Organic and Biological Chemistry

Intermolecular Orbital Theory. III. Thermal and Photochemical Dimerization of Unsaturated Ketones[1]

Alain Devaquet[2] and Lionel Salem

Contribution from Laboratoire de Chimie Théorique, Faculté des Sciences, Orsay (Essonne), France. *Received January 22, 1969*

Abstract: The theory of the interaction between conjugated molecules with overlapping p orbitals[3] has been extended to include the effect of electron repulsion. Self-consistent field π orbitals on the separate molecules are used as starting point. The total interaction energy is expressed in terms of the overlap $S_{rr'}$ between interacting orbitals and of the net electronic charge Δq_r on the atoms. The results are used to draw incipient reaction paths for the Diels–Alder dimerization of acrolein and to calculate stabilization energies in the photodimerization of 3,5-diene-7-one and 4,6-diene-3-one type keto steroids. The high selectivity in the thermal reaction can be ascribed to the combined effect of favorable overlap and polar interactions. In the photodimerization reactions the product is determined, among the few sterically allowed configurations of approach, by favorable overlap interactions in the first case but no simple physical interpretation of the selectivity can be found in the second case.

In parts I[3a] and II[3b] the energy of interaction between two conjugated molecules was obtained by second-order perturbation theory within the framework of a one-electron-interaction Hamiltonian. The method suffered from the neglect of Coulomb repulsion between electrons on the two systems, as well as from the use of unsophisticated orbitals as starting point for the separate systems. These two defects can be remedied by including explicit two-electron interactions in the interaction Hamiltonian, and by improving the starting wave functions. A convenient framework uses self-consistent field (SCF) π molecular orbitals and energies, and also a SCF-type interaction Hamiltonian, as starting point for an intermolecular calculation. In the present paper we first give those results which are easily amenable to physical interpretation. Details of the theory will be provided elsewhere.[4] The theory has been used to evaluate the total energy of interaction in the initial stages of concerted cycloadditions between polar molecules. In the second part this is effected for the Diels–Alder dimerization of acrolein, and in the third and final part for the photodimerization of unsaturated keto steroids. In both cases the interaction energy can be divided into overlap (exchange), polar (electrostatic), and eventually "cross" contributions, and the controlling force for a given reaction can generally be ascertained.

Assumptions and Results of the Theory. The major assumption is that the molecular interaction in its incipient stages can be treated by second-order perturbation theory, the interaction energy being small relative to the energy of the separate systems. The molecular orbitals of the two systems are then assumed to be appropriate starting points for calculating this interaction energy.

The theory assumes[3] that intermolecular bonding is brought about by incipient overlap between $2p\pi$ orbitals. Rehybridization is assumed to occur in a significant manner only at a later stage. Furthermore Coulombic interactions, in particular those between net charges, are considered concurrently with this overlap effect. Although it is now well established that net charges in conjugated systems arise from both σ and π electrons, we restrict consideration, in a first approximation, to the net π charges.

The intermolecular orbitals are combinations of the π molecular orbitals of the separate molecules. They are chosen as eigenfunctions of the Hartree–Fock operator for the composite system of two molecules

$$F^\circ = t + (c + c') + 2J^\circ - K^\circ \qquad (1)$$

where t is the kinetic energy operator, c is the field of the core of the first molecule (unprimed notation), and c' that of the core of the second molecule (primed notation). The operators J° and K° are the Coulomb and exchange operators[5] built in the usual manner over the eigenfunctions of F°. We define the interaction operator I by the identity

$$F^\circ = 0.5(F + F') + I \qquad (2)$$

---

(1) Research supported in part by National Institutes of Health Grant GM 12343. The Laboratoire de Chimie Théorique is also part of the Laboratoire Associé de Physico-Chimie des Rayonnements supported by the CNRS.

(2) Work performed in partial fulfillment of the requirements for the degree of Docteur-és-Sciences at the University of Paris, Faculté des Sciences d'Orsay.

