Determination of Reactivities by Molecular Orbital Theory
Part IV. Application of IMO Method to Some Thermal Diels-Alder Reactions

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Abstract The intermolecular orbital theory was applied to the Diels-Alder reactions of naphthalene, phenanthrene and 1,2-benzanthracene with maleic anhydride. The expected positions of thermal addition in the alternant hydrocarbons were in agreement with experiment. It was also possible to explain the relative proportions of two isomeric adducts with the calculated stabilization energies. Comparison of the results with paralocalization energies of Brown gave a good linear correlation.

Introduction

The Diels-Alder reaction is the addition of a diene and a dienophile such as maleic anhydride (MA). In this type of reaction, many aromatic hydrocarbons behave as dienes and yield polycyclic adducts.

The first theoretical treatment of the Diels-Alder reaction by quantum mechanical methods is that by Brown, who applied the standard linear combination of atomic orbitals (LCAO) molecular orbital (MO) method to the study of the addition of polycyclic hydrocarbons and the polynenes. He proposed a reactivity index, paralocalization energy, \( L_p \), defined as the loss in \( \pi \) bonding energy that results when two carbons having a mutual para orientation are removed from a \( \pi \) network. For the formation of adducts with MA he has shown that aromatic hydrocarbons apparently give an adduct under usual experimental conditions only when the corresponding paralocalization energy is less than 3.60.

Later Dewar confirmed the theoretical results of Brown by the use of the nonbonding molecular orbital (NBMO) method. To a first approximation, he suggested that the paralocalization energy should be equal to the sum of the individual localization energies at the two carbon atoms. Comparison of the two carbon atoms. Comparison of the values so calculated with the more accurate results of Brown gave an excellent agreement. Hopff and Schweizer have shown the validity of the Dewar's simple localization approximation.

The free electron molecular orbital (FFMO)
method was used for the first time by Basu in the study of this type of synthesis. His treatment was limited to a small number of molecules. Sebastian extended this method to a number of aromatic hydrocarbons. The results obtained were in good agreement with those calculated by the LCAO-MO method as well as with the experimental results for MA addition. He concluded that the FEMO method had the same general validity as the LCAO-MO method for the Diels-Alder reaction.

Both the LCAO-MO and FEMO-MO and FEMO method have the common weakness that they deal only with a single reactant, diene or dienophile.

The perturbational molecular orbital method has also been applied by several authors. They calculated the relative stability of endo and exo transition states. Recently Salem developed the intermolecular orbital (IMO) theory postulating the formation of new orbitals between the two interacting molecules. Whangbo and Lee applied this method to the photochemical reaction of benzene and MA. In this work we have applied the IMO method to the thermal reactions of other aromatic alternant hydrocarbons with MA.

Calculations

Molecular orbitals of MA used in the calculation were the same as described previously and those of alternant hydrocarbons were obtained from the "Dictionary of π-electron" by Coulson and Streitwieser. Atoms of the molecules are numbered in the usual manner as shown in Fig. 1.

For thermal reaction the interaction energy concerned is that between monoelectres in their ground states. As it was pointed out previously, two different ways of calculating interaction energies had to be adopted depending on the energy differences of interacting orbitals. Whenever the energy differences are smaller than 0.7h, the following secular determinant was solved directly.

\[
\begin{vmatrix}
E_f - E & H_{ij} - S_{ij}E \\
H_{ik} - S_{ik}E & E_k - E
\end{vmatrix} = 0
\]

(1)

Except the cases where equation (1) was used, we followed the expression given by Salem:

\[
E_{int} = \sum \left( q_i + q_j \right) \eta_{ij} S_{ij} - \frac{2 \sum \sum' \left( \sum C_{ij} C_{ij'} \eta_{ij} \right)^2}{E_{ij} - E_{ij'}} + \frac{1}{4} \left( E_i - E_j \right) \left( \sum C_{ij} C_{ij'} S_{ij} \right)^2
\]

(2)

The actual calculation of interaction energies was carried out using IBM 1130 at the computing center of the Seoul National University.

