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A MOLECULAR ORBITAL STUDY OF THE ORIENTING EFFECT IN HOMOCONJUGATED SYSTEMS

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Abstract Polarization of double bonds in homoconjugated systems has been studied by the use of MO theory and the results obtained have been compared with experimental findings. It has been suggested that the substituent effects are reduced by a structurally determined factor 1/10 ~ 1/100 when they are transmitted through homoconjugation and that the rate of attenuation of the effects would also depend on substituents, being slower in the case of strongly electron-releasing or withdrawing groups and faster in the case of weakly electron-releasing or withdrawing groups. An aspect of polarization in multicyclic conjugated molecules induced by the attacking electrophiles has been discussed in some detail, yielding a fair agreement between the theoretical conclusion and the experimental results accumulated so far.

Conjugation between two double bonds in a molecule separated by tetravalent carbons has been suggested to play a significant role in determining chemical reactivities of multicyclic unsaturated systems.[1,2] Simonetta and Winstein discussed for the first time the importance of homoconjugation theoretically in stabilizing molecular systems as early in 1954.[3] Placing a particular emphasis on interactions between conjugated constituents of bicyclic molecules, an interesting concept "bicycloaromaticity" was introduced.[4,5] On the other hand, some photoelectron spectroscopic studies of a variety of multicyclic molecules have been performed recently in order to disclose quantitatively the nature of homoconjugation.[6,7]

Experiments so far carried out have shown that the selectivities in heterolytic and homolytic additions to multicyclic conjugated molecules are more or less affected by the presence of intramolecular conjugation between fragmentary pi bonds. It may be worthy to clarify here some basic aspects of the orienting effects of homoconjugation by applying the molecular orbital perturbation theory. The results obtained from a simplest theoretical model will be compared with experimental findings. The qualitative discussion will also be supplemented by *ab initio* MO calculations. The concept of orbital intermixings is used to describe the charge polarization in a double bond induced statically by substituent groups and dynamically by attacking electrophiles.

A simplest interaction model

In order to investigate basic aspects of homoconjugation, we set up a simplest model as shown in Fig. 1. The fragment A is a substituent group X and the fragments B and C are ethylenic double bonds separated by tetravalent carbons. The substituent fragment A is in conjugation with B at the C atom C_1, the interaction being represented by the integral h_{1X}. The homoconjugation between the fragments B and C is denoted by the integrals $h_{14} = h_{23} = \Delta \cdot h$, where h is the exchange integral for a normal ethylenic pi bond.

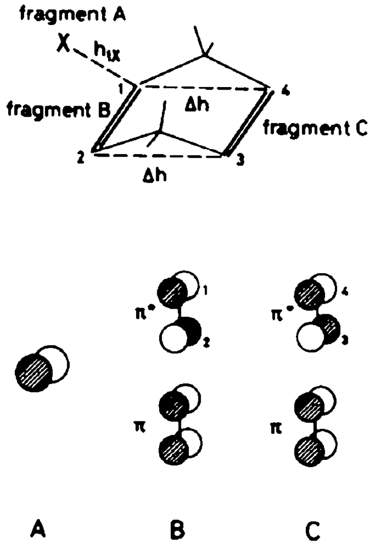


Fig. 1. A simple model of homoconjugation.

The electronic structure of an ethylenic double bond is represented by a mutually orthogonal pair of bonding (π) and antibonding (π^*) MO's. When a substituent is introduced, the π and π^* MO's intermix each other to polarize the bond.[8-12] The effects of substituents may simply be examined by placing a single orbital which interacts with the ethylenic pi MO's. The relevant MO of the fragment A is occupied in the case of electron-releasing substituents and unoccupied in the case of electron-withdrawing substituents. The energy of the substituent orbital is denoted by ε_X.

The occupied MO's of electron-releasing groups are lower in energy than the ethylene π^* MO ($\varepsilon_X < \varepsilon_{\pi^*}$) and the unoccupied MO's of electron-withdrawing groups lie higher than the ethylene π MO ($\varepsilon_X > \varepsilon_\pi$), in general. In the Hückel MO approximation, $\varepsilon_\pi - \varepsilon_{\pi^*} = 2h$ and ε_X may be represented by $1/2(\varepsilon_\pi + \varepsilon_{\pi^*}) + \lambda \cdot h$ $(-1 < \lambda < 1)$. Then, the intermixing of the π and π^* MO's in the fragment B caused by the interaction with the substituent fragment A is given by;[13]