(3) (a) L. Salem, *J. Am. Chem. Soc.*, 90, 543 (1968); (b) L. Salem, *ibid.*, 90, 553 (1968). (c) NOTE ADDED IN PROOF. O. E. Polansky (private communication, 1969) has kindly pointed out some numerical errors in part II: (1) in eq 10 and 11 $\eta_{22'}\eta_{33'}$ and $\eta_{11'}\eta_{44'}$ have coefficients -0.229 (not -0.498) and 0.134 (not -0.136); in eq 13 and 14 the coefficients of $S_{22'}S_{33'}$ and $S_{11'}S_{44'}$ become -2.85 and -3.62. The butadiene excimer has an energy minimum of 0.097β at $S = 0.117$. (2) Equation 16 for E_{VI} should read $-0.35S_{11'}{}^2$, not $-1.35S_{11'}{}^2$. The nonsynchronous character of the *exo* dimerization of butadiene is enhanced; the best path corresponds to $S_{11'}S_{42'} = 1.22$ with a stabilization energy of 0.130β at $S_{11'} = 0.2$. (3) For reactions VII and VIII, eq 16 reads $0.54S_{11'}{}^2$ (not 0.64) and $4.23S_{12'}S_{41'}$ (not 5.20; also 15 has $0.470\eta_{12'}\eta_{41'}$). The corrected stabilization energies are 0.063β for the first stage of VII and 0.062β (first stage) or 0.070β (both bonds closed) for VIII. *Hence, Hückel theory actually gives almost equal energies for the two different exo condensations of acrolein.* Finally, once eq 19 and 19a are corrected accordingly ($-0.35S_{11'}{}^2$ for IX, $0.54S_{11'}{}^2$ for X, and $5.94S_{12'}S$ for XI), only minor changes occur in the ensuing *endo* reaction paths and energies (0.109β for X and 0.179β for XI).

(4) A. Devaquet, submitted for publication.

(5) C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

where F and F' are the Hartree–Fock operators for the separate molecules. The matrix elements of F° between orbitals ψ_j (eigenvalue ϵ_j) and $\psi_{j'}$ (eigenvalue $\epsilon_{j'}$) on different molecules can then be conveniently expressed as

$$F^\circ_{jj'} = 0.5(\epsilon_j + \epsilon_{j'})S_{jj'} + I_{jj'} \tag{3}$$

where $S_{jj'}$ is the overlap integral between ψ_j and $\psi_{j'}$. Orbitals j and j' run through both occupied and unoccupied sets, respectively, for the first and second molecules. If only a particular set (occupied or unoccupied) is considered, it will be specified appropriately.

In the perturbation treatment, two different orders of smallness appear which characterize the two different perturbational effects, "overlap" interaction and "electrostatic" interaction. The extent of covalent bond formation is limited to the size of the overlap $S_{jj'}$. It will therefore be natural to expand the interaction energy in powers of $S_{jj'}$. If the molecular orbitals are expressed as linear combinations of the atomic orbitals φ_r, the expression ultimately involves the atomic orbital overlaps $S_{\mathrm{rr}'}$. The electrostatic interactions ultimately involve the Coulomb attraction or repulsion between net charges on the different atoms. In a conjugated hydrocarbon, for instance, each carbon atom r provides one π electron for conjugation but carries an electronic charge density q_r. The *net electronic charge* on carbon atom r can therefore be measured in atomic units as $\Delta q_\mathrm{r} = q_\mathrm{r} - 1$. In alternant hydrocarbons $\Delta q_\mathrm{r} = 0$ but for nonalternants or for heteromolecules the net charge seldom vanishes and may vary substantially from one atom to another. In neutral systems, however, Δq_r will tend to be small compared with 1 since a too highly nonuniform charge distribution is costly energywise. The total interaction energy can therefore also be expanded in powers of Δq. Altogether the interaction energy is expanded to second order both in S and in Δq, typical terms of highest order being S^2, $S\Delta q$, and Δq^2. *To this order of approximation*

$$I \approx 0.5(c + c') + (J + J') - 0.5(K + K') \tag{4}$$

The interaction operator in (4) is not strictly identical with that in the Hückel-like intermolecular orbital theory,[3] but it contains essentially the same effects. These include the attraction of the nuclear cores and the Coulomb and exchange potentials of the π electronic shells acting on an electron in the intermolecular region. Altogether the Hückel operator v, in which the electronic field is totally smoothed out, is replaced by the operator $c + 2J - K$.

The matrix elements of F° are evaluated in the zero differential overlap approximation.[6] They involve essentially (a) the electronic repulsion integral

$$\gamma_{\mathrm{rr}'} = \int\int \varphi^2_\mathrm{r}(1)\frac{e^2}{\mathrm{r}_{12}}\varphi^2_{\mathrm{r}'}(2)\mathrm{d}\tau_1\mathrm{d}\tau_2 \tag{5}$$

(b) an atomic orbital interaction integral $\eta_{\mathrm{rr}'}$ obtained by expanding $I_{jj'}$ over pairs of *opposite* atoms r and r′ with directly overlapping orbitals on the two molecules

$$\eta_{\mathrm{rr}'} = \int \varphi_\mathrm{r} I \varphi_{\mathrm{r}'}\mathrm{d}\tau \tag{6}$$