Results and Discussion

1. Addition of Naphthalene and MA Dotted lines in Fig. 2 indicate pairs of interacting
The stabilizing effect of second and thirled terms, arising mainly from the mixing of occupied orbitals and unoccupied orbitals is partially diminished by the closed shell repulsive term $-1.917 (\eta_{3s}S_{3s} + \eta_{4s}S_{4s})$. Following Salem, the interaction integral was assumed to be proportional to the overlap integral $S_{rr}$, i.e.,

$$\eta_{rr}/\beta = k S_{rr}$$

and the dimensionless constant $k$ was taken to be 3 (this value will be used henceforth). Then the interaction energy can be represented with overlap integrals only:

$$E_{\text{int}}/\beta = -0.402(S_{3s}^2 + S_{4s}^2) + 4.751 S_{3s}S_{4s}$$

A new bond will be considered to be established when the $p$ orbital overlap reaches the value of 0.2. Thus the overall stabilization energy for $S_{3s} = S_{4s} = 0.2$ becomes $E_{\text{int}} = 0.158 \beta$. This value indicates that the interaction gives stabilization and thus cyclo-addition is favorable thermally in the ground states.

According to Brown, naphthalene has an $L_s$ value of 3.68 so that under usual conditions it would not react with MA since this value greater than 3.60. By the FEMO method, it has come to the same conclusion that the adduct formation is not favorable. Experimentally, however, it was found that naphthalene gives two isomers of adducts with MA thermal reaction. Thus the IMO approach in this case gives better agreement with the experimental result. To obtain the relative stability of exo and endo adducts (See Fig. 3), we estimated the additional interaction energies. The molecular planes of the diene and the dienophile of the Diels-Alder adducts are known to be roughly parallel. The interaction energy between 2,5-position of MA and 2,3-position of naphthalene may be considered to be the secondary interaction energy of the endo form

$$E_{\text{secondary}}/\beta = 3.535(S_{2s}^2 + S_{3s}^2) + 8.51S_{3s}S_{4s}$$

And that of the exo form is similarly

$$E_{\text{secondary}}/\beta = 1.803(S_{2s}^2 + S_{10s}^2) - 3.70S_{2s}S_{10s}$$

From equation (6), we can see that the secondary interaction energy for the exo form has destabilizing effect when overlap begins. The detailed structures of the two isomers are not definitely known. We can not, therefore, calculate the additional stabilization energy accurately. If we adopt the value of overlap integral in the secondary interaction to be 0.2 again as we did for the primary interactions, it would certainly be an over-estimation. However for the purpose of comparing the relative stabilities of the two conformations,
the choice of the value of overlap integral is immaterial. Thus we have used the same value of 0.2 in our calculations of the secondary interactions. Substitution of this value into equations (5) and (6) now gives 0.771β and respectively. This indicates that for the same extent of orbital overlaps endo adduct is the preferred confirmation. This prediction is consistent with the experimental findings that larger proportion of endo form is obtained in the adducts.

2. Addition of phenanthrene and MA

No cycloaddition of phenanthrene with MA has yet been discovered through thermal process,\textsuperscript{15} To ascertain whether phenanthrene can react thermally with MA or not, we calculated the interaction energies between possible position of phenanthrene and MA. The interaction energy between 1,4-position of phenanthrene and 3,4-position of MA is given by

\[
E_{int}/\beta = -0.469S_{2,2}^2 - 0.625S_{2,4}^2 + 4.446S_{2,2}^2 S_{2,4}^2
\]

(7)

In equation (7), there are two repulsive square terms which arise mainly from the interaction between occupied orbitals of each molecules. On the other hand the cross term involving simultaneous two-bond overlap is attractive.

The overall stabilization for \( S_{2,2} = S_{2,4} = 0.2 \) is \( E_{int} = 0.134β \).

This stabilization energy is small but indicates the possibility of occurrence of addition. Here again two possible adducts may be considered as shown in Fig. 4. For configuration (I), the secondary interaction energy between 2,3-positions of phenanthrene and 2,5-positions of MA is given by

\[
E_{int}/\beta = -2.124S_{2,2}^2 - 1.896S_{2,4}^2
\]

\[+0.068S_{2,4}^2 S_{2,5}^2\] (8)

The secondary interaction in this case is repulsive and hinders the new bond formation between phenanthrene and MA. Accordingly the stabilization energy of bond 1,3 and 4,4 will decrease as the secondary overlap begins. If the secondary overlap also reaches the value of 0.2 then it gives the destabilizing energy of \(-0.183β\). Hence the thermal 1,4-addition of configuration (I) should be energetically unfavorable provided of course that the secondary overlap reaches 0.2.