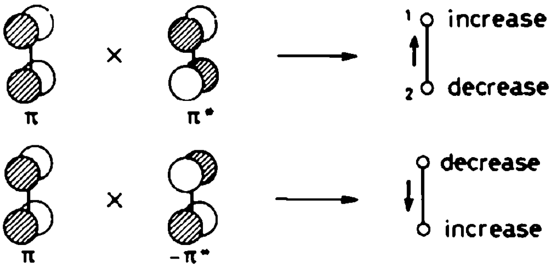
For electron-releasing substituents

$$\sim 2h_{1X}^2/\{(\varepsilon_\pi - \varepsilon_{\pi^*})(\varepsilon_{\pi^*} - \varepsilon_X)\}$$
$$= -(h_{1X}/h)^2 \cdot 1/(1 + \lambda) < 0$$

For electron-withdrawing substituents (1)

$$\sim 2h_{1X}^2/\{(\varepsilon_\pi - \varepsilon_{\pi^*})(\varepsilon_\pi - \varepsilon_X)\}$$
$$= (h_{1X}/h)^2 \cdot 1/(1 - \lambda) > 0$$

in which the phase of MO's has been taken as illustrated in Fig. 1. The positive and negative mixings of the π and π^* MO's increase the electron density at C_1 and C_2, respectively.[9-11]



Stronger donor groups have higher ε_X values and stronger acceptor groups possess lower ε_X values to make the denominator smaller in each case. The magnitude of polarization can then be estimated by the orbital intermixings as well.

The influence of the substituent A on the electronic structure of the fragment C should be examined next. The intermixing of the π and π^* MO's in the fragment C due to the interaction with the pi MO's of the fragment B perturbed by the substituent A is derived in a similar manner as given by;

For electron-releasing substituents

$$\sim 1/2 \cdot (h_{1X}/h)^2 \Delta^2 \cdot (2 + \lambda)/(1 + \lambda)^2 > 0 \qquad (2)$$

For electron-withdrawing substituents

$$\sim -1/2 \cdot (h_{1X}/h)^2 \Delta^2 \cdot (2 - \lambda)/(1 - \lambda)^2 < 0$$

The intermixing of the π and π^* MO's in the fragment C is seen to be opposite in sign to that in the fragment B in each case. Thus, in line with our chemical intuition, the polarization of the C_3–C_4 bond induced through homoconjugation is shown clearly to take place in the inverse direction to the polarization of the C_1–C_2 bond. The main question that we are concerned about here is how efficiently the influence of substituents is transmitted through homoconjugation.

According to eqns (1) and (2), the ratio of the orbital mixing in the fragment C to that in the fragment B caused by the introduction of an electron-releasing group and an electron-withdrawing group is given by $-1/2 \cdot \Delta^2(2 + \lambda)/(1 + \lambda)$ and $-1/2 \cdot \Delta^2(2 - \lambda)/(1 - \lambda)$, respectively. It is seen that the polarization in .the fragment C is attenuated rapidly by a factor Δ^2 in comparison with the polarization in the fragment B. The structural parameter Δ may be estimated to be 0.3 or smaller.[14,15] It is suggested, therefore, that the substituent effects on the redistribution of the electron density transmitted via homoconjugation should be pretty weak, being 1/10 ~ 1/100 of the direct influence of substituents.

The results of our *ab initio* (STO-3G) MO and CNDO/2 MO calculations on substituted norbornadiene are shown in Fig. 2.[16]

The substituent was chosen tentatively to be a nitro group which may show us a general trend. The calculated changes in the pi electron densities seem to be consistent with the conclusion derived above from our simple interaction model.

Let us look at experimental results. The substituent effects in addition reactions have been studied most extensively in regard to benzonorbornadienes **1**. Electron-releasing group attached to the benzene ring increases the electron density of the C_5 atom and, therefore, the C_2–C_3 bond is polarized through

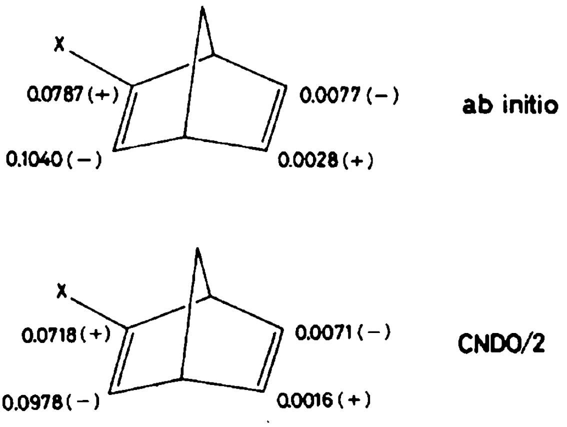
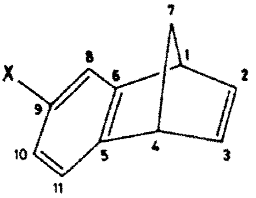