The integral $\gamma_{\mathrm{rr}'}$ represents the Coulombic interaction between an electron in atomic orbital φ_r and an electron in atomic orbital $\varphi_{\mathrm{r}'}$. It can be written as the interaction energy between two negative charges located on nuclei r and r′ corrected by a penetration term of order S^2

$$\gamma_{\mathrm{rr}'} = \frac{1}{R_{\mathrm{rr}'}} + \left(\gamma_{\mathrm{rr}'} - \frac{1}{R_{\mathrm{rr}'}}\right) \tag{7}$$

where $R_{\mathrm{rr}'}$ is the distance between nuclei r and r′. This penetration term remains small through the important region of incipient overlap ($R > 4$ au), as shown in Figure 1. In this figure, the comparison of $\gamma_{\mathrm{rr}'}$, calculated for two end-on SCF carbon 2p orbitals,[7] and $1/R_{\mathrm{rr}'}$ shows that in fact for any value of $R_{\mathrm{rr}'}$ no smaller than 2 au, the difference $[\gamma_{\mathrm{rr}'} - (1/R_{\mathrm{rr}'})]$ is never more than 12% of $\gamma_{\mathrm{rr}'}$. The maximum deviation occurs for $R_{\mathrm{rr}'} = 3.5$ au. The theory neglects this penetration term and writes

$$\gamma_{\mathrm{rr}'} \approx \frac{1}{R_{\mathrm{rr}'}} \tag{8}$$

Note that this approximation is by no means self-evident, since one would have expected the difference between $\gamma_{\mathrm{rr}'}$ and $1/R_{\mathrm{rr}'}$ to increase steadily as $R_{\mathrm{rr}'}$ decreases.

The final approximations concern the relative values of $\eta_{\mathrm{rr}'}/S_{\mathrm{rr}'}$ and $\Delta q_{\mathrm{r}'}/R_{\mathrm{rr}'}$ on one hand, and on the other hand the energy difference between an unoccupied orbital k' on one molecule and an occupied orbital j on the other. It is assumed that the ratio $\eta_{\mathrm{rr}'}/S_{\mathrm{rr}'}$ is large in front of the average excitation energy (see I,[3a] eq 32)

$$\frac{\eta_{\mathrm{rr}'}}{S_{\mathrm{rr}'}} \gg \epsilon_{k'}{}^{(\mathrm{unocc})} - \epsilon_j{}^{(\mathrm{occ})} \tag{9}$$

On the other hand we assume

$$\frac{\Delta q_{\mathrm{r}'}}{R_{\mathrm{rr}'}} \ll \epsilon_{k'} - \epsilon_j \tag{10}$$

The left-hand side should seldom exceed 1 eV ($\Delta q \sim 0.3$, $R \sim 6$ au), whereas the right-hand side is almost always greater than 3 eV.

The expressions for the total energy of interaction are similar to those of the simple theory,[3] but certain additional terms appear because of the inclusion of electron repulsion. For two identical molecules in their ground state the simple theory led to the interaction energy (I, eq 15a)

$$E_\mathrm{int} = -\textstyle\sum_{\mathrm{rr}'}(q_\mathrm{r} + q_{\mathrm{r}'})\eta_{\mathrm{rr}'}S_{\mathrm{rr}'} - 2\displaystyle\sum_j^{\mathrm{occ}}\sum_{k'}^{\mathrm{unocc}} \times \frac{(\sum_{\mathrm{rr}'}c_{j\mathrm{r}}c_{k'\mathrm{r}'}\eta_{\mathrm{rr}'})^2}{E_{k'} - E_j} - 2\sum_{j'}^{\mathrm{occ}}\sum_{k}^{\mathrm{unocc}}\frac{(\sum_{\mathrm{rr}'}c_{k\mathrm{r}}c_{j'\mathrm{r}'}\eta_{\mathrm{rr}'})}{E_k - E_{j'}} \tag{11}$$

in which the one-electron energies were denoted by E_j (orbital j). In this expression the first term represents the *repulsion* between the two molecules arising from their closed-shell character. It is proportional to the π charge densities q_r and $q_{\mathrm{r}'}$ on pairs of interacting atoms r and r′. The terms with the double sums represent an *attractive* energy due to the mixing between occupied orbitals on one molecule and vacant orbitals on the other. These terms are crucial in determining favorable reaction paths for nonpolar systems. In the present

---

[6] R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 446, 767 (1953); J. A. Pople, *Trans. Faraday Soc.*, 49, 1375 (1953).

[7] R. B. Hermann, *J. Chem. Phys.*, 42, 1027 (1965).

