

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

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요약 IMO 이론을 naphthalene, phenanthrene 및 1,2-benzanthracene 과 maleic anhydride 와의 Diels-Alder 반응에 적용하였다. Alternant hydrocarbon 에서 열적 부가반응이 일어 나리라 예상되는 위치가 실험결과와 잘 일치하였다. 계산된 안정화 에너지로부터 부가생성물 중의 이성체들의 상대적 양이 설명되었으며 또 Brown 의 paralocalization 에너지와 안정화에너지 사이에 좋은 직선성이 있음을 알았다.

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.¹

The first theoretical treatment of the Diels-Alder reaction by quantum mechanical methods is that by Brown,² 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 polyenes. He proposed a reactivity index, paralocalization energy, L_p , defined as the loss in π bonding energy that results when two

carbons having a mutual para orientation are removed from a π 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.³ 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.⁴

The free electron molecular orbital (FFMO)

*The following paper will be taken as part III in this series; M. H. Whangbo and I. Lee, *J. Amer. Chem. Soc.*, **93**, 2 330 (1971)

method was used for the first time by Basu⁵ in the study of this type of synthesis. His treatment was limited to a small number of molecules. Sebastian⁶ 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 however have the common weakness that they deal only with a single reactant, diene or dienophile.⁷

The perturbational molecular orbital method has also been applied by several authors.⁸ They calculated the relative stability of endo and exo transition states. Recently Salem⁹ developed the intermolecular orbital (IMO) theory postulating the formation of new orbitals between the two interacting molecules. Whangbo and Lee¹⁰ 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 previously¹⁰ and those of alternant hydrocarbons were obtained from the "Dictionary of π -electron" by Coulson and Streitwieser.¹¹ 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 molecules in their ground states. As it was pointed out previously,¹⁰ two different ways of calculating interaction energies had to be adopted depending

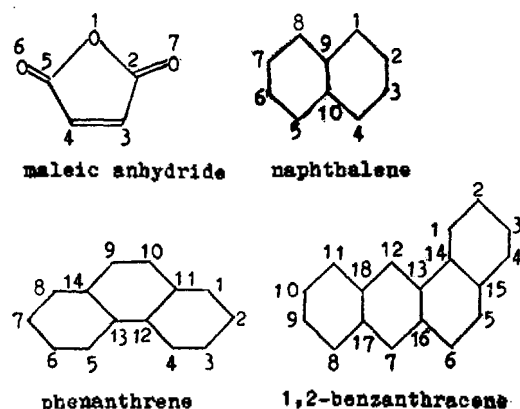


Fig. 1. Numbering of molecules

on the energy differences of interacting orbitals. Whenever the energy differences are smaller than 0.7β , the following secular determinant was solved directly.

$$\begin{vmatrix} E_j - E & H_{jk} - S_{jk}E \\ H_{jk} - S_{jk}E & E_k - E \end{vmatrix} = 0 \quad (1)$$

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

$$\begin{aligned} E_{int} = & -\sum_{r,r'} (q_r + q_{r'}) \eta_{rr'} S_{rr'} \\ & - 2 \sum_j^{ccc} \sum_{j'}^{ccc} \left\{ \frac{(\sum_{r,r'} C_{jr} C_{k'r'} \eta_{rr'})^2}{E_k - E_j} \right. \\ & \left. + \frac{1}{4} (E_k - E_j) (\sum_{r,r'} C_{jr} C_{k'r'} S_{rr'})^2 \right\} \\ & - 2 \sum_{j'}^{ccc} \sum_j^{ccc} \left\{ \frac{(\sum_{r,r'} C_{k'r} C_{j'r'} \eta_{rr'})^2}{E_k - E_j} \right. \\ & \left. + \frac{1}{4} (E_k - E_j) (\sum_{r,r'} C_{k'r} C_{j'r'} S_{rr'})^2 \right\} \quad (2) \end{aligned}$$