Fig. 2. Changes in the pi electron densities due to the introduction of a nitro substituent in norbornadiene. The signs + and − indicate the increase and decrease in the density, respectively.

homoconjugation so as to make the C_2 atom more negative than the C_3 atom.



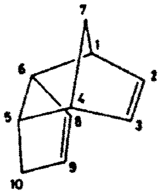
Electrophiles will attack C_2 preferentially. On the contrary, electron-withdrawing substituent in the benzene ring will enhance the reactivity of the C_3 atom to electrophiles.

Acetoxythallation of methoxybenzonorbornadiene ($X = CH_3O$) and chlorobenzonorbornadiene ($X = Cl$) afforded cis-exo products, a preferable attack on C_2 and C_3 by positive moiety being occurred respectively:[17] the ratio (C_2/C_3) was about 9/1 in the case of $X = CH_3O$ and about 2/8 in the case of $X = Cl$. Electrophiles such as H^+ (HCl addition) and Al^- (carbalumination) attack preferentially C_2 in the case of $X = CH_3O$ and C_3 in the case of $X = F$, the ratio C_2/C_3 being 8/2 and 3/7, respectively.[18,19] On the other hand, carbalumination of methylbenzonorbornadiene ($X = CH_3$) afforded a regioisomeric mixture of 53/47 with the attack of aluminium moiety on C_2/C_3.[19]

Another interesting point to be noted here concerning the substituent effects in homoconjugated systems is that the ratio of the polarizations in the fragments B and C is not only structurally determined but also contains a substituent dependent part $(2 + \lambda)/(1 + \lambda)$ in the case of electron-releasing groups and $(2 - \lambda)/(1 - \lambda)$ in the case of electron-withdrawing groups. A larger λ yields a smaller value for $(2 + \lambda)/(1 + \lambda)$. This means that the effect of weaker electron-releasing substituents should be attenuated more rapidly than the effect of stronger electron donating substituents is reduced when they are transmitted through homoconjugation. A similar trend may also be expected in the case of electron-withdrawing groups. Methyl group is obviously a weak donor. The very low selectivity in the carbalumination of methylbenzonorbornadiene in comparison with other cases may partly be related to the characteristic aspect of the substituent effect in homoconjugated systems disclosed above. Further accumulation of experimental results is anticipated.

Polarization in nonpolar homoconjugated molecules

Nonpolar molecules in an isolated state may be polarized under the influence of the approaching reagent. Let us examine some basic aspects of polar additions to dicyclopentadiene **2**, as an example, which has two unsymmetrically located double bonds in the molecular framework. Hydroxymercuration (*cis-exo*) of **2** shows a preferable attack of positive mercury moiety on C_3 than on C_2 with the ratio, $C_3/C_2 = 7/3$.[20] Acetoxythallation in methanol or chloroform gives a regioisomeric mixture of *cis-exo* adducts, involving a preferable attack of positive thallium moiety on C_3 ($C_3/C_2 = 3 \sim 5/1$).[21] A recent report on hydration revealed that the attack of proton took place with the ratio $C_3/C_2 = 2/1$.[22] Carbalumination followed by hydrolysis has been reported to give an isomeric mixture of alkyl derivatives of **2** where one isomer predominates ($2.4 \sim 2.6:1$).[23] The position of preferential attack of aluminium moiety has not been decided yet.



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If the charge polarization of the C_2–C_3 bond originally existing in an isolated state of **2** is responsible for the observed trend, additions should be selective whether they take place stepwise or not. The experimental results suggest that this is unlikely. Addition of nitrosyl chloride ($^{\delta-}Cl$–$^{\delta+}NO$) is known to give an almost 1:1 mixture of addition products.[20] Hydroboration of **2** showed also low selectivity, the boron moiety attacking slightly more favorably C_3 than C_2 ($C_3/C_2 = 1.4/1$).[20] These reactions are supposed to take place via 4-centered transition states.[24–27] Thus, we are prompted to look for some other factors possibly affecting the reaction courses.

