*Tetrahedron* Vol. 42, No. 2, pp. 515 to 522, 1986
Printed in Great Britain.

0040-4020/86 $3.00 + .00

# MO APPROACH TO THE AROMATICITY OF TRANSITION STATES OF THE GENERALIZED PERICYCLIC REACTIONS*

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(*Received in Japan* 1 *July* 1985)

**Abstract** — The aromaticity of transition states of generalised pericyclic reactions has been examined by the HMO method. Established thereby is a secular equation from which all the specific secular equations for different types of pericyclic reactions can be derived and with which the generalisation of Woodward and Hoffmann can be substantiated.

## INTRODUCTION

The principal merit of the approach to pericyclic reactions in terms of aromatic transition state (TS) theory is that energy changes in this kind of reactions can be interpreted by the concept of aromaticity that was developed in empirical organic chemistry and gains support from modern quantum theory[1-3]. However, so far treatment of the potential aromaticity of the TSs of pericyclic reactions has had to resort to the Hückel-Möbius aromaticity criterion for normal cyclic polymethines. In order to devise a sounder theoretical basis for aromatic transition state theory, we have approached the TSs of various types of pericyclic reactions by MO method and thereby obtained the energy levels of the MOs of TSs and, in turn, the activation energies of the reactions. The evidence thus provided indicates that pericyclic reactions are thermally allowed, provided their TSs are aromatic, so that their activation energies are lower than those of the non- or antiaromatic ones. In the light of such an approach, we are in a position to clarify the feasibility to predict the electronic and topological requirements for the allowance and prohibition of the pericyclic reactions by means of aromaticity concept for the normal molecules of cyclic polymethines[4].

In the present work we are attempting to treat the TSs of the generalised pericyclic reactions, so as to find out the generalised structural and topological requirements for the TSs of diversified reacting systems as they partake of the aromatic or antiaromatic properties.

As is well known, Woodward and Hoffmann have formulated for the pericyclic reactions an empirical generalisation in which various types of this kind of reactions are regarded as intra- or intermolecular cycloadditions. In the present approach pericyclic reactions are likewise so regarded and the results thus obtained are compared and analysed in contrast with those attained by Woodward and Hoffmann[1].

## MATHEMATICAL APPROACH

The topological structures of TSs of differentiable types of pericyclic reactions have one thing in common that they are equivalent to those of the corresponding cyclic polymethines containing as many electrons as take part in first order pericyclic transformation of bonding relationships, ( bond breaking and making) since these reactions can be treated as concerted intra- or intermolecular

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*Project supported by the Science Fund of Chinese Academy of Science.

cycloaddition processes as Woodward and Hoffmann pointed out several years before. Based on such a generalisation we are in a position to devise a mathematical approach to the TS of the generalised pericyclic transformation.

Let the total number of the components taking part in the pericyclic reactions be n ($n \geqslant 2$) and $r_1, r_2, \ldots r_n$ be the numbers of carbon atoms constituting the conjugated chains of the corresponding components. If the total number of carbon atoms of the atomic chain of the TS, $N = \sum_{i=1}^{n} r_i$, is even, we may take all the $r_i$ be even; if, however, N is odd, we may take that there is only one component with $r_n$ being odd. It is remarkable what is postulated here is the generalised mode rather than the individual special one, because of the following: (1) It is both theoretically and practically inconceivable to have two or more components with an odd number of carbon atoms irrespective of whether anions, cations or radicals containing $4q + 1$ or $4q + 3$ carbon atoms the components may be. (2) Since electrocyclic and sigmatropic reactions can all be regarded as intramolecular concerted cycloaddition, it is sheerly unnecessary to single out two or more components containing an odd number of carbon atoms.

The interactions between the two terminal atomic orbitals of two neighboring components taking part in the formation of the TS of a generalised pericyclic reaction is shown in Fig. 1 where $\pm b_i\beta$ ($i = 1, 2, \ldots n$) stand for the interactions between two terminal $p_z$ atomic orbitals of neighboring components with + or − indicating overlaps in phase and out of phase respectively; $a_i\beta$ and $a'_i\beta$ represent the interactions between $p_z$ orbitals of the terminal atoms and the neighboring ones within the same component.