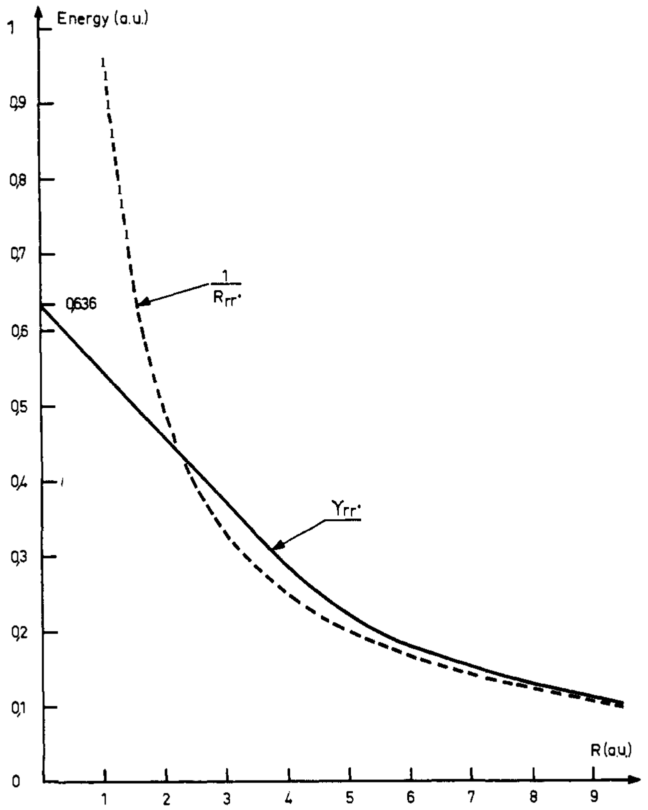


Figure 1.

theory the interaction energy contains two parts. The first part is an *interaction energy due to overlap* proper, E_{overlap}, and is given precisely by eq 11, in which the E_j's are replaced by ϵ_j's in the one-electron energy denominators. The second part is an *electrostatic energy*, E_{polar}, given by

$$E_{\text{polar}} = \sum_{\text{rr}'} \Delta q_{\text{r}} \Delta q_{\text{r}'} \frac{1}{R_{\text{rr}'}} \tag{12}$$

which can be simply interpreted as the interaction between the net charges on the two molecules. Equation 12 actually results from a cancellation of several effects: a core–core repulsion energy, each core being represented as a set of positive charges +1 located at the nuclear positions, a core–electron attractive energy, and an electron–electron repulsion energy.

If one molecule is excited (excitation $\psi_j \rightarrow \psi_k$), the simplest case occurs when the orbital splitting due to the molecular interaction is sufficient to ensure that the lowest excited state of the dimer is well represented by the one-electron configuration of lowest energy (Figure 2; orbitals j' and k' on the second molecule are degenerate respectively with j and k).[8] In this case the simple theory gave for the change ΔE_{int} in interaction energy upon excitation (I, eq 21a)

$$\Delta E_{\text{int}}^{(j \rightarrow k)} = -\left(\left|\sum_{\text{rr}'} c_{j\text{r}} c_{j'\text{r}'} \eta_{\text{rr}'}\right| + \left|\sum_{\text{rr}'} c_{k\text{r}} c_{k'\text{r}'} \eta_{\text{rr}'}\right|\right) + \sum_{\text{rr}'} (c^2_{j\text{r}} - c^2_{k\text{r}}) \eta_{\text{rr}'} S_{\text{rr}'} + \sum_{\substack{\text{all } j' \\ (\neq j)}} \frac{\left(\sum_{\text{rr}'} c_{j\text{r}} c_{j'\text{r}'} \eta_{\text{rr}'}\right)^2}{E_{j'} - E_j} - \sum_{\substack{\text{all } j' \\ (\neq k)}} \frac{\left(\sum_{\text{rr}'} c_{k\text{r}} c_{j'\text{r}'} \eta_{\text{rr}'}\right)^2}{E_{j'} - E_k} \tag{13}$$

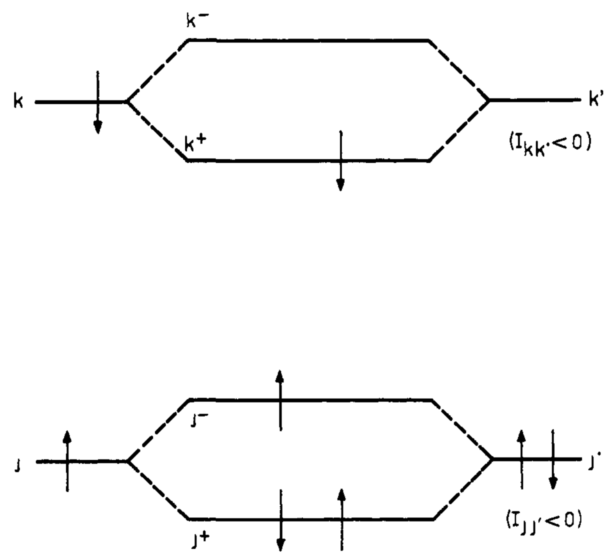


Figure 2.

