond B. The preference of the delocalization for the antiperiplanar relation is also controlled by the orbital phase continuity (Fig. 5).

The orbital phase is extending the coverage over organic chemistry. Most fundamentally, the orbital phase determines the bonding and antibonding properties of chemical bonds. The orbital phase continuity conditions originally developed for catalytic action[10] cover the Woodward-Hoffmann stereoselection rule and the Hückel aromaticity rule.[11]. A prerequisite for the application of the conditions has given birth to a new concept, continuity and discontinuity of cyclic conjugation.[12] Kinetic stability of cyclic conjugated molecules can be predicted from the phase continuity requirements.[18] The orbital phase also determines thermodynamic stability of acyclic conjugated molecules (cyclic orbital interaction in acyclic conjugation, acyclic aromaticity).[19] Regioselectivity of organic reactions can also be explained in terms of the phase continuity,[20] while so far in terms of the frontier orbital amplitudes. In the present work, the orbital phase is an important factor controlling the bond-to-bond delocalization of σ-electrons which is related to such stereoelectronic effects as anomeric effects,[1] gauche effects,[2] a concept of σ-assistance and σ-resistance[21] and so on.

Ab initio molecular orbital calculations with GAUSSIAN 80 and MONSTERGAUSS programs were carried out on a HITAC M-680H computer at the Institute for Molecular Science and on a FACOM M-782 computer at Nagoya University Computer Center, respectively. We are grateful to Prof. Kimihiko Hirao for permitting us to use MONSTERGAUSS program. The configuration analysis was carried out on a FACOM M-360 computer at Gifu University Computing Center. This work was supported by a Grant-in-Aid for Scientific Research Nos. 63550620, 62303002 from the Ministry of Education, Science and Culture.

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