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Extended Hückel Theory Applied to Chemical Reactivity

I. Diels-Alder Reactions of Cyclopentadiene, Cyclopentadienone, and Maleic Anhydride

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Wave functions and energies are calculated for cyclopentadiene, cyclopentadienone, and maleic anhydride under the LCAO–MO approximation with a basis set of atomic orbitals which is comprised of all valence electrons. The geometries of the molecules, required as inputs to the MO calculations, are determined with a procedure which minimizes the ring angular deformation energy. The various possible Diels-Alder reactions of these compounds are then considered. Second-order perturbation theory, with variable overlap integrals and including all interactions, is used to estimate the energies of transition intermediates or states which correspond closely to π complexes. Predicted endo-exo isomeric adduct ratios are in agreement with experimentally known values. Predictions of the relative rates for Diels-Alder reactions reflect the correct order and magnitude of reactivity, where experimental results are known.

Für Cyclopentadien, Cyclopentadienon und Maleinsäureanhydrid werden Wellenfunktionen und Energien berechnet, wobei die verwendete Basis des LCAO–MO-Verfahrens die atomaren Orbitale aller Valenzelektronen umfaßt. Die Geometrie der Moleküle wird durch Minimisierung der winkelabhängigen Deformationsenergie des Ringes bestimmt. Eine Störungsrechnung 2. Ordnung mit Einschluß aller Wechselwirkungen und variablen Werten für die Überlappungsintegrale ermöglicht die Abschätzung der Energien von Übergangszuständen oder Zuständen, die π-Komplexen sehr ähnlich sind. Die Voraussagen über das Verhältnis von endo-/exo-isomeren Addukten stimmen mit den experimentellen Werten überein; desgleichen die Aussagen über die relativen Reaktionsgeschwindigkeiten.

Les fonctions d'onde et les énergies sont calculées pour le cyclopentadiène, la cyclopentadienone et l'anhydride maléique, dans l'approximation LCAO–MO, avec une base d'orbitales atomiques englobant tous les électrons de valence. Les géométries moléculaires, données de base du calcul, sont déterminées par un procédé de minimisation de l'énergie de déformation angulaire du cycle. On étudie les différentes réactions de Diels-Alder possibles pour ces composés. Les énergies des intermédiaires réactifs ou des états qui correspondent étroitement à des complexes π, sont estimées a l'aide de la théorie des perturbations au second ordre, avec des intégrales de recouvrement variables et en tenant compte de toutes les interactions. Les rapports ainsi prévus entre les composés d'addition isomères endo et exo sont en accord avec les valeurs expérimentales connues. Les prévisions des vitesses relatives des réactions de Diels-Alder reflètent correctement l'ordre et l'importance de la réactivité expérimentale connue.

Introduction

The cycloaddition of a conjugated diene and an olefinic or acetylenic dienophile is called the Diels-Alder Reaction*, named after its principal investigators,

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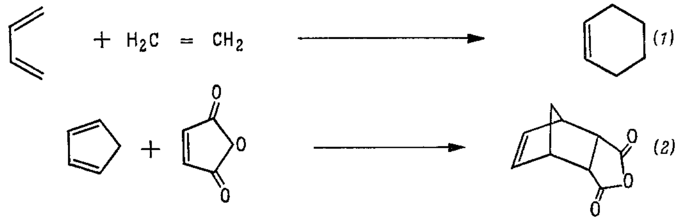
* For recent reviews see BERSON and REMANICK [6], ETTLINGER and LEWIS [13], MARTIN and HILL [31], SAUER [39], TITOV [45], and WASSERMANN [47].

O. Diels and K. Alder. Typical examples are the reaction of butadiene and ethylene to yield cyclohexene, and that of cyclopentadiene and maleic anhydride to give a bicyclic adduct.

The latter reaction illustrates an important facet of the reaction. Two products are possible; the isolated "endo" product [*2*] has the anhydride grouping folded away from the methylene bridge.