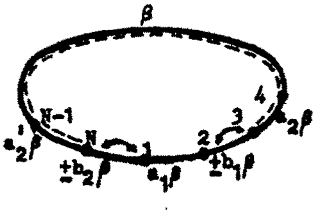

Fig. 1. TS of a generalised pericyclic reaction (an electrocyclic reaction between one $\sigma$ component (involving $C_1, C_2$) and one $\pi$ component (involving $C_3, C_4, \ldots C_N$).

Obviously, $a_i$ and $a'_i$ are identical for components containing two atoms ($r_i = 2$). Moreover, $b_i$, $a_i$ and $a'_i$ are functions of the angles $\varphi$ resulting from rotation of the $p_z$ orbitals from their original axis perpendicular to the plane of the pericyclic ring.

Take, for example, an electrocyclic reaction of a linear conjugated polyene. As the reaction proceeds, the interactions between the terminal carbon atoms and the neighboring carbon atoms change from $\beta$ to $\beta\cos\varphi$. Because of the rotation of the terminal atoms, the axis of the $p_z$ orbitals deviates from its original place by an angle $\varphi$. This angle is refered to as the angle of rotation. At the initial stage of reaction, there is no interaction between the terminal carbon atoms. However, as the reaction proceeds, it increases with increasing the degree of $\varphi$ designated by $\gamma(1 - \cos\varphi)$ or $-\gamma(1 - \cos\varphi)$ depending on whether the orbital interactions are in phase or out of phase, where $\gamma$ is the energy of C–C single bond. If the usual values are adopted for $\gamma$ and $\beta$, then $\gamma/\beta = 1.3$. Hence an electrocyclic reaction can be regarded as the cycloaddition of a $\sigma$ and a $\pi$ component ($r_1 = 2$, $r_2 = N - 2$) in which $n = 2$, $a_1 = 1.3\,(1 - \cos\varphi)$, $a_2 = a'_2 = 1$ and $b_1 = b_2 = \cos\varphi$ (Fig. 1).

Using the notation defined in Fig. 1, the secular determinant $R_N^{TS}$ for the resolution of the MOs of the TS of the generalised pericyclic reaction can be established as follows (page 3), where $x = (\alpha - E)/\beta$.

Expansion of the determinant by the Laplacian theorem and mathematical induction gives the following secular polynomial for the TS of the generalised pericyclic reaction:

$$\text{When } r_n > 1,\ R_N^{TS} = Z_n T_{n-1} - b_{n-1}^2 Y_n S_{n-1} - b_n^2 Y'_n S'_{n-1} + b_{n-1}^2 b_n^2 K_{r_n - 2} S''_{n-1} + (-1)^{k+N+1} 2 \prod_{\substack{1 \leqslant i \leqslant n \\ r_i > 2}} a_i a'_i b_i \prod_{\substack{1 \leqslant j \leqslant n \\ r_j = 2}} a_j b_j = 0 \qquad (1)$$

$$\text{When } r_n = 1,\ R_N^{TS} = XT_{n-1} - b_{n-1}^2 S_{n-1} - b_n^2 S'_{n-1} + (-1)^k 2\, b_n \prod_{\substack{1 \leqslant i \leqslant (n-1) \\ r_i > 2}} a_i a'_i b_i \prod_{\substack{1 \leqslant j \leqslant (n-1) \\ r_j = 2}} a_j b_j = 0 \qquad (2)$$

In Eqs (1) and (2), k is the number of times which the terminal carbon atoms of neighboring components overlap in an out-of-phase manner. In other words, it is the number of times which the components participate in the reaction in an antarafacial manner.