Here the first term represents the *stabilization of the excited electron* (ψ_k) and *the destabilization of the hole* (ψ_j), due to the first-order mixing between ψ_j and ψ_k and their degenerate partners. The second term represents the effect of the change in size of the exclusion shell around atom r upon excitation, and the last terms are small modifications brought by the excitation to the second-order energy. The first term is all important in determining favorable paths for photochemical cycloadditions of nonpolar systems. In the present theory the overlap contribution to the change of interaction energy, $\Delta E_{\text{overlap}}$, is precisely given by (13) with the E_j's replaced by ϵ_j's. The additional contributions which arise depend on whether the excitation occurs to a singlet or to a triplet state. They can be divided into purely Coulombic energies

$$^3\Delta E_{\text{polar}} = \sum_{\text{rr}'} (c_{k\text{r}}^2 - c_{j\text{r}}^2) \frac{\Delta q_{\text{r}'}}{R_{\text{rr}'}} - \left[\frac{1}{4}(J_{jk'} + J_{j'k}) - \frac{1}{2} J_{jk}\right]$$

$$^1\Delta E_{\text{polar}} = {}^3\Delta E_{\text{polar}} - (K_{jk,j'k'} + K_{jk,jk}) \tag{14}$$

$$J_{jk} = \int \psi_j^2(1) \frac{e^2}{\text{r}_{12}} \psi_k^2(2) \text{d}\tau_1 \text{d}\tau_2$$

$$K_{jk,j'k'} = \int \psi_j(1) \psi_k(1) \frac{e^2}{\text{r}_{12}} \psi_{j'}(2) \psi_{k'}(2) \text{d}\tau_2 \text{d}\tau_2$$

and into "*cross*" *interaction energies* between the overlap (exchange) and Coulomb interactions. The latter involve many terms[4] and will not be written out. In (12) the term $\Sigma_{\text{rr}'}(c_{k\text{r}}^2 - c_{j\text{r}}^2)(\Delta q_{\text{r}'}/R_{\text{rr}'})$ arises from the change in net charge distribution on the molecule which is excited. This term, added to (11), gives the interaction between the new net charges. The term $-0.25 \cdot (J_{jk'} + J_{j'k})$ arises from the fact that in the dimer the excited electron, although initially in orbital k of the first molecule (excitation energy $\epsilon_k - \epsilon_j - J_{jk}$), now "belongs" equally to both molecules (excitation energy $\epsilon_{k^+} - \epsilon_{j^-} - J_{j^-k^+}$). Part of the time it therefore feels the effect of the electrons in j' rather than j. The same explanation holds for the term $-(K_{jk,j'k'} + K_{jk,jk})$.

It should be emphasized again that eq 12 holds only in the region where the interaction due to overlap is sufficiently large for a molecular orbital

---

[8] A configuration interaction calculation involving all four configurations (j^-k^+), (j^-k^-), (j^+k^+), (j^+k^-), shows that when the orbital splitting is large enough, (j^-k^+) lies well under the combination $(j^+k^+) + (j^-k^-)$ which is stabilized only by a Coulombic dipole–dipole term.

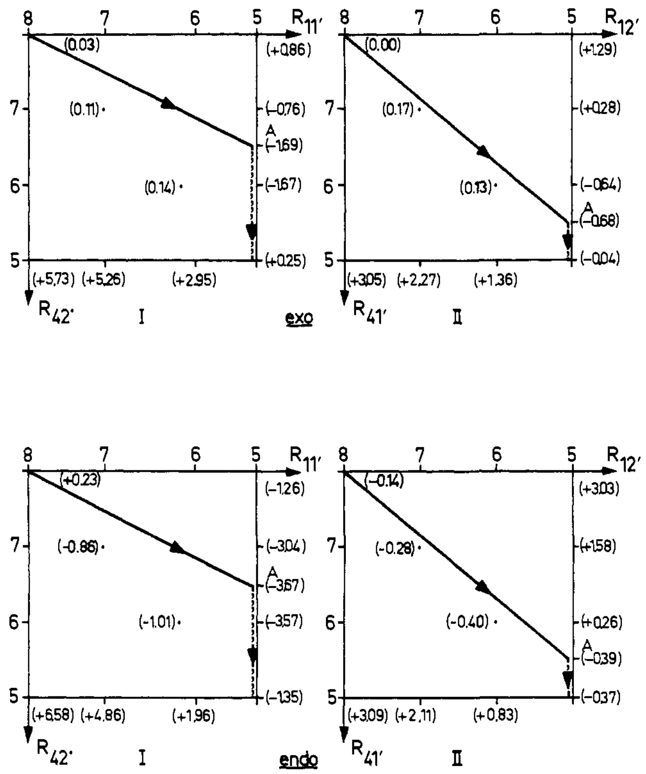
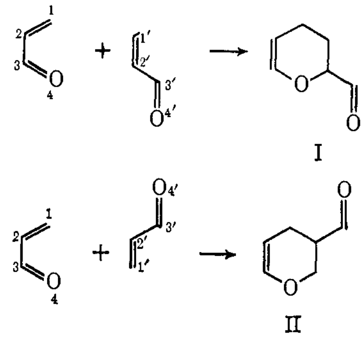