In this paper, we are concerned with the theoretical quantitative prediction of reactivities and adduct structures in the Diels-Alder reactions of cyclopentadiene (CPD), cyclopentadienone (CPDO), and maleic anhydride (MA). Previous theoretical treatments of the Diels-Alder reaction are numerous. This may be a reflection of the interest that attaches to a reaction which only requires mixing of the reactants, and which proceeds as readily in the gas-phase as in solution.

A great deal of the previous theoretical work has made use of the Hückel molecular orbital theory in its π-electron approximation. This work has been reviewed by Streitwieser [*44*], and has dealt mainly with predictions of the site of attack on various aromatic compounds and their relative reactivities. Also Evans [*14, 15*] suggested a cyclic π-electron model for the transition state of Diels-Alder reactions and was reasonably successful in semi-quantitative predictions of activation energies. No developments of his ideas have appeared in the literature.

Theoretical treatments based on transition state theory [*19*] have primarily attempted to discriminate between a one-step, cyclic, concerted mechanism, or a two-step diradical-intermediate reaction pathway [*25, 26, 27, 37, 46*]. Calculations of entropies of activation have generally been in agreement with a concerted cyclic mechanism. A model for the transition state of Diels-Alder reactions, in which one incipient bond is stronger or formed to a greater degree than the other, was first suggested by Woodward and Katz [*48*] and has been gaining acceptance [*5, 27*].

We will assume that Diels-Alder reactions are cyclic, concerted processes. With this assumption Fukui has suggested that an important controlling factor in the Diels-Alder reaction is the symmetry relationship and energy difference between the highest occupied molecular orbital of the diene and the lowest vacant molecular orbital of the dienophile [*16, 17*]. Hoffmann and Woodward [*22, 23*] have given energy and orbital diagrams which illustrate the concept in a neat fashion. Quite subtle effects, for example, preference for endo addition, are explained on the basis that important stabilizing interactions during a reaction will result from the mixing of vacant dienophile with occupied diene levels.

We have determined the orbital energies and wave functions for CPD, CPDO, and MA. The method of calculation is the extended generalized Hückel treatment of all valence electrons, as developed by HOFFMANN [*21*]. The various possible diene reactions are then studied using a perturbation method, which comprises a semi-quantitative extension of the suggestions of FUKUI, and HOFFMANN and WOODWARD.

Methods of Calculation

Extended Hückel Calculation. The molecular orbitals are represented by a linear combination of Slater atomic orbitals which in our case include the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals of the oxygen and carbon atoms and the $1s$ atomic orbitals of the hydrogen atoms. We used Hoffmann's computer program* modified for the IBM 7040 computer to carry out the calculations. The program requires as input, Slater exponents, values of the Coulomb integrals, and Cartesian coordinates for the atoms in the molecular species under study. We used the negative of valence-state ionization potentials taken from the tables of PRITCHARD and SKINNER [*36*] for the requisite Coulomb integrals, and Slater exponents of 1.625, 2.275, and 1.000 were used for carbon, oxygen, and hydrogen respectively. The problem in choosing atomic coordinates is discussed below.

The computer program determines values of all overlap integrals (S_{ij}) and resonance integrals (H_{ij}), which are calculated from a recipe suggested by MULLIKEN [*33*] and first applied by WOLFSBERG and HELMHOLZ [*49*]. The H_{ii}

$$H_{ij} = K \frac{(H_{ii}+H_{jj})}{2} S_{ij} \tag{3}$$

are the Coulomb integrals and the choice of the arbitrary constant $K = 1.75$ has been discussed by HOFFMANN [*21*]. The complete secular determinant $| H_{ij} - ES_{ij} | = 0$ is then solved retaining all off-diagonal terms. The output includes energy levels, wave functions, and Mulliken overlap populations [*32*].

Atomic Coordinates. Bond lengths and angles have been reported for both cyclopentadiene [*41*] and maleic anhydride [*30*]. Error limits for CPD are quite large, and the values given depend upon assumed values for the carbon-carbon ($sp^2 - sp^3$) single bonds (1.53 Å) which are almost certainly too large. In any case, no molecular parameters are available for cyclopentadienone since it has never been isolated. Since consistent and precise atomic coordinates are required for the Hückel calculation, we devised the following procedure to obtain coordinates for all three molecules.