$$\begin{vmatrix}
x & a_1 & 0 & \cdots & & & & & & & \pm b_n \\
a_1 & x & 1 & 0 & \cdots & & & & & & \cdots \\
0 & 1 & x & 1 & 0 & \cdots & & & & & \cdots \\
\cdots & & & & & & & & & & \cdots \\
& 0 & 1 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & 1 & x & a_1' & 0 & \cdots & & & & \cdots \\
\cdots & 0 & a_1' & x & \pm b_1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & \pm b_1 & x & a_2 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & a_2 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & 1 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & & & & & & & & & & \cdots \\
\cdots & 0 & 1 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & 1 & x & a_2' & 0 & \cdots & & & & \cdots \\
\cdots & 0 & a_2' & x & \pm b_2 & 0 & \cdots & & & & \cdots \\
\cdots & & & & & & & & & & \cdots \\
\cdots & 0 & \pm b_{n-2} & x & a_{n-1} & 0 & \cdots & & & & \cdots \\
\cdots & 0 & a_{n-1} & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & 1 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & & & & & & & & & & \cdots \\
\cdots & 0 & 1 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & 1 & x & a_{n-1}' & 0 & \cdots & & & & \cdots \\
\cdots & 0 & a_{n-1}' & x & \pm b_{n-1} & 0 & \cdots & & & & \cdots \\
\cdots & 0 & \pm b_{n-1} & x & a_n & 0 & \cdots & & & & \cdots \\
\cdots & 0 & a_n & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & 0 & 1 & x & 1 & 0 & \cdots & & & & \cdots \\
\cdots & & & & & & & & & & \cdots \\
\cdots & & & & & & \cdots & 0 & 1 & x & 1 & 0 \\
\cdots & & & & & & & \cdots & 0 & 1 & x & a_n' \\
\pm b_n & \cdots & & & & & & & \cdots & 0 & a_n' & x
\end{vmatrix} = 0$$

When $r_i = 2$ $(i = 1,2,3\ldots n)$, $Z_i = X^2 - a_i^2$

$r_n = 3$, $Z_n = x^3 - a_n^2 - a'^2_n X$

$r_i > 3$

$$Z_i = \begin{vmatrix}
X & a_i & 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\
a_i & X & 1 & 0 & \cdot & \cdot & \cdot & \cdot \\
0 & 1 & X & 1 & 0 & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & 0 & 1 & X & 1 & 0 \\
\cdot & \cdot & \cdot & \cdot & 0 & 1 & X & a_i' \\
\cdot & \cdot & \cdot & \cdot & \cdot & 0 & a_i' & X
\end{vmatrix}_{r_i \text{ order}} = x\,(x\,K_{r_i-2} - a_i'^2\,K_{r_i-3}) - a_i^2\,(x\,K_{r_i-3} - a_i'^2 K_{r_i-4}) \quad (3)$$

$Y_i$ is a minor of $(r_i - 1)$ order obtained from the determinant $Z_i$ by deleting the first row and column.

When $r_i = 2$, $Y_i = X$

When $r_i > 2$, $Y_i = X\,K_{r_i-2} - a_i'^2\,K_{r_i-3}$ (4)

$Y_i'$ is likewise a minor of $(r_i - 1)$ order obtained from the determinant $Z_i$ by deleting the $r_i$th row and columns. Thus

when $r_i = 2$, $Y_i' = X$

when $r_i > 2$, $Y_i' = X\,K_{r_i-2} - a_i^2\,K_{r_i-3}$ and $T_i = Z_i T_{i-1} - b_{i-1}^2\,Y_i\,S_{i-1}$ $(i = 1,2,3 \ldots n-1)$ (5), (6)

$T_i$ is a minor of $\sum_{J=1}^{i} r_j$ order obtained from the secular determinant $R_N^{TS}$ by deleting the rows and columns after the $(\sum_{j=1}^{i} r_j)$th ones. Set $T_o = 1$, $S_o = 0$, we have $T_1 = Z_1$ and $S_i$ is a minor of $(\sum_{j=1}^{i} r_j) - 1$ order obtained from the determinant $T_i$ by deleting the $(\sum_{j=1}^{i} r_j)$th row and column.

$$S_i = Y_i' T_{i-1} - b_{i-1}^2 K_{r_i-2} S_{i-1} \quad (i = 1,2,3, \ldots. n-1) \tag{7}$$

Obviously $S_1 = Y_1'$. $S_i'$ is again a minor of $(\sum_{j=1}^{i} r_j) - 1$ order derived from $T_i$ with the first row and column stricken out.

$$S_i' = Z_i S_{i-1}' - b_{i-1}^2 Y_i S_{i-1}'' \quad (i = 2,3, \ldots. n-1) \tag{8}$$