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

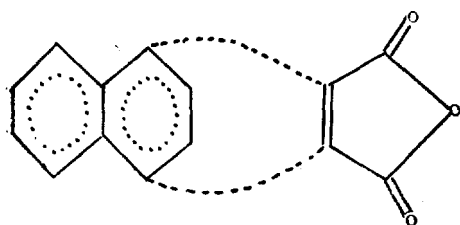


Fig. 2. Configuration of 1,4-addition

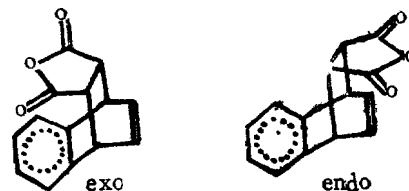


Fig. 3. two isomers of naphthalene-MA adducts

atoms. From equations (1) and (2) the interaction energy of the two ground state molecules is given by equation (3)

$$E_{int} = 1.917 (\eta_{1,3} S_{1,3} + \eta_{4,4} S_{4,4}) + \frac{1}{\beta} \{0.524(\eta_{1,3}^2 + \eta_{4,4}^2) + 0.527 \eta_{1,3} \eta_{4,4}\} + \beta \{0.630(S_{1,3}^2 + S_{4,4}^2) + 0.181 S_{1,3} S_{4,4}\} \quad (3)$$

The stabilizing effect of second and third terms, arising mainly from the maxing of occupied orbitals and unoccupied orbitals is partially diminished by the closed shell repulsive term $-1.917 (\eta_{1,3} S_{1,3} + \eta_{4,4} S_{4,4})$. 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).^{9,10} Then the interaction energy can be represented with overlap integrals only;

$$E_{int} / \beta = -0.402(S_{1,3}^2 + S_{4,4}^2) + 4.751 S_{1,3} S_{4,4} \quad (4)$$

A new bond will be considered to be established when the p orbital overlap reaches the value of 0.2.¹² Thus the overall stabilization energy for $S_{1,3} = S_{4,4} = 0.2$ becomes $E_{int} = 0.158 \beta$. This value indicates that the interaction gives stabilization and thus cyclo-addition is favorable thermally in the ground states.

According to Brown², naphthalene has an L_p 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 conclusion⁶, that the adduct formation is not favorable. Experimentally, however, it was found that naphthalene gives two isomers of adducts with MA thermal reaction.¹³ 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.¹⁴ 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

$$E_{2,5}^{2,3} / \beta = 3.535(S_{2,2}^2 + S_{3,5}^2) + 8.516 S_{2,2} S_{3,5} \quad (5)$$

And that of the exo form is similarly

$$E_{2,5}^{2,3} / \beta = 1.803(S_{9,2}^2 + S_{10,5}^2) - 3.703 S_{9,2} S_{10,5} \quad (6)$$

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.¹⁵ 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 conformation. This prediction is consistent with the experimental findings that larger proportion of endo form is obtained in the adducts.¹⁶

2. Addition of phenanthrene and MA

No cycloaddition of phenanthrene with MA has yet been discovered through thermal process.¹⁶ 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

$$E_{int}/\beta = -0.469S_{1,3}^2 - 0.621S_{4,4}^2 + 4.446S_{1,3}S_{4,4} \quad (7)$$

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 $S_{1,3}=S_{4,4}=0.2$ is $E_{int}=0.134\beta$,

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

$$E_{int}/\beta = 2.124S_{2,2}^2 - 1.895S_{3,5}^2 - 0.058S_{2,2}S_{3,5} \quad (8)$$

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 -0.163β . 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

$$E_{int}/\beta = -1.762S_{11,2}^2 - 2.233S_{12,5}^2 + 1.426S_{11,2}S_{12,5} \quad (9)$$

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 ev as Salem did, this stabilization energy is merely $-2,144$ 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

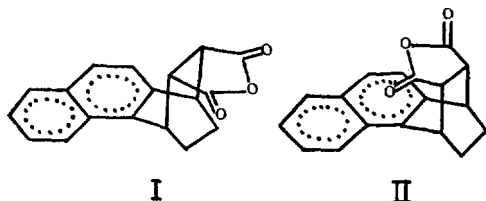


Fig. 4. Two hypothetical adducts

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.¹⁷ The **interaction** energy between 9,10-positions of phenanthrene and 3,4-positions of MA is

$$E_{int}/\beta = -0.391 (S_{9,3}^2 + S_{10,4}^2) - 7.035 S_{9,3} S_{10,4} \quad (10)$$

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.¹⁸ The L_p value of the 7,12-position is 3.41, indicating that the reaction is favorable. The interaction energy for this position is given by equation (11).

$$E_{int}/\beta = 0.418 S_{12,3}^2 + 0.690 S_{7,4}^2 + 6.599 S_{12,3} S_{7,4} \quad (11)$$

The overall stabilization energy for $S_{12,3} = S_{7,4} = 0.2$ is $E_{int} = 0.308\beta$, $\beta_{int} = 0.308\beta$. The two possible isomers of adduct is shown in Fig. 5.

