

화학반응성의 분자궤도론적 연구(제 7 보).  
시클로펜타디엔과 아크릴로니트릴 치환체간의  
Diels-Alder 반응에 대한 SCF-IMO 연구

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Determination of Reactivities by Molecular Orbital Theory(VII).  
SCF-IMO Studies on the Diels-Alder Reactions between  
Cyclopentadiene and 2-Substituted Acrylonitriles

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**요 약.** 바닥상태에 대한 자기무당착장 상호작용 에너지 이론을 2-치환-아크릴로니트릴과 시클로펜타디엔의 Diels-Alder 반응에 적용하여 반응성과 입체 선택성을 조사하였다. 출발점으로는  $\sigma$  전자와  $\pi$  전자를 다 고려하는 CNDO/2 MO가 사용되었다. 1차 상호작용 에너지 계산으로 정성적인 반응성이 얻어 졌으며 활성화 에너지 값은 실측치 범위의 것이 계산되었다. 2차 상호작용 에너지 계산으로 얻은 입체 선택성은 치환기에 대하여 모두 *endo* 선택성을 보여주었다. 비대칭 폐환의 원인을 반응원자의 원자가 비활성 전자밀도로서 설명하였다.

**ABSTRACT.** The ground state SCF IMO theory was applied to the Diels-Alder reactions of cyclopentadiene with 2-substituted acrylonitriles. The CNDO/2 MO of the separate systems, including both  $\sigma$  and  $\pi$  electrons, was used as starting point.

The qualitative prediction of the relative reactivity was made with the calculated primary interaction energies. Here the calculated activation energies appeared to be realistic. The stereoselectivity determined by the calculated secondary interaction energies represented the *endo*-selectivity for all the substituents. The reason for the slightly unsymmetrical ring closure at the transition state was discussed in terms of valence inactive electron densities of the reacting atoms.

INTRODUCTION

The Diels-Alder reaction occurs readily between a conjugated chain and a dienophile in which the reacting double bond may also belong to a conjugated chain (Fig. 1). The reactions

between cyclopentadiene and 2-substituted acrylonitriles, which play the part of diene and dienophile respectively, belong to the typical Diels-Alder reaction.<sup>1</sup>

Recently a great amount of interest has been focussed on the intermolecular cycloadditions of

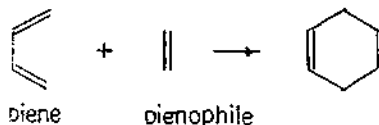


Fig. 1. Diels-Alder Reaction.

conjugated systems since several characteristics of the reaction are amenable to theoretical treatments. Recent developments in this field of intermolecular cycloaddition reactions involve the use of quantum perturbation theory and the direct quantum-mechanical calculation of potential energy surfaces. The basic idea of quantum perturbation method is that one may start with molecular wave functions for isolated, separated molecules and then calculate the energy change resulting from the mutual perturbing influence of one molecule upon the other.

In the independent electron Hückel type method for  $\pi$  electron, which is usually referred to the perturbational molecular orbital (PMO) theory<sup>2</sup>, the interaction energy is expressed as equation (1).

$$\Delta E = -2 \left\{ \sum_j^{\text{occ}} \sum_{k'}^{\text{uno}} \frac{(\sum_{rr'} c_{jr} c_{kr'} \eta_{rr'})^2}{\epsilon_{k'} - \epsilon_j} + \sum_{j'}^{\text{occ}} \sum_k^{\text{uno}} \frac{(\sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'})^2}{\epsilon'_{j'} - \epsilon_k} \right\} \quad (1)$$

where  $\eta_{rr'}$  is the matrix element of the interaction energy between a pair of atoms  $r$  and  $r'$ , and other notations have their usual significances.

The effect of coulombic repulsion is neglected in this treatment, and this effect coupled with the zero-overlap approximation precludes application of this form to the reaction of highly polar substances. The neglect of overlap also leads to the neglect of the intermolecular repulsion interactions of filled orbitals. Therefore it would seem most appropriate to use this simplest PMO theory only when the starting molecular orbitals are Hückel MO's calculated with the same basic assumption.