Values for the lengths of the various types of bonds found in these molecules were taken from the compilations of LIDE [*28*] and STOICHEFF [*43*].

The preferred values of the internal bond angles were then taken to be 120° in the case of trigonally hybridized atoms and 109° 28′ in the case of tetrahedrally hybridized atoms. Since bond-stretching force constants are larger than angle deformation force constants, the strain energy in each molecule was then assumed to be distributed only over the five internal angles of each ring. A potential function of the type $E = k_\theta(\theta - \alpha)^2$ was chosen to represent the strain energy for each

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* Available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Indiana, U.S.A.

bond angle, and the total strain energy was minimized with respect to the size of all five internal angles. θ and α are the preferred value of the angle and the actual value respectively. k_θ, the bond-bending force constant, was assumed to be the same for all angles, an assumption which is probably not too incorrect.

Bonds to hydrogen and oxygen atoms exterior to the ring were presumed to bisect the exterior ring angle at their point of attachment to the ring. Reference to Fig. 1, which gives the values of the bond lengths and angles used in this work, will illustrate the method. To exemplify, the angles in maleic anhydride are given by the formulae

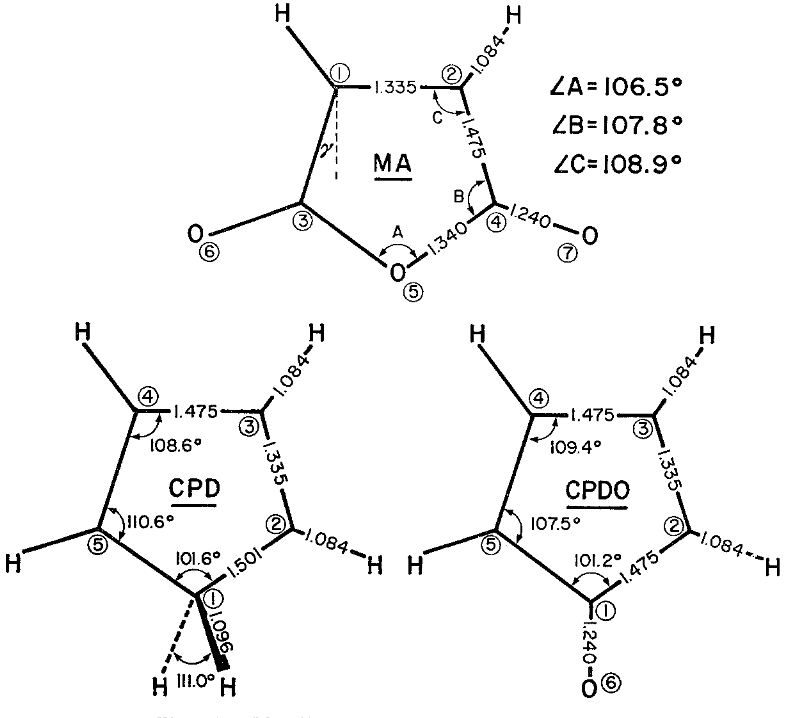

Fig. 1. Bond lengths and angles for CPD, CPDO, and MA

$$C = 90^\circ + \gamma$$

$$B = 180^\circ - \gamma - A/2$$

$$A/2 = \arcsin \{[(1.335/2) + 1.475 \sin \gamma]/1.340\}\,.$$

A graph of total strain energy divided by the force constant versus γ was then constructed and the required value of γ was determined at the minimum value of the energy. Our calculated bond angles for the two known molecules are reasonable, and they fall within the limits of error of the X-ray determinations. A table of the Cartesian coordinates is available upon request.