Finally, let $S_1' = Y_1$, then $S_i$ is the minor of $(\sum_{j=1}^{i} r_j) - 2$ order derived from $T_i$ by striking out the first and the $(\sum_{j=1}^{i} r_j)$th rows and columns.

$$S_i'' = Y_i' S_{i-1}' - b_{i-1}^2 K_{r_i-2} S_{i-1}'' \quad (i = 2,3, \ldots. n-1) \tag{9}$$

Set $S_1'' = K_{r_1-2}$, then $K_{r_1-2}$, $K_{r_1-3}$, .... represent the characteristic polynomials of open chain conjugated polyenes containing $r_1 - 2$, $r_1 - 3$ ... carbon atoms, respectively. It is of course well known that for conjugated open chain polyenes with g carbon atoms, the characteristic polynomial can be expanded to give

$$K_g = \sum_{f=0}^{g/2 \text{ or } (g-1)/2} (-1)^f \frac{(g-f)!}{f!(g-2f)!} x^{g-2f} \tag{10}$$

of which $K_o = 1$, $K_1 = x$.

It is worth mentioning here that from the expressions for the polynomials of the TSs of the generalised pericyclic reactions (1) and (2), all the secular polynomials of differentiable types of pericyclic reactions can be deduced, we would like to put off this problem for the time being and take into consideration the aromaticity of the TSs of generalised pericyclic reactions.

## RESULTS AND DISSCUSION

Equation (10) is now being employed to analyse Eq (1), so as to examine the aromaticity of the TSs of concerted cycloaddition processes containing n components.

### 1. Systems containing an even number of carbon atoms

When the sum N of the number of carbon atoms of all components participating in the pericyclic transformation is even, the TS may be regarded as composed of $E_{4q+2}$ components containing 4q + 2 carbon atoms each and $E_{4q}$ components containing 4q carbon atoms each. By application of Eq (10) it can be seen that neither $K_{4q-2}$ nor $K_{4q}$ involves terms of odd ordinal powers of x but only terms of even ordinal powers of x and a constant. $K_{4q+3}$ and $K_{4q+1}$ contain terms of odd ordinal powers of x. Hence, $Z_i$ does not contain x to odd ordinal powers, but x to even ordinal ones and a constant, thus neither $Y_i$ nor $Y_i'$ contains terms of even ordinal powers of x and constant, but terms of odd ordinal powers of x. Therefore, $T_1 = Z_1$. $T_1$ does not contain odd ordinal powers of x but even ones and a constant, whereas

$$\begin{aligned} T_2 &= Z_2 T_1 - b_1^2 Y_2 S_1 \\ &= Z_2 Z_1 - b_1^2 Y_2 Y_1 \end{aligned}$$

Therefore, $T_2$ does not contain odd ordinal powers of x but even ones and constant which emerges from $Z_2 Z_1$, and

$$\begin{aligned} T_3 &= Z_3 Z_2 - b_2^2 Y_3 S_2 \\ &= Z_3 Z_2 Z_1 - b_1^2 Z_3 Y_2 Y_1' - b_2^2 Y_3 (Y_2' Z_1 - b_1^2 K_{r_2-2} Y_1') \end{aligned}$$

Hence, $T_3$, just like $T_1$ or $T_2$, does not contain odd ordinal powers of x, but even ones and a constant which emerges from $Z_1 Z_2 Z_3$. Therefore, $T_{n-1}$ does not contain odd ordinal powers of x, but even ones and a constant. Consequently, the term $Z_n T_{n-1}$ in Eq (1) does not contain x to odd ordinal powers, but even ones and a constant.

In the same manner, it can be shown that $S_{n-1}$ and $S'_{n-1}$ contain neither even ordinal power of x nor a constant, but odd ones. However, because neither $Y_n$ nor $Y'_n$ contains even ordinal powers of x and constant, yet they contain odd ones with the result that $-b^2_{n-1} Y_n S_{n-1}$ and $-b^2_n Y'_n S'_{n-1}$ in Eq (1) contain no odd ordinal powers of x but even ones. Yet there is no constant in both of them.