Dicyclopentadiene **2** possesses no particular symmetry and the occupied π_1 MO and the unoccupied π_1^* MO of the C_2–C_3 bond intermix through the interaction with the occupied π_2 and the unoccupied π_2^* MO's of the C_8–C_9 bond.[28] By taking the phase of the MO's as shown in Fig. 3, the orbital mixing is given by;

$$\sim -\frac{(\Delta_{28}{}^2 - \Delta_{39}{}^2)h^2}{(\varepsilon_{\pi_1} - \varepsilon_{\pi_1^*})(\varepsilon_{\pi_2} - \varepsilon_{\pi_1^*})} + \frac{(\Delta_{28}{}^2 - \Delta_{39}{}^2)h^2}{(\varepsilon_{\pi_1} - \varepsilon_{\pi_1^*})(\varepsilon_{\pi_1} - \varepsilon_{\pi_2^*})} \quad (3)$$

where the integrals $\Delta_{28} \cdot h$ and $\Delta_{39} \cdot h$ ($\Delta_{28} > \Delta_{39} > 0$) represent the interaction between the carbons 2 and 8

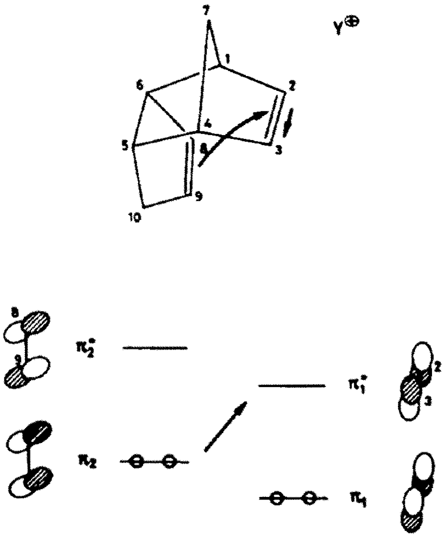


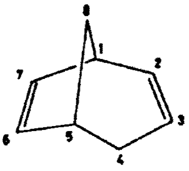
Fig. 3. A schematic illustration of the bond polarization due to the intramolecular charge transfer induced by an attacking electrophile.

and that between the carbons 3 and 9, respectively.[29] In an isolated state, $(\varepsilon_{\pi_2} - \varepsilon_{\pi_1^*}) = (\varepsilon_{\pi_1} - \varepsilon_{\pi_2^*})$ and, therefore, the charge polarization in the C_2–C_3 bond should not be significant.

Attacking electrophiles remove a fractional charge from the C_2–C_3 bond region. A partial charge will then be donated from the C_8–C_9 bond to the C_2–C_3 bond through homoconjugation to neutralize the positive charge which is concentrated on the sites under attack. That is, in the presence of a cationic moiety approaching the C_2–C_3 bond, the orbital levels are changed in such a manner as to make the energy gap $(\varepsilon_{\pi_2} - \varepsilon_{\pi_1^*})$ smaller than $(\varepsilon_{\pi_1} - \varepsilon_{\pi_2^*})$. Thus, the first term on the right-hand side of eqn (3) giving the intermixing of the π_1 and π_1^* MO's with negative sign through the interaction with the occupied π_2 MO is reinforced, while the second term arising from the interaction with the unoccupied π_2^* MO is depressed. The outcome of the cooperation between the intramolecular charge transfer through homoconjugation and the induced polarization in the C_2–C_3 bond is the accumulation of the electron density mainly on C_3 donated from the C_8–C_9 bond region. The reactivity of the C_3 atom toward the attacking electrophile is intensified.

When a cationic moiety and an anionic moiety attack the C_2–C_3 bond simultaneously, the polarization of that bond induced through homoconjugation will not be specific. Both the first and the second terms on the right-hand side of eqn (3) will be intensified and, therefore, they cancel each other. Thus, it may be concluded that stepwise additions initiated by the attack of strong electrophiles will lead to relatively good selectivity. It should be recognized also that the intramolecular transfer of a minor portion of the electronic charge through homoconjugation is responsible for the specificity in polarization and, naturally, the selectivity would not be high, in general. The slightly larger overlap population between the attacking proton and C_3 than that between proton and C_2 in the models shown in Fig. 4 appears to symbolize the slightly more favorable C_3 attack by cationic moieties. More effective electron-transfer leads obviously to the formation of a tighter bond.[30]

Other experimental findings which are consistent with our present discussion are polar additions to bicyclo [3.2.1] octa-2,6-diene **3**. Acetoxythallation, acetoxymercuration, addition of acetic acid and bromination of **3** have shown that positive thallium moiety, mercury moiety, proton and bromine attack selectively the C_6 atom.[21,31–33]



3

Polarization of bonds in reactants through the interaction with reagents is one of the basic features of chemical reactions, as has been revealed theoretically[8,11] and in MO calculations.[27] Thus, the specificity in the polarization of double bonds induced by the reagent and assisted by the homoconjugation with another double bond in the molecule is suggested to be of significance in governing the reaction path.

