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STEREOSPECIFICITY WITH REFERENCE TO SOME CYCLIC REACTIONS

Kenichi Fukui
Department of Fuel Chemistry, Kyoto University
Kyoto, Japan

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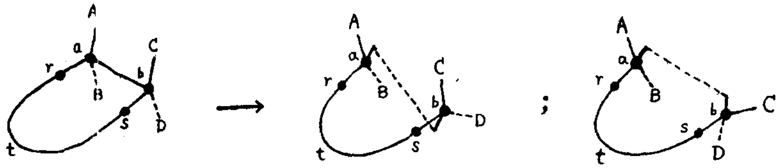
THE recent communication of Woodward and Hoffmann[1] aroused interest of organic chemists. It reported that the steric course involved in the ring-opening reaction of some cyclic olefins and also of the cyclization of linear polyenes seemed to follow an extremely simple rule in which the symmetry of the highest occupied molecular orbital (HO) of the conjugated system should play an essential role. They defined the two steric courses, the conrotatory and the disrotatory ones, and concluded that an open-chain system with $4n\pi$ electrons should undergo conrotatory displacement, while a $(4n+2)\ \pi$-electron system disrotatory one in their ground state. The basic concept seems to originate from the idea that the symmetry of HO favors the former and the latter displacements through the overlap of orbital parts on opposite faces and on the same face of the system, respectively, so as to effectuate the terminal bonding interaction. However, their explanation seems to leave room for some revisions, since to consider an overlap stabilization of one and the same molecular orbital appears very strange from quantum-mechanical point of view. The following will be of service to a more plausible explanation for the interesting remark of Woodward and Hoffmann.

The importance of the symmetry of HO and LV (lowest vacant molecular orbital) in relation to the Diels-Alder reactivity between two planar conjugated molecules was already clearly pointed out by the present author, based upon the frontier orbital concept[2]. In principle the same way of interpretation will be applicable also to the present problem. In this connection it seems more convenient to discuss the problem of ring-opening and ring-closure separately.

(1). Stereospecificity associated with the ring-opening of cyclic olefins.

The model for the mode of chemical interaction involved in the present process is represented by the following scheme. Consider



conrotatory disrotatory

a cyclic olefin which consists of a linear conjugated part, r---t---s, having (k-2) carbon 2pπ orbitals, and two sp^3 carbon atoms, a and b, bonded to each other and to the two sp^2 carbon atoms, r and s, respectively, where k is the number of π electrons of the linear polyene molecule to be produced by the ring-opening. We concentrate our attention only to the interaction between the two a-b bonding electrons and (k-2) π electrons in r---t---s part. At the initial stage they have evidently no conjugation. According as the ring-cleavage begin to proceed, a π-type conjugation will take place between the two "incipient" orbitals appearing at the carbon atoms, a and b, and the conjugated part. As is seen in the illustration, there exist two ways of interaction, in which the components, of the two incipient orbitals, perpendicular to the molecular plane are parallel and antiparallel to each other, corresponding to what are referred to as conrotatory and disrotatory processes, respectively. The problem is concerned with the question as to which of the two ways of interaction mentioned above is favorable. The change in energy of the system, ΔE, may be calculable, for instance simply by a Hückel MO (molecular orbital) perturbation treatment, if we regard the above mentioned π-like conjugation as a small perturbation. A most simple expression for ΔE may be as follows:

$$\Delta E = A + \left\{ \sum_j \nu_j \frac{(C_r^j C_a' \gamma_a + C_s^j C_b' \gamma_b)^2}{\varepsilon_j - \varepsilon_0'} - \sum_j (2-\nu_j) \frac{(C_r^j C_a \gamma_a + C_s^j C_b \gamma_b)^2}{\varepsilon_j - \varepsilon_0} \right\} + O(\gamma^4) \quad \cdots (1)$$

where

ε_0 and ε_0' : the energies of a-b bonding and antibonding orbitals which are denoted by $\chi = C_a \varphi_a + C_b \varphi_b$ and $\chi' = C_a' \varphi_a + C_b' \varphi_b$, respectively, in which φ_a and φ_b are the carbon sp^3 hybridized orbitals of the bond a-b.

ε_j : the energy of $_j$th MO of the (k-2) π-electron system which is written as

$$\psi_j = \sum_t C_t^j \phi_t$$

where ϕ_t is $_t$th 2pπ atomic orbital.

ν_j : the number of electrons occupying jth MO.

A : the term which is involved in common in both conrotatory and disrotatory processes.

γ_a and γ_b : the "resonance" intergrals (although this terminology may be queer for their positive value) between the two incipient orbitals appearing at the carbon atoms, a and b, with the adjacent $2p\pi$ orbitals at the carbon atoms, r and s.

The equations of such a kind are easily obtained by a perturbation method presented by the present author's group[3], and a similar equation was already used in the discussion of Diels-Alder reactions[2], in which both γ_a and γ_b were equal and negative. In the present case, however, γ_a and γ_b would become to have their sign in such a manner that it may favor the minimization of energy requirement of the total system, resulting in either one of the two steric courses. As is clearly understood from the illustration, their positive and negative values correspond to conrotatory and disrotatory courses, respectively.