For configuration II, the secondary interaction energy between 11,12-position of phenanthrene and 2,5-position of MA is

\[
E_{int}/\beta = -1.762S_{3,12}^2 - 2.233S_{3,12}^2
\]

\[+1.426S_{3,12}^2 S_{3,12}^2\] (9)

If the secondary overlaps are assumed to be 0.2 as in the case (I) the interaction energy is \(-0.103β\). Thus the secondary interaction for (II) is also unfavorable for the addition. The total stabilization energy of configuration (II) is 0.031β. Taking the value of \( β \) to be \(-3 \text{ eV}\), as Salem did, this stabilization energy is merely \(-2.144 \text{ kcal/mole}\). This is very small for the formation of thermal adduct to occur.

We therefore conclude that the cycloaddition of MA to 1,4-position of phenanthrene can proceed initially on account of stabilizing primary interaction, but as the reaction proceed further destabilizing effect of secondary interaction may interfere and the addition becomes more and more unfavorable. Since the secondary overlaps may not proceed as far as 0.2, the preferred configuration (II) may
form in small amount. The $L_p$ value of the
1,4-position of phenanthrene is 3.77, and
based on this Brown concluded that no adduct
will be formed under usual conditions.
Other possible positions for phenanthrene to
react with MA may be 9, 10-positions.\(^\text{17}\) The
interaction energy between 9, 10-positions of
phenanthrene and 3, 4-positions of MA is

$$E_{\text{int},\beta} = -0.391 \left( S_{\text{th},3} + S_{\text{th},4} \right) - 7.085 S_{\text{th},3} S_{\text{th},4} \quad (10)$$

We can see from this that the interaction energy
is repulsive for any value of overlap integral.
Thus the thermal addition of MA to 9, 10-
positions will not occur.

3. Addition of 1, 2-benzanthracene and MA

MA undergoes thermal addition to 7, 12-position
of 1, 2-benzanthracene.\(^\text{18}\) The $L_p$ value of the
7, 12-positions is 3.41, indicating that the
reaction is favorable. The interaction energy for
this position is given by equation (11).

$$E_{\text{int},\beta} = 0.418 S_{\text{th},3} + 0.690 S_{\text{th},4} + 6.598 S_{\text{th},3} S_{\text{th},4} \quad (11)$$

The overall stabilization energy for $S_{\text{th},3}=S_{\text{th},4} = 0.2$ is $E_{\text{int}} = 0.308 S_{\text{th},3} S_{\text{th},4} = 0.308 \beta$. The two possible isomers of adduct is shown in Fig. 5.

![Fig. 5. Two possible isomers of adducts.](image)

For configuration (I) and (II), the secondary
interaction energies are given by equations (12)
and (13) respectively.

$$E^{(1)}_{\text{int},\beta} = -1.767 S_{\text{th},3} - 0.988 S_{\text{th},5} + 0.019 S_{\text{th},3} S_{\text{th},5} \quad (12)$$

$$E^{(2)}_{\text{int},\beta} = -1.084 S_{\text{th},3} - 1.156 S_{\text{th},5} - 0.058 S_{\text{th},3} S_{\text{th},5} \quad (13)$$

These secondary interaction energies have
destabilizing effects as in the case of 1,4-
addition of phenanthrene. If we suppose that
the secondary overlaps have the value of 0.2,
then the destabilization energies are $E^{(1)} = -
0.110 \beta$ and $E^{(2)} = -0.092 \beta$. With these and
the stabilization energy of equation (11),
configuration (I) has the total stabilization
energy of $E_{\text{int}} = 0.198 \beta$ and that of (II) is
$E_{\text{int}} = 0.216 \beta$. Thus we may draw a conclusion
that configuration (II) will be predominant.