Figure 3. Reaction paths for Diels–Alder dimerization of acrolein (energies in kilocalories/mole).

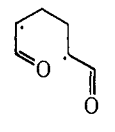
description to be valid. It definitely breaks down at large distances.[9] With this restriction, our results allow for the distinction between interaction energies for excited singlets and excited triplets arising from the same one-electron excitation. This distinction may be useful in understanding the different behavior of singlets and triplets in photochemical cycloadditions.

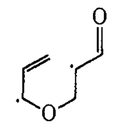
Diels–Alder Dimerization of Acrolein. In their study of the mechanism of the Diels–Alder reaction[10] Woodward and Katz pointed out that the selective dimerization of acrolein[11] to give product I rather than II agreed with predictions based on the more stable hypothetical diradical intermediate (III rather than IV). They also showed, however, that the formation of I could be accounted for by a *concerted*, two-stage mechanism with a highly structured *endo* transition state in which secondary forces played an important role.



I

II


III


IV

In our first calculations on the dimerization process[3b] we did find concerted pathways for the initial bond closures for both additions. Addition I was found to occur rather unsymmetrically, with bond 11′ "formed" ($S_{11'} = 0.2$) while bond 42′ was still at a very early stage ($S_{42'} = 0.07$). Addition II followed a quasi-symmetrical pathway with bonds 12′ and 41′ closing at equal rates. Yet the lowest energy attained in the first addition (−4.3 kcal/mol) was slightly higher than that attained in the second addition (−4.9 kcal/mol) in contradiction with the experimental facts. The consideration of an *endo* structure[12] with secondary interactions of the type 3′ ↔ 3, 4′ ↔ 2 in I, or 3′ ↔ 2, 4′ ↔ 3 in II brought no change to the matter. Although the stabilization energies were larger (−7.5 kcal/mol for I, −12.4 kcal/mol for II), the theory still favored process II.

It was our feeling that overlap interactions alone were inadequate to account for the specificity of this reaction. As Klopman and Hudson have pointed out,[13] controlling forces in reactions include both overlap—"frontier"[14] control—*and* polar interactions—"charge" control. We therefore performed a calculation by the method outlined in the previous section, in which both effects are included.

The π SCF molecular orbitals were evaluated by the method of Bloor and Gilson,[15] whose closed-shell SCF-LCAO MO program was kindly provided by the Quantum Chemistry Program Exchange. Their method adopts the Mataga–Nishimoto formalism for calculating electron repulsion integrals between π orbitals.[16] The numerical evaluation of the interaction energy required a value for the ratio

$$k = \frac{\eta_{rr'}}{S_{rr'}} \qquad (15)$$

which is assumed to be constant.[17] The value

$$k = -14 \text{ eV}$$

was chosen throughout our calculations.[18]

---

[9] In no manner does the requirement that the distance of approach lie in the "intermediate" range (5 to 8 au) contradict the assumption that the overlap *integral* is small enough for a power expansion to be valid. It was shown[3] that the $p\sigma$–$p\sigma$ end-to-end overlap never exceeds 0.27.

[10] R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

[11] E. C. Coyner and W. S. Hillman, *J. Am. Chem. Soc.*, **71**, 324 (1949).

[12] W. C. Herndon and L. Hall, *Tetrahedron Letters*, 3095 (1967), have offered an alternative explanation for the *endo* mechanism, in which only the different size of the primary overlaps is involved.

[13] (a) G. Klopman and R. F. Hudson, *Theoret. Chim. Acta*, **8**, 165 (1967); *Tetrahedron Letters*, 1103 (1967); (b) G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).

[14] (a) K. Fukui, T. Yonezawa, and C. Nagata, *J. Chem. Phys.*, **20**, 722 (1952); **22**, 1433 (1954); (b) K. Fukui in "Molecular Orbitals in Chemistry, Physics and Biology," P. O. Löwdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1964, p 573.

[15] (a) J. E. Bloor, P. N. Daykin, and P. Boltwood, *Can. J. Chem.*, **42**, 121 (1964); (b) J. E. Bloor and N. Brearley, *ibid.*, **43**, 1761 (1965).