In addition to this, it can easily be shown that there is no odd ordinal powers of x in the term, $b^2_{n-1}\, b^2_n K_{r_n-2} S''_{n-1}$ of Eq (1), but there is even ones and a constant.

It is, therefore, evident that if N is even, the secular polynomial of TS, Eq (1), contains only even ordinal powers of x but no odd ones. Thus the distribution of energy levels of MOs is symmetric above and below $E = \alpha$ being reminiscent of the normal conjugated cyclic polymethines.

It can be shown that the constant term is made of

$$(-1)^t \prod_{\substack{1\le i\le n\\ r_i>2}} a_i^2 a_i'^2 K_{r_i-4} \prod_{\substack{1\le j\le n\\ r_j=2}} a_j^2$$

emerging from $Z_n T_{n-1}$

$$(-1)^n \prod_{1\le i\le n} b_i^2 K_{r_i-2}$$

emerging from $b^2_{n-1}\, b^2_n\, K_{r_n-2}\, S''$ and

$$(-1)^{k+N+1}\, 2 \prod_{\substack{1\le i\le n\\ r_i>2}} a_i\, a_i'\, b_i \prod_{\substack{1\le j\le n\\ r_j=2}} a_j\, b_j$$

by summing them up altogether algebraically, t being the number of components participating in the reaction and containing two carbon atoms.

Since the constants in $K_{4q+2}$ and $K_{4q}$ are $-1$ and $+1$ respectively, it follows that the constant terms in Eq (1) can be denoted by

$$(-1)^{E_{4q+2}} \prod_{\substack{1\le i\le n\\ r_i>2}} a_i^2 a_i'^2 \prod_{\substack{1\le j\le n\\ r_j=2}} a_j + (-1)^{E_{4q+2}} \prod_{1\le i\le n} b_i^2 + (-1)^{k+1}\, 2 \prod_{\substack{1\le i\le n\\ r_i>2}} a_i a_i' b_i \prod_{\substack{1\le j\le n\\ r_j=2}} a_j b_j \tag{11}$$

If the number of components taking part in the reaction and containing $4q + 2$ atoms is odd, i.e. $E_{4q+2} = 2m + 1$ ( $m = 0,1,2,\ldots.$) and moreover if $k = 2l + 1$ ($l = 0,1,2, \ldots.$), then the delocalised system of TS is of Möbius type with $N = 4p + 2$ ( $p = 1,2,3, \ldots.$). Therefore, the constant term in Eq (1) i.e. the term (11) itself is

$$-\Big(\prod_{\substack{1\le i\le n\\ r_i>2}} a_i a_i' \prod_{\substack{1\le j\le n\\ r_j=2}} a_j - \prod_{1\le i\le n} b_i\Big)^2$$

Obviously, when

$$\prod_{\substack{1\le i\le n\\ r_i>2}} a_i\, a_i' \prod_{\substack{1\le j\le n\\ r_j=2}} a_j = \prod_{1\le i\le n} b_i$$

the constant in Eq (1) is zero, leading to a pair of roots $x_i = 0$. Consequently the TS of diradical nature with antiaromatic properties. Such being the case, the pericyclic reaction is thermally prohibited. Hence the rotation angle $\varphi_u$, which makes the term (11) equal zero, is refered to as antiaromatic characteristic angle. This situation may be so rationalised that as the reaction proceeds the angle of rotation of the terminal p orbital becomes $\varphi_u$ which makes the delocalised system of the reaction partake of the diradical nature, so that the formation of closed shell is impossible and the pericyclic reaction is thermally prohibited. For intermolecular cycloaddition containing n components, the characteristic antiaromatic angle $\varphi_u$ can be found from the term (11). Under such cases, $a_i = a_i = \cos\varphi_u$ and $b_i = 1.3(1 - \cos\varphi_u)$. Therefore, as $t = 0$, $\varphi_u = 48.13^\circ$; $t = n$, $\varphi_u = 55.06^\circ$; when $0 < t < n$, then $48.13^\circ < \varphi_u < 55.06^\circ$.

As to electrocyclic reactions and [m,n] sigmatropic reactions, the $\varphi_u$ can be easily calculated to give $\varphi_u = 48.13^\circ$ and $60^\circ$ respectively[4].