Perturbation Method. The perturbation treatment for reactivity follows that of DEWAR [*12*] in all its essentials. We choose a particular configuration of the two reactions to represent a stage along the reaction pathway. The Hamiltonian for this stage is thus $H_R + P$ where H_R is the Hamiltonian for the isolated reactant molecules and P is a relatively small perturbation Hamiltonian. The intermolecular interaction is multicenter since many atoms of the diene are relatively close to various atoms in the dienophile. The perturbation involves increases in the resonance integrals between the atoms of diene and those of dienophile from initial values of zero (isolated molecules) to values which are characteristic of the interacting state.

The perturbation can be defined in terms of the basis set of atomic orbitals ϕ_m (diene) and ϕ_n (dienophile) as a matrix element $\int \phi_m \, P \, \phi_n \, d\tau = P_{mn}$ in the secular determinant for the perturbed system. If only the π orbitals contribute, the interaction can then be described in terms of $M \times N$ resonance integral where M is the number of diene π orbitals and N is the number of dienophile π orbitals. As DEWAR [*12*] has shown, there is no first-order perturbation energy, and the second-order change in total energy for the perturbed state is given by Eq. (4).

$$\varDelta E = 2 \left[\sum_{m}^{\text{occ.}} \sum_{n}^{\text{vac.}} - \sum_{m}^{\text{vac.}} \sum_{n}^{\text{occ.}} \right] \frac{\left[\sum_{i,j} a_{m,i} \, b_{n,j} \, P_{mi,nj} \right]^2}{(E_m - E_n)} \,. \tag{4}$$

The superscripts occ., vac., refer to summations over all occupied molecular orbitals and unoccupied molecular orbitals respectively. The coefficients of the atomic orbitals are a_{mi} (diene) and b_{nj} (dienophile). The sum subscripted i, j is over all pairs of atoms i, j through which diene interacts with dienophile in the perturbed state. $P_{mi,nj}$ is the resonance integral for the interaction between atoms i, j.

With the assumption of the particular geometry of the interacting molecules one can determine the $M \times N$ overlap integrals. We took these from large graphs drawn through points determined from the overlap integral formulas of MULLIKEN, et al. [*34*]. We then calculated the resonance integrals for each pair interaction as directly equal to the negative product of the arithmetic mean of the valence state ionization potentials of interacting pair of atoms and the overlap integral. There was, in this case, no compelling reason to use a proportionality constant other than one.

Finally, the coefficients for use in Eq. (3) were obtained from the extended Hückel calculation, and a computer program was written to do the actual summations.

Results and Discussion

Wave Functions. The energies and symbols of the irreducible representations for some of the molecular orbitals of cyclopentadiene, cyclopentadienone, and maleic anhydride are given in Tab. 1. In each case, the lowest vacant MO and the highest occupied MO are both π type MO's. In every case there are also several relatively energetic σ-type occupied MO's.

The wave functions for the π-molecular orbitals are given in Tab. 2. In these wave functions, ϕ_i represents the $2p_z$-function of atom i (the z-axis being perpendicular to the plane of the molecule). Note that the π-system for cyclopentadiene includes contributions from the hydrogen atoms and carbon atom of the methylene group. An extended Hückel wave function for the lowest vacant MO, ψ_{12}, of maleic anhydride has been reported [*23*] as $\psi = 0.442\,(\phi_1 - \phi_2) + 0.506\,(\phi_3 - \phi_4) - 0.343\,(\phi_6 - \phi_7)$. The differences are probably due to a different choice of molecular geometry.

Table 1. *Energies and Symmetry Species of Extended Hückel Molecular Orbitals for* CPD, CPDO, *and* MA