[16] (a) N. Mataga and K. Nishimoto, *Z. Physik. Chem.* (Frankfurt), **13**, 140 (1957); (b) R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, Inc., New York, N. Y., 1963, p 90.

[17] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[18] The constant k is evaluated in the following manner. The matrix element $\eta_{rr'}$ in (6) is calculated for two opposite isolated carbon atoms by the Mulliken approximation. To first order in the overlap this yields $\eta_{rr'} = 0.5(c_{rr'} + \gamma_{11} + \gamma_{11'})$ where $c_{rr'}$ is the matrix element of the core potential c and is equal to I − kinetic energy. Here I is the ionization potential for a $p\pi$ electron on isolated carbon atom. Making the usual approximation $\gamma_{11} = I - A$, where A is the π electron affinity of a hybridized carbon atom in its valence state, we obtain $k = 0.5(-A -$ kinetic energy $+ \gamma_{11'})$. Calculations give A = 0.03 eV,[19] kinetic en-

We assumed that the two acrolein molecules remained planar during the initial stages of the cycloaddition. Energies were calculated for reactions I and II for several configurations of approach. In "symmetric" configurations the molecular planes are parallel, the terminal atoms of the diene lie exactly above the double bond to which they add, and both incipient-bond lengths are equal. In "asymmetric" configurations, the bond lengths are different, but the projections of the terminal atoms of the diene on the plane of the dienophile still lie symmetrically about the double bond to which they add. All distances were measured on actual Dreiding stereomodels of the molecules. The results are given in Figure 3 (for *exo* cycloadditions, and for *endo* cycloadditions, with the additional secondary interactions postulated earlier[12]). The numbers in these figures refer to the energy in kilocalories/mole for various values of the incipient-bond lengths, between 5 and 8 au. It is also possible to draw approximate reaction paths by joining the origin to the point A where, one bond being "formed" (R = 5 au), the energy is a minimum. The paths are indicated by the full lines with arrows. Dotted lines indicate that the interaction energy increases. It is possible that these dotted paths are not actually followed by the molecules which find alternate means (rehybridization) of lowering the over-all energy.

The remarkable feature of these figures is that cycloaddition I now leads to a lower interaction energy than cycloaddition II. Comparison of the π stabilization energies at A show I (−1.69 kcal/mol) to be preferred by 1 kcal/mol to II (−0.68 kcal/mol) in the *exo* approach, the difference increasing to 3.3 kcal/mol (I, −3.67 kcal/mol, II, −0.39 kcal/mol) in the *endo* approach. The experimental observations can then be understood in terms of a concerted *endo* approach of the molecules in configuration I, in agreement with the Woodward and Katz hypothesis, with bond 11′ closing roughly twice as fast as bond 42′.

The interpretation of the difference between I and II in terms of "overlap energy" and "polar energy" is illuminating. In both *exo* and *endo* approaches the major contribution (60 to 70%) to the stabilization of I relative to II arises from the electrostatic terms in E_{polar}, as shown by the terms of Table I. However, in both cases the overlap energy also favors configuration I, an improvement over the previous calculations[3b,3c] based on Hückel molecular orbitals. Hence part of the previous failure[3b,3c] to agree with experiment appears to have been due to the unreliability of the Hückel molecular orbitals.

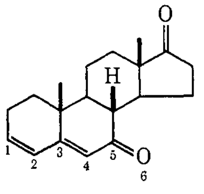
Table I. Interaction Energies[a] for Diels–Alder Dimerization of Acrolein

	I (*exo*)	II (*exo*)	I (*endo*)	II (*endo*)
E_{overlap}	−0.66	−0.36	−1.33	+0.19
E_{polar}	−1.03	−0.32	−2.34	−0.58
E_{total}	−1.69	−0.68	−3.67	−0.39

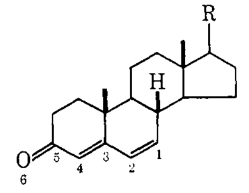
[a] In kilocalories/mole.

The slow decay of the Coulomb interaction $1/R$ with distance does not allow for a simple interpretation of the origin of E_{polar}; charge–charge interactions between all pairs of atoms play an important role. However, the experimentally observed difference can be interpreted in the following manner. In reaction II the most favorable polar attraction (oxygen 4 with carbon 1′) runs counter to an unfavorable overlap energy, so that the molecules are forced to compromise and choose a symmetrical path which gives mediocre overlap and polar energies. In reaction I, however, the polar energy is rather insensitive to the relative bond distances $R_{11'}$ and $R_{42'}$, so that the molecules can choose the path with the best overlap stabilization.