However, if $k = 2l$ ( $l = 0,1,2, \ldots.$), then the delocalised system of the TS is no longer of Möbius type with $4p + 2$ atoms, but of Hückel one. There does exist in Eq (1) a constant other than zero:

$$-\Big(\prod_{\substack{1\leq i\leq n\\ r_i>2}} a_i a_i' \prod_{\substack{1\leq j\leq n\\ r_j=2}} a_j + \prod_{1\leq i\leq n} b_i\Big)^2 \neq 0$$

Therefore, Eq (1) has no solution, $x_i = 0$, but has $(2p + 1)$ positive and negative roots each. The corresponding energy levels are then distributed above and below the energy level with $E = \alpha$. If the system contains $4p + 2$ electrons they will accomodated to all the energy levels below $E = \alpha$, resulting in the formation of a closed electron shell with aromatic properties. Under such circumstances, the pericyclic reactions are, therefore, thermally allowed.

So far systems with odd number of components containing $4p + 2$ atoms have been examined. The discussion on systems of this kind but with an even number of components, i.e. $E_{4q+2} = 2m$ is now in order. Under such cases, $N = 4p$ $(p = 1,2,3,\ldots.)$. If $k = 2l$ $(l = 0,1,2,\ \ldots.)$, Then the TS can be ascribed to delocalised systems of Hückel type with $4p$ atoms. The constant term in Eq (1) i.e. (11) is

$$\Big(\prod_{\substack{1\leq i\leq n\\ r_i>2}} a_i a_i' \prod_{\substack{1\leq j\leq n\\ r_j=2}} a_j - \prod_{1\leq i\leq n} b_i\Big)^2.$$

When

$$\prod_{\substack{1\leq i\leq n\\ r_i>2}} a_i a_i' \prod_{\substack{1\leq j\leq n\\ r_j=2}} a_j = \prod_{1\leq i\leq n} b_i$$

the constant term of Eq (1) is zero, with the result that the TS is diradical in nature and antiaromatic in properties. Under such a circumstance, pericyclic reactions are thermally prohibited and the characteristic angle of the antiaromatic TS is all the same as pointed out before.

If $k = 2l + 1$ $(\ l = 0,1,2,\ \ldots.)$, then TS is ascribed to Möbius system containing $4p$ atoms, and the constant term of Eq (1) is not equal to zero. Therefore, there is no root, $x_i = 0$, but $2p$ positive and negative roots each. Moreover, the corresponding energy levels are symmetrically distributed above and below $E = \alpha$. At TS the $4p$ electrons taking part in first order change of the bonding relationship can well accomodate to energy levels below $\alpha$ with the result that the TS is aromatic and the reaction is thermally allowed.

Up to now, all cases where $N$ is even have been run over, the conclusion thus far attained is that all the TSs of pericyclic reactions follow the same rule of aromaticity as normal molecule of conjugated cyclic polymethines do. In short, all allowed pericyclic reactions proceed through aromatic TSs.

2. Systems containing an odd number of carbon atoms.

The reaction systems containing an odd number of carbon atoms may be regarded as composed of $E_{4q+2}$ and $E_{4q}$ components containing $4q + 2$ and $4q$ atoms respectively and, in addition to this, a single component containing odd number of atoms which is always denoted by $r_n$. Although $T_{n-1}$ does not contain terms of odd ordinal power of x but even ones and a constant, yet $Z_n$ does with the result that $Z_n T_{n-1}$ is composed of terms of odd ordinal powers of x but no terms of even ones or a constant. Evidently, $Y_n$ and $Y_n'$ do not contain terms of odd ordinal power of x, neither $S_{n-1}$ nor $S_{n-1}'$ contains even ordinal powere of x but odd ones with the result that $-b_{n-1}^2 Y_n S_{n-1}$ and $-b_n^2 Y_n' S_{n-1}'$ do not contain any terms of even powers of x or a constant but terms of odd powers of x. Because there is no odd ordinal power of x in $S_{n-1}''$, whereas there is in $K_{r_n-2}$, $b_{n-1}^2\ b_n^2 K_{r_n-2} S_{n-1}''$ is likewise composed of terms of odd ordinal powers of x only. Under such cases, there are terms of odd ordinal powers of x and a constant in (1), thus the constant of which does not equal to zero i.e.