The simplest intermolecular orbital (IMO) theory<sup>3</sup> introduces atomic overlaps into the PMO theory. The mathematical expression of the intermolecular interaction energy is represented as equation (2).

$$\Delta E = - \sum_{rr'} (q_r + q_{r'}) \eta_{rr'} S_{rr'} - 2 \left\{ \sum_j^{\text{occ}} \sum_{k'}^{\text{uno}} \frac{(\sum_{rr'} c_{jr} c_{kr'} \eta_{rr'})^2}{\epsilon_{k'} - \epsilon_j} + \sum_{j'}^{\text{occ}} \sum_k^{\text{uno}} \frac{(\sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'})^2}{\epsilon_k - \epsilon_{j'}} \right\} \quad (2)$$

where  $q_r$  is the Hückel charge density at atom  $r$  and  $S_{rr'}$  is the atomic matrix element of the overlap between the  $2p$  orbitals on the atom  $r$  and  $r'$ . This interaction energy expression is identical with the PMO theory except for the repulsive first term, which arises because each molecule has a closed shell into which other electrons cannot penetrate. This method suffers from the neglect of coulombic repulsion or attraction between atoms on the two systems, as well as from the use of unsophisticated orbitals as starting point for the separate systems. Thus this method is not favorable for the polar interactions<sup>4</sup>.

Finally the self-consistent field (SCF) IMO theory<sup>5</sup> is derived by use of SCF  $\pi$  orbitals on the separate molecules as basis set. This theory remedies the defects in both PMO and simple IMO theories by including explicit two-electron interactions in the Hamiltonian and by improving the starting wave function. The interaction energy is now given by equation (3).

$$\Delta E = - \sum_{rr'} (q_r + q_{r'}) \eta_{rr'} S_{rr'} - 2 \left\{ \sum_j^{\text{occ}} \sum_{k'}^{\text{uno}} \frac{(\sum_{rr'} c_{jr} c_{kr'} \eta_{rr'})^2}{\epsilon_{k'} - \epsilon_k} + \sum_{j'}^{\text{occ}} \sum_k^{\text{uno}} \frac{(\sum_{rr'} c_{kr} c_{j'r'} \eta_{rr'})^2}{\epsilon_k - \epsilon_{j'}} \right\} + \sum_{rr'}^{\text{all}} \Delta q_r \cdot \Delta q_{r'} \frac{1}{R_{rr'}} \quad (3)$$

where  $q_r$  is the net charge on atom  $r$  and  $R_{rr'}$  is the distance between the atoms  $r$  and  $r'$ . The last term in this expression represents the coulombic interaction between the net charges on the two molecules. Using this expression, Salem and Devaquet made a successful interpretations of dimerization reactions between highly polar substances. But the major weakness of the theory and its application lies in the consideration of the  $\pi$  electrons alone. Therefore the calculated reaction paths by this theory are valid only in the very initial stages of the cycloadditions. The low, often negative, interaction energies which are obtained by sole consideration of these  $\pi$  electrons clearly indicate that the major source of the activation energy lies in the rearrangement of the  $\sigma$  core<sup>3,5</sup>.

In this work we intend to examine whether the defects of the SCF IMO theory can be remedied by using the CNDO/2 MO<sup>6</sup> as a basis for the separate systems. It is natural and important that the assumptions from the consideration of  $\pi$  electrons alone will vanish in our method since the CNDO/2 wave function includes both  $\sigma$  and  $\pi$  electrons. However the mathematical expression of the SCF IMO theory will be originally used in evaluating the total interaction in the initial stages of the thermal cycloadditions between cyclopentadiene and 2-substituted acrylonitriles.

## CALCULATION

**Molecular Coordinates.** The geometries of the reactant molecules were assumed to be planar and were constructed from the probable bond angles and lengths<sup>7</sup> as shown in Fig. 2. With given bond angles, bond lengths, and dihedral angle the calculation of atomic cartesian coordinates of the molecular system for the input of the CNDO/2 program was carried out with an aid of a modified version of QCPE (Quantum Chemistry Program Exchange at Indiana Univer-

sity) No. 136 program by means of IBM 1130 at Inha University.

The transition state models were constructed by putting the reactants in parallel planes at 5 a.u. distances. There are two transition state geometries corresponding to possibilities of *endo*- and *exo*-stereoselectivity for the acrylonitriles with respect to cyclopentadiene as illustrated in Fig. 3. The overall interatomic distances corresponding to the interplanar distances of 8, 7, 6 and 5 a.u. for the *endo*- and *exo*-transition state model were likewise obtained from the above program. The overall interatomic distances are needed in the calculation of the polar interaction energy.