Molecular Orbital		Energy (eV)	Symmetry Species
a) CPD (C_{2v}) $\Gamma = 11a_1 + 2a_2 + 9b_1 + 4b_2$			
ψ_8	$(\pi)_{\text{vacant}}$	9.84163	b_2
ψ_{12}	$(\pi)_{\text{vacant}}$	-6.35932	a_2
ψ_{13}	$(\pi)_{\text{vacant}}$	-8.33929	b_2
ψ_{14}	$(\pi)_{\text{occ.}}$	-12.27606	a_2
ψ_{15}	$(\sigma)_{\text{occ.}}$	-13.16091	b_1
ψ_{16}	$(\sigma)_{\text{occ.}}$	-13.20156	a_1
ψ_{17}	$(\pi)_{\text{occ.}}$	-13.42169	b_2
ψ_{20}	$(\pi)_{\text{occ.}}$	-15.60461	b_2
b) CPDO (C_{2v}) $\Gamma = 12a_1 + 2a_2 + 10b_1 + 4b_2$			
ψ_{11}	$(\pi)_{\text{vacant}}$	-6.17229	b_2
ψ_{12}	$(\pi)_{\text{vacant}}$	-6.34459	a_2
ψ_{13}	$(\pi)_{\text{vacant}}$	-11.08085	b_2
ψ_{14}	$(\pi)_{\text{occ.}}$	-12.29975	a_2
ψ_{15}	$(\sigma)_{\text{occ.}}$	-13.03907	b_1
ψ_{16}	$(\sigma)_{\text{occ.}}$	-13.50409	a_1
ψ_{18}	$(\pi)_{\text{occ.}}$	-14.32856	b_2
ψ_{22}	$(\pi)_{\text{occ.}}$	-18.15499	b_2
c) MA (C_{2v}) $\Gamma = 12a_1 + 3a_2 + 11b_1 + 4b_2$			
ψ_{10}	$(\pi)_{\text{vacant}}$	-6.05953	a_2
ψ_{11}	$(\pi)_{\text{vacant}}$	-7.82368	b_2
ψ_{12}	$(\pi)_{\text{vacant}}$	-10.66316	a_2
ψ_{13}	$(\pi)_{\text{occ.}}$	-13.52167	b_2
ψ_{14}	$(\sigma)_{\text{occ.}}$	-13.80116	b_1
ψ_{15}	$(\sigma)_{\text{occ.}}$	-13.82614	a_1
ψ_{18}	$(\pi)_{\text{occ.}}$	-17.69527	b_2
ψ_{21}	$(\pi)_{\text{occ.}}$	-18.14098	a_2
ψ_{23}	$(\pi)_{\text{occ.}}$	-18.59090	b_2

Spectra. The molecules all have C_{2v} point-group symmetry and the ground state in each case belongs to the totally symmetric singlet species, $^1A_1$. The first excited singlet state for CPD and CPDO is the product $a_2b_2^*$, and for maleic anhydride is $b_2a_2^*$. Both states are $^1B_1$ and the $\pi \rightarrow \pi^*$ transition is thus allowed in each case with polarization perpendicular to the C_2 axis and in the plane of the molecule. A second $\pi \rightarrow \pi^*$ transition, which is $^1A_1$ to $^1A_1$ for all three molecules is allowed according to polarization along the molecular C_2 axis. All other $\pi \rightarrow \pi^*$ transitions are also symmetry-allowed.

$n \rightarrow \pi^*$ singlet-singlet transitions are possible in the two compounds which contain oxygen. For CPDO, the transition to configuration $\psi_{15}\psi_{13}^*$ $(b_1b_2^*)$ or $^1A_1 \rightarrow {}^1A_2$, and which involves a lone pair of electrons on oxygen is forbidden. Transition to configuration $\psi_{16}\psi_{13}$ $(a_1b_2^*)$ would be $^1A_1 \rightarrow {}^1B_2$ and is allowed. For MA, the first allowed $n \rightarrow \pi^*$ singlet-singlet transition is to configuration $\psi_{14}\psi_{12}^*$

Table 2. *Extended Hückel wave functions for the π-molecular orbitals of* CPD, CPDO, *and* MA

a) CPD[a]