$$(-1)^k\, 2 \prod_{\substack{1\leq i\leq n\\ r_i>2}} a_i a_i' b_i \prod_{\substack{1\leq j\leq n\\ r_j=2}} a_j b_j \neq 0 \tag{12}$$

If $k = 2l + 1$ $(l = 0,1,2,\ \ldots.)$, i.e. the TS is of Möbius type, then the value of the left hand side of the inequality (12) is negative; if $k = 2l$ $(\ l = 0,1,2,\ \ldots.\ )$ i.e. TS is of Hückel type, then the value of the left side of (12) is positive. This situation is sheerly reminiscent of the secular polynomial of Hückel-Möbius system of normal cyclic polymethines containing an odd number of carbon atoms. Under such cases, the energy level distributions of the MOs of the TSs are closely similar to that of normal conjugated cyclic polymethinas. If the energy level diagram for the TSs of Hückel type is reflected symmetrically, with reference to $E = \alpha$ there will give rise to the Möbius one. The TS likewise follow the same rule of aromaticity as do the normal molecules of conjugated cyclic polymethines. Cationic TSs of Möbius type and anionic TSs of Hückel type with total number of carbon atoms $N = 4p + 1$, and cationic TSs of Hückel type and anionic TSs of Möbius type with total number of carbon atoms $N = 4p + 3$ all partake of the closed electron shell of aromatic structure through which the pericyclic reactions proceed thermally. In contrast to this, cationic TSs of Hückel type and anionic TSs of Möbius type with total number of carbon atoms $N = 4p + 1$ and cationic TSs of Möbius type and anionic TSs of Hückel type with total number of carbon atoms $N = 4p + 3$ are nonaromatic and it is unlikely for them to play the role of the role of TSs of pericyclic reactions.

A brief account concerning Eq (2) is worth mentioning. Actually this equation emerges from the special case where the number of carbon atoms of the component containing odd number of carbon atoms is unity, i.e. $r_n = 1$. It can be seen that if such is the case, the rules of aromacity for TSs of pericyclic reaction deduced from Eq (2) is entirely the same as those deduced above from Eq (1).

In the following section we are attempting to deduce the generalisation for pericyclic reaction from the concept of aromaticity of the TS of this kind of reactions.

1. Systems with even N

In the foregoing presentation we have explained pretty fully that when $E_{4q+2} = 2m + 1$ ($m = 0,1,2, \ldots.$), $k = 2l$ ( $l = 0,1,2, \ldots.$), then TS is of Hückel type containing $4p + 2$ atoms with aromaticity. Such being the case pericyclic reactions are thermally allowed. Now, let $A_{4q+2}$ and $S_{4q+2}$ stand, respectively, for the numbers of the antarafacial and suprafacial components containing $4q + 2$ electrons and $A_{4q}$ and $S_{4q}$ represent, respectively, the numbers of the antarafacial and suprafacial components containing $4q$ electrons, we have

(a) when $A_{4q+2} = 2u$ ($u = 0,1,2, \ldots.$), then $S_{4q+2} = 2 ( m - u ) + 1$

and the number of antarafacial components $A_{4q}$ in ($4q$) component should be

$$A_{4q} = k - A_{4q+2} = 2(l - u)$$

resulting in

$$S_{4q+2} + A_{4q} = 2(l + m - 2u) + 1$$

This indicates that in aromatic TSs the total number of $(4q + 2)_s$ and $(4q)_a$ components is odd;

(b) when $A_{4q+2} = 2u + 1$, we have $S_{4q+2} = 2(m - u)$

$$A_{4q} = 2(l - u) - 1$$

with the result that

$$S_{4q+2} + A_{4q} = 2(l + m - 2u) - 1$$

This again indicates that the total number of $(4q + 2)_s$ and $(4q)_a$ components is odd.

Hence the requirement of aromaticity of the TSs of $(4p + 2)$ Hückel type of a thermally allowed pericyclic reaction implies that the total number of $(4q + 2)_s$ and $(4q)_a$ components is odd.