**CNDO/2 calculator:** The wave functions, the energy values, and the charge densities for the isolated reactants were calculated using program of Pople<sup>8</sup>. Input parameters in this program are

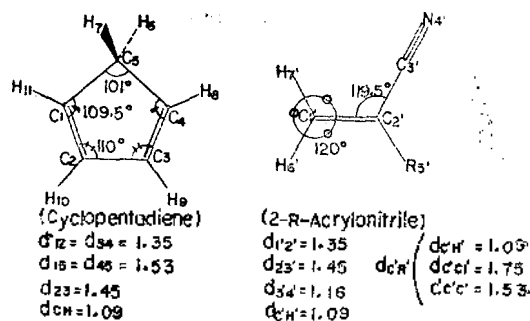


Fig. 2. Bond angles and bond lengths (in Å units) of reactant molecules. All molecules are assumed to be planar.

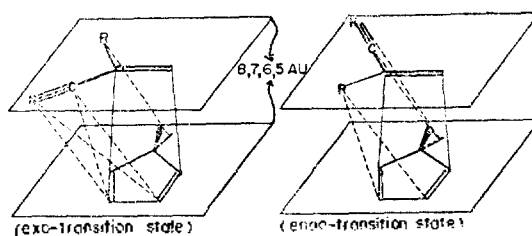


Fig. 3. Transition state models in biplanar system. The solid line between two planes indicates the primary interaction, and the dotted line describes the secondary interaction which only influences upon the stereoselectivity.

the atomic numbers and the cartesian coordinates of each atom in Å units.

**Overlap Integral  $S_{rr'}$ .** There are two kinds of  $\pi$  orbital overlap calculations in our reaction model. One is the primary orbital overlap, namely the " $\sigma$ " overlap  $S$ , between two end to end orbitals which are orthogonal to each other. The value of overlap integral is taken simply to be 0.2 in the significant range of distance, about 5 a.u. where the core repulsive wall is small. The other is the secondary orbital overlap which requires the geometrical adjustment for the secondary interaction as in the case of the stereochemical study of Salem<sup>3</sup> because the secondary  $p\pi$  orbitals are not at all orthogonal to the direction of approach. The following formula was used in this case.

$$S_{rr'} = S_{rr'}(\sigma, \sigma) \cos^2 \theta_{rr'} - S_{rr'}(\pi, \pi) \sin^2 \theta_{rr'} \quad (4)$$

where  $\theta_{rr'}$  is the angle between the interatomic line and the normal on the molecular plane.  $S_{rr'}(\sigma, \sigma)$  and  $S_{rr'}(\pi, \pi)$  are known through the extensive tables by Mulliken.

**Interaction Energy  $\Delta E$ .** The total thermal interaction energy for one reaction consists of three parts; repulsion of the filled core, delocalization energy, and the polar energy as shown in equation (3). The sum of the first two energies represents the overlap energy which is a function of overlap alone. Actual calculations involved the following procedures. (a). To know the relative influence upon the total energy of interaction, repulsion, delocalization and polar energies were calculated separately. (b). For the interaction of

one sets of reactants, we also attempted to calculate the primary interaction energy which takes part directly in the reaction, and the secondary interaction energy which does not participate directly in the reaction but gives the distinction as to the *endo*- and *exo*-configurations. Thus the relative reactivity of our reaction model depended upon the primary interaction energy and the stereoselectivity depended upon the secondary interaction energy ( $c$ ). We then compared the frontier orbital interaction energy with the full orbital interaction energy.

## RESULTS and DISCUSSION

**Relative Reactivity.** The results of calculation by equation (3) for the primary interaction energy of the cycloaddition reaction of cyclopentadiene with 2-substituted acrylonitriles are shown in Table 1.

The repulsion between exclusion shells is largest for the 2-CH<sub>3</sub> substituted and smallest for the 2-Cl substituted acrylonitriles. This is in accord with the fact that the CH<sub>3</sub> group is an electron releasing while the Cl is an electron withdrawing group. The increase in electron density of interacting atoms will give larger repulsion, but it will also result in an increase in delocalization. This is also seen in Table 1. The absolute values of repulsive energies are larger than those of the delocalization stabilization energies. Since the total interaction energies are all repulsive and large, the reaction will require considerable amo-

Table 1. Primary interaction energies(kcal/mol).

2-Substituent	Repulsion		Delocalization.		$\Delta E_t$	
	Full	Frontier	Full	Frontier	Full	Frontier
H	44.3657	42.8087	-21.4047	-14.4311	22.9610	28.3776
Cl	43.2450	38.1452	-21.0560	-11.4602	22.1890	26.6850
CH <sub>3</sub>	51.1628	45.6143	-24.5238	-15.4284	26.6390	30.1859

unt of activation energy. The total interaction energy for the overlap of  $S=0.2$  for both reacting centers may be considered to be activation energy involved in the reaction<sup>9</sup>. The calculated values are shown in Fig. 4.