$\psi_8 = -0.1389\,(\phi_2 + \phi_5) + 0.0253\,(\phi_3 + \phi_4) + 1.1915\ \phi_1 - 0.9736\,(\phi_{H\alpha} - \phi_{H\beta})$
$\psi_{12} = -0.5054\,(\phi_2 - \phi_5) + 0.7344\,(\phi_3 - \phi_4)$
$\psi_{13} = -0.6697\,(\phi_2 + \phi_5) + 0.4150\,(\phi_3 + \phi_4) + 0.1766\ \phi_1 + 0.2178\,(\phi_{H\alpha} + \phi_{H\beta})$
$\psi_{14} = -0.5519\,(\phi_2 - \phi_5) - 0.3798\,(\phi_3 - \phi_4)$
$\psi_{17} = -0.2141\,(\phi_2 + \phi_5) - 0.5047\,(\phi_3 + \phi_4) + 0.2996\ \phi_1 + 0.2240\,(\phi_{H\alpha} - \phi_{H\beta})$
$\psi_{20} = -0.2308\,(\phi_2 + \phi_5) - 0.1415\,(\phi_3 + \phi_4) + 0.4885\ \phi_1 - 0.3311\,(\phi_{H\alpha} + \phi_{H\beta})$

b) CPDO[a]

$\psi_{11} = -0.6072\,(\phi_2 + \phi_5) + 0.2598\,(\phi_3 + \phi_4) + 0.8192\ \phi_1 - 0.2561\,\phi_6$
$\psi_{12} = 0.5046\,(\phi_2 - \phi_5) - 0.7355\,(\phi_3 - \phi_4)$
$\psi_{13} = 0.2760\,(\phi_2 + \phi_5) - 0.4644\,(\phi_3 + \phi_4) + 0.6181\ \phi_1 - 0.2883\,\phi_6$
$\psi_{14} = 0.5515\,(\phi_2 - \phi_5) + 0.3784\,(\phi_3 - \phi_4)$
$\psi_{18} = 0.3379\,(\phi_2 + \phi_5) + 0.4055\,(\phi_3 + \phi_4) + 0.2251\ \phi_1 - 0.1822\,\phi_6$
$\psi_{22} = 0.0261\,(\phi_2 + \phi_5) + 0.0061\,(\phi_3 + \phi_4) + 0.2131\ \phi_1 + 0.9299\,\phi_6$

c) MA[a]

$\psi_{10} = 0.7242\,(\phi_1 - \phi_2) - 0.5121\,(\phi_3 - \phi_4) + 0.1569\,(\phi_6 - \phi_7)$
$\psi_{11} = 0.2985\,(\phi_1 + \phi_2) - 0.6965\,(\phi_3 + \phi_4) + 0.2429\,(\phi_6 + \phi_7) + 0.3925\,\phi_5$
$\psi_{12} = 0.4375\,(\phi_1 - \phi_2) + 0.5460\,(\phi_3 - \phi_4) - 0.2468\,(\phi_6 - \phi_7)$
$\psi_{13} = 0.5706\,(\phi_1 + \phi_2) + 0.1615\,(\phi_3 + \phi_4) - 0.1159\,(\phi_6 + \phi_7) - 0.2006\,\phi_5$
$\psi_{18} = 0.0036\,(\phi_1 + \phi_2) + 0.0032\,(\phi_3 + \phi_4) - 0.5303\,(\phi_6 + \phi_7) + 0.6672\,\phi_5$
$\psi_{21} = 0.0159\,(\phi_1 - \phi_2) + 0.1475\,(\phi_3 - \phi_4) + 0.6621\,(\phi_6 - \phi_7)$
$\psi_{23} = 0.0280\,(\phi_1 + \phi_2) + 0.1916\,(\phi_3 + \phi_4) + 0.4109\,(\phi_6 + \phi_7) + 0.6479\,\phi_5$

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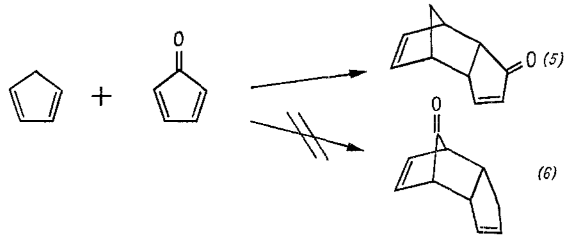
[a] See Fig. 1 for the numbering of the atomic orbitals.