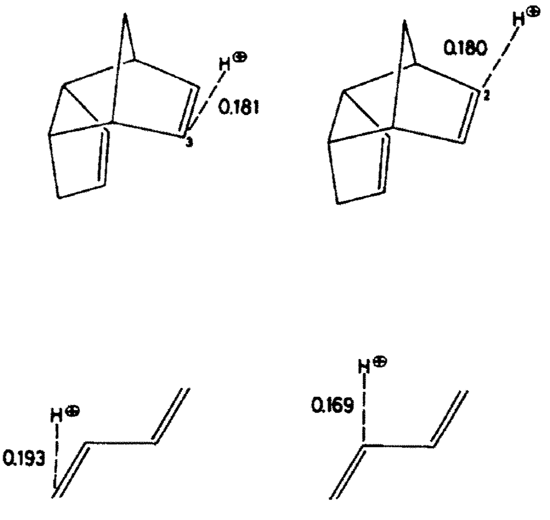


Fig. 4. Overlap populations between the proton 1s orbital and the carbon 2pπ atomic orbitals in the models of electrophilic addition to dicyclopentadiene. Proton was placed tentatively 1.5 Å above the carbon atoms perpendicular to the $C_1C_2C_3C_4$ plane. Calculations were made by the use of *ab initio* STO-3G MO method. The results on protonated butadienes were shown for reference.

Concluding remark

We should note that experimental results discussed in this paper by the use of the molecular orbital perturbation theory may be explicable by simply applying classical electrostatic theory and/or resonance theory. In addition, we have disregarded the possible influence of the sigma electron system intervening between the pi bonds. The sigma core might play a significant role, though the evaluation of its effect appears to be rather complicated.[34] The present analysis, as a crudest model, will hopefully offer a better understanding of some basic aspects of the orienting effect in homoconjugated systems and related problems, connecting the familiar concepts in organic chemistry with quantitative MO calculations available these days.

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[34] Our preliminary calculation on a system composed of two unsymmetrically located ethylene molecules and proton gave, however, a similar result as that obtained for the system consisting of **2** and proton.

APPENDIX

By neglecting the differential overlap integrals, the i th MO of the fragment B perturbed through the orbital interactions with the MO's ψ of the fragment A is given by:

$$\phi_i' = \left\{1 - 1/2\sum_k^{A} h_{ik}^2/(\varepsilon_i - \varepsilon_k)^2\right\}\phi_i$$

$$+ \sum_k^{A} h_{ik}/(\varepsilon_i - \varepsilon_k)\psi_k$$

$$+ \sum_{j(\neq i)}^{B} \sum_k^{A} h_{ik}h_{jk}/\{(\varepsilon_i - \varepsilon_k)(\varepsilon_i - \varepsilon_j)\}\phi_j +$$

A general formula representing the intermixing of the MO's ϕ_i and ϕ_j in the fragment B through the orbital interactions is derived as;

$$-4 \sum_k^{\text{occ}+\text{uno}} h_{ik}h_{jk}/\{(\varepsilon_i - \varepsilon_k)(\varepsilon_i - \varepsilon_j)\}$$

$$+ 4\sum_k^{\text{occ}} h_{ik}h_{jk}/\{(\varepsilon_k - \varepsilon_i)(\varepsilon_k - \varepsilon_j)\}$$

$$= -4\sum_k^{\text{occ}} h_{ik}h_{jk}/\{(\varepsilon_i - \varepsilon_j)(\varepsilon_k - \varepsilon_j)\}$$

$$+ 4\sum_l^{\text{uno}} h_{il}h_{jl}/\{(\varepsilon_i - \varepsilon_j)(\varepsilon_i - \varepsilon_l)\}$$

where Σ^{occ}, Σ^{uno} and $\Sigma^{\text{occ}+\text{uno}}$ signify the summation over the occupied, unoccupied and all MO's of A, respectively.