Experimentally the similar type of reaction is known to have an activation energy amounting to the order of 10 kcal/mol<sup>10</sup>. It seems that the CNDO/2 wave functions give reasonable prediction of activation energy. It is also seen from Table 1 that the frontier orbital<sup>11</sup> alone always gives correct relative interaction energies, and therefore will give the right prediction of relative order of reactivities.

Judging from the calculated total interaction energy, the reaction of 2-Cl acrylonitrile is the most favorable and that of 2-CH<sub>3</sub> acrylonitrile is the least favorable one. This tendency becomes more pronounced in the frontier interaction energies.

The reaction paths calculated in Fig. 4 show explicitly the relative reactivity for the three

reactions considered. All the reactions proceed in a concerted fashion in accord with the view of Woodward and Katz<sup>12</sup>, but the bond 41' is predicted to close slightly earlier than the bond 12'. The reason for such asymmetrical closure can be explained with the calculated valence inactive electron density (VIED)<sup>13</sup> in Table 2. The VIED at C1' is larger than that at C2' and therefore C1' will be more reactive than C2'.

**Stereoselectivity.** The results of calculation of the secondary interaction energies for the *endo* and *exo* additions between cyclopentadiene and 2-substituted acrylonitriles are listed in Table 3. All the secondary interaction energies,  $\Delta E_s$ , which include both overlap and polar interactions, are repulsive but the *endo* form is always less repulsive than the *exo* form. This means that the reactions will show *endo*-selectivity for all substituents. This trend accords qualitatively with the experimental results<sup>14</sup>, except for the unsubstituted acrylonitrile for which the *endo* form is shown to be slightly less favorable. Inclusion

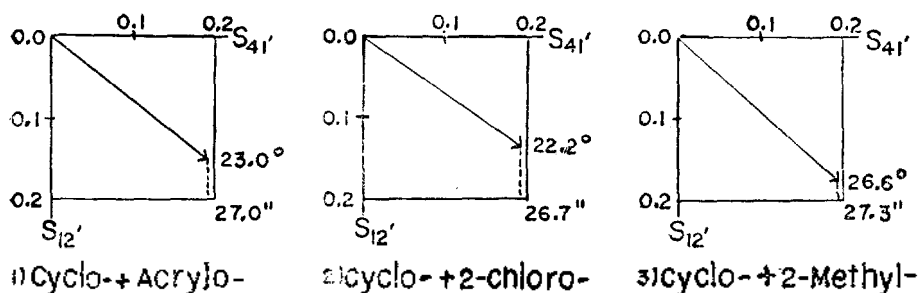


Fig. 4. Initial stages of reaction path.

°; interaction energy to stabilize the reaction between two pi orbitals.

''; activation energy (until both orbital overlaps arrive at the value of 0.2).

Table 2. Valence inactive (VIED) and active (VAED) electron densities.

subst	VIED			VAED		
	H	Cl	CH <sub>3</sub>	H	Cl	CH <sub>3</sub>
C1'	2.0193	2.0104	2.0467	1.9969	1.9967	1.9965
C2'	1.9893	1.9173	1.9474	1.9993	1.9957	1.9986

of the polar term does not change the trend since the polar energy term is negligibly small due to the nonpolar character of the reactants. The nonpolar nature can be seen clearly from Fig. 5

where the results of population analysis<sup>15</sup> are given for all the compounds studied. The net charge densities of atoms in molecules are quite small, and the reacting carbon atoms have less

Table 3. Secondary interaction energies (kcal/mol).

		$\Delta E_{\text{polar}}$	Full orbital		Frontier	Experimental** % product
			$\Delta E_{\text{overlap}}$	$\Delta E_t$	$\Delta E_t$	
H	endo	-0.0942	1.2386	1.1444	1.4302 (1.4104)	45.1
	exo	0.1127	3.6706	3.7833	5.1272 (5.2526)	54.9
Cl	endo	-0.0770	2.0635	1.9865	1.9095 (3.6364)	80.5
	exo	0.0939	3.8336	3.9275	4.0214 (5.5421)	19.5
CH <sub>3</sub>	endo	0.1595	5.4081	5.5976	5.7271 (7.2074)	82.9
	exo	-0.1399	7.1030	7.9631	6.8232 (8.4800)	17.1

\* The frontier orbital interaction energy is the sum of interaction energies between the HOMO(diene) and LUMO(dienophile) and that between HOMO(dienophile) and LUMO(diene). The energies for the former alone is given in parenthesis.