$(b_1 a_2^*)$, i.e. ${}^1A_1 \rightarrow {}^1B_2$, and involves the lone electrons on the ether-like oxygen atom.

In CPDO, we are disappointed to find the inverted relative positions of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, the so-called K and R bands for $\alpha - \beta$ unsaturated carbonyl compounds. The predicted wave-lengths of the lowest energy bands for CPD, CPDO, and MA are 315 mμ, 1018 mμ, and 434 mμ respectively. These are in very poor agreement with the experimental bands: 238.5 mμ [*40*], 395 mμ (for a monosubstituted derivative [*18*], and 227 mμ (determined in this laboratory), respectively. As HOFFMANN has pointed out [*21*], this result is to be expected of these simple wave functions which have not been scaled by the introduction of a spectrally-calibrated resonance integral. The use of other recipes for the resonance integral, especially parabolic relationships between overlap integral and resonance integral [*8*, *38*] has given better results, and we will report on these at a later date.

Reactivity in the Diels-Alder Reaction. We turn now to a comparison of predicted and known reactivity for this system of compounds.

Fig. 2 illustrates the fact that the signs of the highest occupied MO of the diene and the lowest vacant MO of the dienophile are favorable for reaction in all possible combinations of reactants. The smaller the difference in energy between these two MO's, the more likely interaction or reaction should be, and this "energy gap" is also given in Fig. 2. Predicted reactivities are in accord with the known properties of these compounds. Thus CPD and MA is a more reactive pair than CPD and CPD [*4*, *7*, *24*], and CPDO dimerizes so rapidly that it has never been isolated [*1*, *11*]. Also, the relative size of the energy gaps for the two possible reactions of CPD with CPDO, accounts for the fact that generating CPDO in the presence of a large excess of CPD leads only to product in which CPDO acts as dienophile [*9*, *10*]. Reaction 5 occurs; Reaction 6 does not occur.



The predominant formation of endo-adducts is accounted for by secondary interactions between atoms which do not become bonded in the adduct, just as suggested by Hoffmann and Woodward [*23*].

A more quantitative treatment seems desirable, and this is accomplished by the perturbation method outlined in the previous section. We assume a particular geometry for an interacting state of diene and dienophile and calculate the stabilization energy of that state by the perturbation method. We assume that entropy changes to achieve that state will be constant among all reacting pairs. We chose this system of compounds because of their very similar geometries and the necessity for minimizing the entropy effects.

The first reaction stage we decided to investigate was one in which the two reactant molecules had approached one another to the limit of their van der Waals radius in the geometry required to give either an endo or exo adduct. The two reactants were assumed to be in parallel planes and no changes were postulated for bond lengths or angles. Fig. 3 depicts the reaction intermediates for the

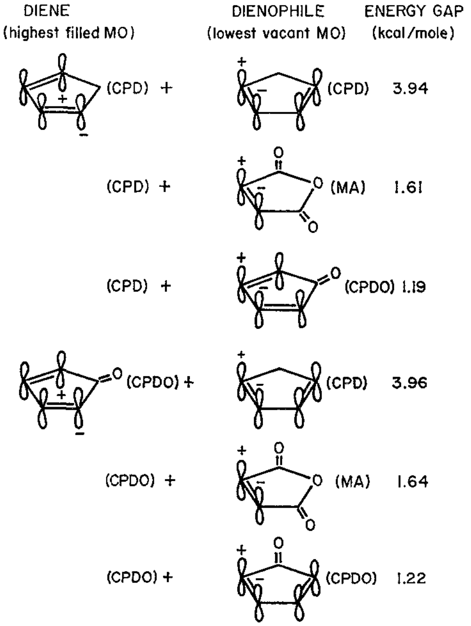


Fig. 2

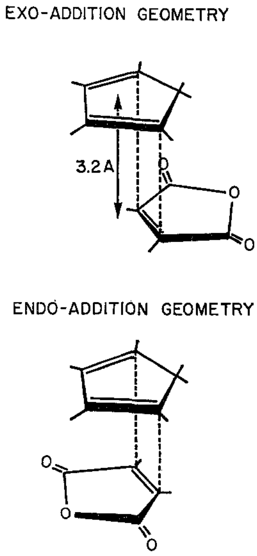


Fig. 3

Fig. 2. Energy gaps and orbital signs for Diels-Alder reactions (see text)

Fig. 3. Two possible interacting states for the reaction CPD + MA

MA-CPD pair. 3.2 Å is approximately twice the van der Waals radius of a double bond [35].