For the sake of simplicity, Eq. (1) is reduced to the following form by taking into account most contributing terms only:

(a) For the case of the ground state π-electron system:

$$\Delta E \sim A - 2\left\{\frac{(C_r^{HO}C_a'\gamma_a + C_s^{HO}C_b'\gamma_b)^2}{\varepsilon_0' - \varepsilon_{HO}} + \frac{(C_r^{LV}C_a\gamma_a + C_s^{LV}C_b\gamma_b)^2}{\varepsilon_{LV} - \varepsilon_0}\right\} \qquad (2)$$

(b) For the case of the first excited state π-electron system:

$$\Delta E \sim A - \left\{\frac{(C_r^{LV}C_a'\gamma_a + C_s^{LV}C_b'\gamma_b)^2}{\varepsilon_0' - \varepsilon_{LV}} + \frac{(C_r^{HO}C_a\gamma_a + C_s^{HO}C_b\gamma_b)^2}{\varepsilon_{HO} - \varepsilon_0}\right\} \qquad (3)$$

where the super- and subscript HO and LV signify the highest occupied and the lowest vacant MO's in the ground state. In view of the numerical relation[4] among ε_{HO}, ε_{LV}, ε_o and ε_o', the first terms in the parentheses of Eqs. (2) and (3) seem to be more important than the second ones.

On investigating Eqs. (3) and (4), we reach at once the following conclusion: In order that ΔE may be minimized,

(a). In the case of ground state:

- (i). For k=4n: γ_a and γ_b should have opposite signs since $c_r^{HO}c_a'$ and $c_s^{HO}c_b'$, and, $c_r^{LV}c_a$ and $c_s^{LV}c_b$, have the opposite signs, leading to the conrotatory course;
- (ii). For k=4n+2: γ_a and γ_b should have the same sign since $c_r^{HO}c_a'$ and $c_s^{HO}c_b'$, and, $c_r^{LV}c_a$ and $c_s^{LV}c_b$, have the same sign, leading to the disrotatory course.

(b). In the case of excited state:

- (i). For k=4n: γ_a and γ_b should have the same sign since $c_r^{LV}c_a'$ and $c_s^{LV}c_b'$, and, $c_r^{HO}c_a$ and $c_s^{HO}c_b$, have the same sign, leading to the disrotatory course;
- (ii). For k=4n+2: γ_a and γ_b should have opposite signs since $c_r^{LV}c_a'$ and $c_s^{LV}c_b'$, and, $c_r^{HO}c_a$ and $c_s^{HO}c_b$, have opposite signs, leading to the conrotatory course.

(2). Stereospecificity associated with the ring-closure of linear polyenes.

It seems to me more acceptable to adopt, for the problem of cyclization, a different way of interpretation from what has been given for the reverse process mentioned above, since in this case the explanation of experimental facts is extremely simple and evident if we employ the well-known relation[5] that the mode of energy change accompanying the bonding between the two termini of a linear polyene having k π orbitals is opposite to each other in the cases of k=4n and k=4n+2. The formulation is very easy since in this case we have

$$\Delta E = A + 2\sum_j \nu_j C_a^j C_b^j \gamma + O(\gamma^2) \qquad (4)$$

where C_a^j and C_b^j are the coefficients of $2p\pi$ atomic orbitals at the carbon atoms, a and b, respectively, of jth MO of the k π-orbital system; γ is the resonance integral of the $p\sigma$-type conjugation between the two π orbitals at the terminal carbons. In order that Δ E is small as possible, γ should be negative when $\sum_j \nu_j C_a^j C_b^j$ is positive while it should be positive when the latter is negative. The quantity, $P_{ab}=\sum_j \nu_j C_a^j C_b^j$, is of the same form as what is known as the bond order, although the meaning is not competely the same. It is easily concluded, therefore, that:

(a). In the case of ground state:

  (i). For k=4n: P_{ab} is negative so that γ is positive, resulting in the *conrotatory* process;

  (ii). For k=4n+2: P_{ab} is positive so that γ is negative, resulting in the *disrotatory* process.

(b). In the case of excited state:

  (i). For k=4n: P_{ab} is positive so that γ is negative, resulting in the *disrotatory* process;

  (ii). For k=4n+2: P_{ab} is negative so that γ is positive, resulting in the *conrotatory* process.

All of the conclusions are completely the same as that of

Woodward and Hoffmann, in agreement with experimental results so far obtained. Also the present method of interpretation leads to the same predictions as theirs, although their standpoint is quite different from mine.

Finally I have to mention that some reservations should be made with respect to the limit of applicability of such a theoretical result, since the "steric" circumstances among the four groups, A, B, C, and D, attached to the terminal carbons, a and b, must be always influential.

REFERENCES

1. R. B. Woodward, R. Hoffmann, J. Am. Chem. Soc. 87, 395 (1965).
2. K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology" edited by P.-O. Löwdin and B. Pullman, Academic Press Inc., New York, p. 525 (1964).
3. K. Fukui, C. Nagata, T. Yonezawa, H. Kato, K. Morokuma, J. Chem. Phys. 31, 287 (1959).
4. K. Fukui, H. Kato, T. Yonezawa, K. Morokuma, A. Imamura, C. Nagata, Bull. Chem. Soc. Japan 35, 38 (1962).
5. See for instance K. Fukui, A. Imamura, T. Yonezawa, C. Nagata, Bull. Chem. Soc. Japan 33, 1591 (1960).