\*\*H, CH<sub>3</sub> in benzene at 80°<sup>14</sup>; Cl in benzene at 40°<sup>14</sup>.

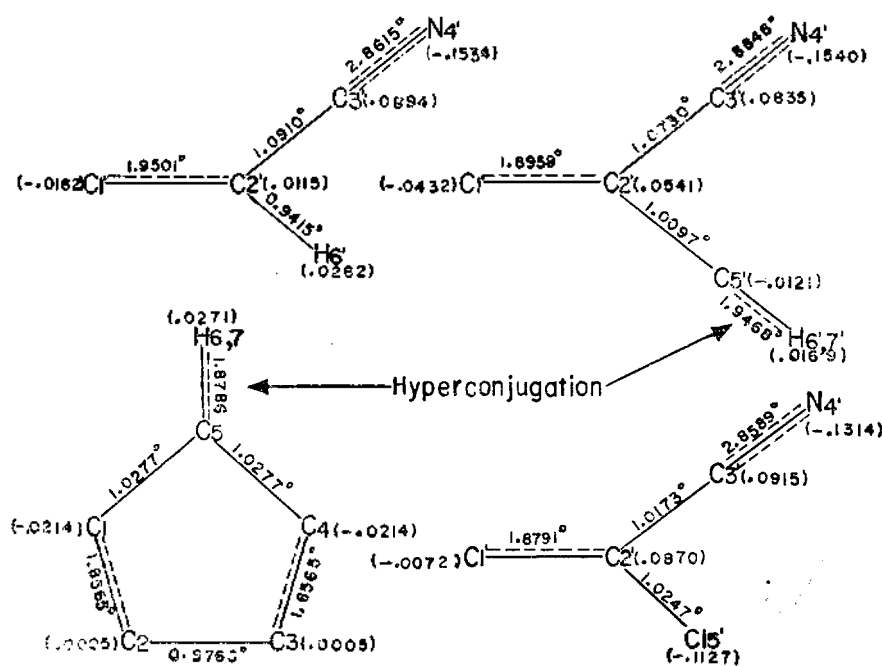


Fig. 5. Net charge densities and bond indices obtained from CNDO/2 calculation. ( ) ; net charge density, °; bond index.

than 0.1 electronic charge unit in all cases. Here again the frontier orbital interactions also give the same trends as the full orbital interactions.

Though appropriateness of the value 2.6 Å assumed for the interplanar distance in the present study is questionable and the steric requirements in the calculation of the orbital overlap  $S_{rr}$  are not so proper as in Salem's model for secondary interaction<sup>3</sup>, there is no doubt that the nitrile group of acrylonitrile has the nonbonding "attractive"<sup>2</sup> interaction with the methylene of cyclopentadiene. This is contrary to the prediction of Mellor and Webb<sup>14</sup> that nonbonding repulsive interactions of substituents of the dienophile are important with the methylene group of cyclopentadiene in determining stereoselectivity. Experimental products ratio of *endo* to *exo* adducts in the case of unsubstituted acrylonitrile was 45% to 55%. On the contrary the yields of *endo* adducts for the substituents, Cl and CH<sub>3</sub> exceed the *exo* adducts by about 60%. Thus there may be some uncertainty in the experimental results for the unsubstituted acrylonitrile since this is the only dienophile which gave greater yield for the *exo* adducts even though the difference is small. More investigations are needed to decide experimentally the stereoselectivity of the reaction.

Attention to the frontier orbital interactions alone rather than the full term value is found to be a more judicious choice at least for predictive purpose. Furthermore the interaction energies between the highest occupied molecular orbitals (HOMO) of diene and the lowest unoccupied MO(LUMO) of dienophiles alone are shown to play the major part of the  $\Delta E_f$ .

In conclusion, it has been shown that (1) the cycloadditions of cyclopentadiene with 2-substituted acrylonitriles are essentially concerted, (2)

2-methyl acrylonitrile requires the largest while 2-Cl-acrylonitrile requires the least activation energy, (3) *endo*-adducts are favored to the *exo*, (4) frontier orbital interactions always give the correct prediction of relative reactivity and stereoselectivity, and (5) polar interaction energies are negligible for all the reactions considered.

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