The stabilization energies for all possible reactant pairs are given in Tab. 3. These figures result from a treatment including all interactions, summed over all occupied and vacant orbitals according to Eq. (4), for only the $2p_z$ atomic orbitals (those perpendicular to the planes of the molecules). We carried out calculations including all other valence electrons ($2s$, $2p_x$, $2p_y$) and find that their contribution to the stabilization energy is less than 2 percent.

The major portion of the stabilization energy is due to the primary interaction, that between highest occupied MO of diene and lowest vacant MO of dienophile. For example, it provides respectively 64 percent, 73 percent, 82 percent, and 65 percent of the stabilization energy for the first two (endo and exo) reactions of Tab. 3. This accounts for the fact that qualitative predictions can be made using only the highest filled and lowest vacant orbitals. However, since this percentage is highly variable it seems best to base a quantitative treatment on the complete set of molecular orbital interactions.

Table 3. *Stabilization Energies for Diels-Alder Reactions*

Reaction	Stabilization energy (kcal/mole)	
	endo geometry	exo geometry
CPD + CPD	11.8	9.5
CPD + MA	18.9	14.5
CPDO + CPDO	41.7	29.2
CPDO + MA	20.6	13.2
CPD(diene) + CPDO	28.0	—
CPDO(diene) + CPD	21.8	—

Data for comparison with the figures of Tab. 3 are sparse, but where available are always in agreement. The difference in stabilization energies (ΔSE) for two reactions can be compared with the difference in activation energies (ΔE_A) for the same two reactions. For CPD + MA (endo addition) versus CPD + CPD (endo addition), $\Delta SE = 7.1$ kcal/mole, $\Delta E_A = 9.4$ to 5.6 kcal/mole (depending upon the solvent) [47]. The difference in transition state energies for formation of *endo*- and *exo*-dicyclopentadiene is estimated to be 3.0 ± 2.0 kcal/mole [29] and we find $\Delta SE = 2.3$ kcal/mole.

The stabilization energies of Tab. 3 account both qualitatively and semi-quantitatively for the reactivity of CPDO. Thus, CPDO reacts primarily as a dienophile with CPD ($SE = 28.0$) rather than as diene ($SE = 21.8$) [10]. Also, the reaction of CPDO with MA ($SE = 20.6$) has not been observed; CPDO evidently prefers to undergo self-dimerization ($SE = 41.7$) [10].

The reaction of CPDO with CPDO is predicted by the figures of Tab. 3 to be some 16 powers of 10 faster than the reaction of CPD and MA. GARBISCH [18] estimates a diffusion controlled reaction for CPDO, $k > 10^{10}$ l/mole-sec, which would predict a difference in reactivity for the reactions under consideration of at least 10^{12}.

The reaction stage which we have chosen to investigate in this initial effort may be a very poor model for the transition state of the Diels-Alder reaction.

However, it is in agreement with an interpretation of the small isotope effects observed during some Diels-Alder reactions, which requires that the transition state lie only a little way along the reaction coordinates [*42*]. Furthermore, the usual exothermicity of the Diels-Alder reaction would indicate an electronic correspondance of initial and transition states, according to the HAMMOND postulate [*20*]. Also, our postulated intermediate stage closely resembles a π-complex, and such complexes are possible intermediates in the Diels-Alder reaction [*3*].

In our calculations the source of an energy of activation is not apparent since the stabilization energies would only tend to increase as the reacting molecules approached one another more closely. We are, therefore, rather surprised to find such good agreement with experimental results. Calculations with more realistic potential functions are being carried out and will be reported in later papers.

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