In compliance with the above inference, it can be affirmed that when TS of a pericyclic reaction meets the requirement of aromaticity of $(4p)$ Möbius type, the total number of $(4q + 2)_s$ and $(4q)_a$ component is necessarily odd. Such being the case, the pericyclic reactions are thermally allowed. But with Möbius systems of $(4p + 2)$ type and Hückel, $(4p)$ one, the reaction is thermally prohibited. Since under such circumstances the TSs are necessarily antiaromatic and the total number of $(4q + 2)_s$ and $(4q)_a$ components must be even.

2. Systems with odd N

Set $A'_{4q+2}$, $S'_{4q+2}$ to represent correspondingly the number of the antarafacial and suprafacial components containing $(4q + 2)$ atoms in the conjugated chains, and $A'_{4q}$, $S'_{4q}$ stand, respectively, for the number of antarafacial and suprafacial components with $4q$ atoms in the conjugated chains. It should be noted that anionic and cationic components containing $r_n = 4q + 1$ atoms are ascribed to $(4q + 2)$ and $(4q)$ components respectively; whereas anionic and cationic components containing $r_n = 4q + 3$ atoms belong to $(4q)$ and $(4q + 2)$ components respectively.

When $N = 4p + 1$, the TS of cationic Möbius type is aromatic. Two cases stem from such a situation: firstly, $E_{4q+2} = 2m + 1$, $r_n = 4q + 3$; and secondly, $E_{4q+2} = 2m$, $r_n = 4q + 1$.

If $E'_{4q+2} = 2m + 1$, $r'_n = 4q + 3$

(1) If $A'_{4q+2} = 2u + 1$, $S'_{4q+2} = 2(m - u)$

Suppose the nth component participates in the reaction in suprafacial manner, then

$S_{4q+2} = S'_{4q+2} + 1 = 2(m - u) + 1$

$A_{4q} = k - A_{4q+2} = 2(l - u)$ where $k = 2l + 1$

Therefore,

$S_{4q+2} + A_{4q} = 2(l + m - 2u) + 1$

In case the nth component takes part of the reaction in an antarafacial manner, then

$S_{4q+2} = S'_{4q+2} = 2(m - u)$,

$A_{4q+2} = A'_{4q+2} + 1 = 2(u + 1)$ and

$A_{4q} = k - A_{4q+2} = 2(l - u) - 1$

Hence,

$S_{4q+2} + A_{4q} = 2(l + m - 2u) - 1$

(2) If $A'_{4q+2} = 2u$, it can be easily shown in the same manner, that under such circumstances the total number of $(4q + 2)_s$ and $(4q)_a$ is odd.

With the cases where $E_{4q+2} = 2m$, $r_n = 4q + 1$, the conclusion is self-evident and needs no further remarks.

We are now in a position to conclude that when $N = 4p + 1$, cationic TSs of Möbius type are aromatic; such being the case, the systems must fulfil the requirement of the Woodward-Hoffmann rule, i. e. the sum of the $(4q + 2)_s$ and $(4q)_a$ components must be odd for a pericyclic reaction to be thermally allowed.

When N is odd, TSs having aromatic properties still include anionic TSs of Hückel type with $N = 4p + 1$, cationic TSs of Hückel type and anionic TSs of Mobius type with $N = 4p + 3$, In all such systems the total sums of the number of $(4q + 2)_s$ and $(4q)_a$ components are necessarily odd. All such conclusions can easily be substantiated in exactly the same manner and we are not to dwell upon this point redundantly.

To sum up, the aromatic TS theory and the general rule of the principle of conservation of orbital symmetry can be regarded as the same concept described in different terminology. These two theorems have been being intricated together only because of ambiguity of the terminology.

In short the TS of a thermally allowed pericyclic reaction is aromatic wherein the total sum of the $(4q + 2)_s$ and $(4q)_a$ components is necessarily an odd number.

Acknowledgements — The authors wish to express their gratitude to Chinese Academy of Science for providing funds. Thanks are also due to Professor J. Wirz of Institut für Physikalische Chemie, Universitat Basel, Switzerland for reading the manuscript.

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