Unfortunately lack of experimental data
prohibits the comparison of our prediction with
experimental results as to which configuration
is actually formed or predominant.

From equation (11) we can see that the
bonds 12, 3 and 7, 4 should close at the same
time but not at the same rate. By considering
the reaction path$^9$ for this reaction, we may
expect that the 7, 4 bond will close a little
more rapidly than 12, 3 bond.

It is no surprise the reaction will occur
asymmetrically since the configuration certainly
has no symmetry in it. The other possible
positions of 1, 2-benzanthracene MA addition
would take place are 11, 8-position and 1, 4-
position. The interaction energies calculated
for these position are as follows.

For 11, 8-position,

$$E_{\text{int},\beta} = 0.223 S_{\text{th},3} + 0.472 S_{\text{th},4} + 0.024 S_{\text{th},3} S_{\text{th},4} \quad (14)$$

For 1, 4-position,

$$E_{\text{int},\beta} = 0.742 S_{\text{th},3} - 0.250 S_{\text{th},4} + 0.384 S_{\text{th},3} S_{\text{th},4} \quad (15)$$

Assuming that the overlaps have the value 0.2,
we obtain the overall stabilization energies:
from equations (14) and (15). The overall
stabilization energies, of 11, 8-position and 1, 4-position are 0.1933 and 0.1143, respectively. By comparing these values with the overall stabilization energy for 7, 12-position, 0.303, we can see that 7, 12-position is the most favorable for the thermal addition of 1, 2-benzanthracene with MA. This prediction is in agreement with the experimental results of Kloetzel [28].

4. Comparison of IMO Method $L_p$ Method. Brown's $L_p$ gives a reasonable linear correlation when plotted against the relative equilibrium constants of the reaction between MA and diene molecules related to anthracene [19].

A better procedure for the calculation of paralocalizations energies based on the use of a semi-empirical SCF-MO by Dewar showed a good correlation with the constants of the Diels-Alder reactions of some alternant hydrocarbons [20].

For lack of available experimental data to compare with our results, the $L_p$ values are to test whether IMO theory would give the same relations with kinetic data as the $L_p$ values.

The stabilization energies the thermal reactions are compared with $L_p$ values of Brown in Table 1.

Fig. 6 shows a good linearity and implies the validity of IMO theory as a reactivity index for Diels-Alder reactions. From Fig. 6, it can be seen that the reactions between the aromatic hydrocarbons and MA will have stabilizations energies only if $L_p$ is less than about 4.0, although Brown predicted that reactions are possible only when $L_p$ is less than 3.60. Thus we expect the occurrence of addition with MA at the position where the $L_p$ value is less than 4.0. One can predict the position of

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Position</th>
<th>$L_p$</th>
<th>Stabilization Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1, 4</td>
<td>4.00</td>
<td>0.021*</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1, 4</td>
<td>3.68</td>
<td>0.158</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>1, 4</td>
<td>3.77</td>
<td>0.124</td>
</tr>
<tr>
<td>1, 2-Benzanthracene</td>
<td>7, 12</td>
<td>3.41</td>
<td>0.308</td>
</tr>
<tr>
<td></td>
<td>8, 11</td>
<td>3.64</td>
<td>0.193</td>
</tr>
<tr>
<td></td>
<td>1, 4</td>
<td>3.78</td>
<td>0.114</td>
</tr>
</tbody>
</table>

*From reference (10)
the Diels-Alder addition in large molecule by seeking out the position of lowest $L_e$ value $^4$. But para-localization theory can not be applied to the photochemical reactions while the IMO theory can be applied to both thermal and photochemical reactions between conjugated molecules. Furthermore, IMO method enables one to predict the theoretical reaction pathway for a given reaction. It also useful for determining the stereochemical structures of the adducts.

But as Salem pointed out $^6$ IMO theory has some weaknesses such as (a) neglect of explicit intermolecular coulomb interactions, (b) neglect of explicit interaction with the $\sigma$ electrons, (c) existence of the parameter $k$. If and when calculated results do not agree with the experimental results, the disagreement may be ascribed to these weaknesses.

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References

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(16) Ref. (12) b.
(17) Ref. (18) p. 171
(19) Ref. (12) p. 433