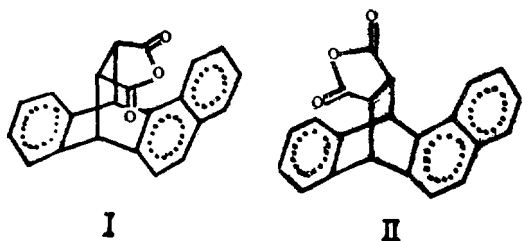


Fig. 5. Two possible isomers of adducts

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

$$E_{int}^{(I)}/\beta = -1.787 S_{13,2}^2 - 0.988 S_{16,5}^2 + 0.019 S_{13,2} S_{16,5} \quad (12)$$

$$E_{int}^{(II)}/\beta = -1.084 S_{18,2}^2 - 1.156 S_{17,5}^2 - 0.058 S_{18,2} S_{17,5} \quad (13)$$

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 $E_{int}^{(I)}/\beta = -0.110\beta$ and $E_{int}^{(II)}/\beta = -0.092\beta$. With these and the stabilization energy of equation (11), configuration (I) has the total stabilization energy of $E_{int} = 0.198\beta$ and that of (II) is $E_{int} = 0.216\beta$. 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 path⁹ 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,

$$E_{int}/\beta = -0.325 S_{11,3}^2 + 0.472 S_{8,4}^2 + 4.024 S_{11,3} S_{8,4} \quad (14)$$

For 1,4-position,

$$E_{int}/\beta = -0.743 S_{1,3}^2 - 0.250 S_{4,4}^2 + 0.3845 S_{1,3} S_{4,4} \quad (15)$$

Assuming that the overlaps have the value 0.2, we obtain the overall stabilization energies from equations (14) and (15). The overall

Table 1. L_p and stabilization energy

Molecule	Position	L_p	Stabilization Energy
Benzene	1,4	4.00	0.021*
Naphthalene	1,4	3.68	0.158
Phenanthrene	1,4	3.77	0.134
1,2-Benzanthracene	7, 12	3.41	0.308
	8, 11	3.64	0.193
	1,4	3.78	0.114

*From reference (10)

stabilization energies, of 11,8-position and 1,4-position are 0.193β and 0.114β , respectively. By comparing these values with the overall stabilization energy for 7,12-position, 0.30β , 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 Kloetzel¹⁸

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 anthracene¹⁹.

A better procedure for the calculation of parlocalizations 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 hydrocarbons²⁰

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

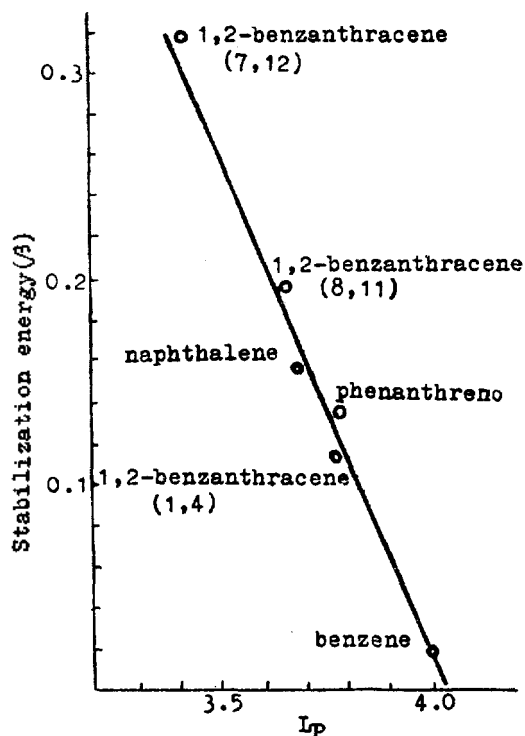


Fig. 6. Plot of stabilization energy vs. L_p

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

the Diels-Alder addition in large molecule by seeking out the position of lowest L_p value²¹. 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 out⁹ IMO theory has some weaknesses such as (a) neglect of explicit intermolecular coulomb interactions, (b) neglect of explicit interaction with the σ 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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