Photodimerization of Steroidal β,δ-Dienones. The remarkable specificity of the photodimerization of the 3,5-diene-7-one V[20] and the 4,6-diene-3-one VI[21] has recently been pointed out.[22,23] In both cases only one product is obtained: the 11′,22′ adduct (VIIa) for V, and the 14′,23′ adduct (VIIIc) for VI.

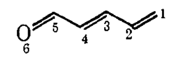


V



VI

The first question to ask is the nature of the excited state for which the photodimerizations occur. Probably the lowest over-all electronic state in the conjugated all-*trans* β,δ-hexadienone system



is the *triplet* $\pi \rightarrow \pi^*$ state. Indeed in the shorter enones both the photochemical behavior (cyclopentenone and cyclohexenone[24]) and theoretical calculations (acrolein[25]) indicate that the n → π^* and $\pi \rightarrow \pi^*$ triplets already lie very close to each other. The addition of a double bond to the conjugated chain will certainly raise the energy of the top π-bonding level in a significant manner relative to the n orbital on the oxygen; our calculations suggest an increase of 0.9 eV from acrolein to the linear hexadienone. The lowest singlet, however, is certainly the singlet *n → π^* state.* The intense singlet $\pi \rightarrow \pi^*$ absorption band still lies at energies (2850 Å ≈ 4.3 eV)[26] well above the singlet n → π^* level at roughly 3.2 eV (3860 Å).[27] In principle,

---

ergy = 33.4 eV for an isolated pπ orbital,[7] and $\gamma_{11'} \approx 5$ eV in the region of intermediate distances.[9]

(19) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962).

(20) M. B. Rubin, D. Glover, and R. G. Parker, *Tetrahedron Letters*, 1075 (1964).

(21) (a) H. P. Throndsen, G. Cainelli, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **45**, 2342 (1962); (b) M. B. Rubin, G. E. Hipps, and D. Glover, *J. Org. Chem.*, **29**, 68 (1964).

(22) P. J. Kropp in "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 1.

(23) For convenience we have numbered only the atoms of the conjugated chain from the carbon and to the oxygen atom.

(24) (a) P. de Mayo, private communication to the authors, 1968; (b) O. L. Chapman, T. H. Koch, F. Klein, P. J. Nelson, and E. L. Brown, *J. Am. Chem. Soc.*, **90**, 1657 (1968); (c) for the recent example of 4-bromotestosterone acetate, see D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).

(25) M. Jungen and H. Labhart, *Theoret. Chim. Acta*, **9**, 345 (1968).

(26) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, p 216.

(27) J. M. Hollas, *Spectrochim. Acta*, **19**, 1425 (1963); J. C. D. Brand and D. G. Williamson, *Discussions Faraday Soc.*, **35**, 184 (1963).

Table II: Interaction Energies (kcal/mol) for the Photodimerization of the Linear β,δ-hexadienone System[a]

Configuration		a(11′,22′)	b(12′,21′)	c(14′,23′)	d(13′,24′)	e(34′,43′)
Ground state	E_0	36,5	33,5	32	32	29
Triplet $\pi \rightarrow \pi^*$	$\Delta E_{\text{overlap}}$	−56	−38	−60.5	−52.5	−62
	ΔE_{polar}	44.5	49	37.5	42.5	38
	ΔE_{cross}	−4	−14	−12.5	−2	−1
	${}^3\Delta E_{\text{total}}$	−15.5	−3	−35.5	−12	−25
	${}^3E = {}^3\Delta E_{\text{total}} + E_0$	21.0	30.5	−3.5	20	4
Singlet $\pi \rightarrow \pi^*$	${}^1\Delta E_{\text{total}}$	−54	−34	−67.5	−41	−61
	${}^1E = {}^1\Delta E_{\text{total}} + E_0$	−17.5	−0.5	−35.5	−9	−32
Steric feasibility of dimer		Allowed (V) Allowed (VI)	Allowed (V) Allowed (VI)	Forbidden (V) Allowed (VI)	Forbidden (V) Forbidden (VI)	Forbidden (V) Allowed (VI)

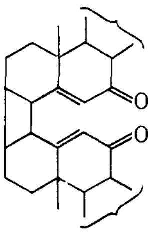
[a] For configurations c and d there is only a slight difference (0.1 kcal/mol) in the polar interaction energy depending on whether the unprimed or primed molecule is initially excited.[20] This difference arises from terms of type $\Sigma_{rr'}(c^2_{kr} - c^2_{jr})(\Delta q_{r'}/R_{rr'})$ in (14). The table shows the average energy of the two possibilities.

therefore, the reaction should occur either from the singlet n → π^* level or from the triplet $\pi \rightarrow \pi^*$ level. Although reactions in upper excited states of given spin symmetry cannot be excluded,[28] the singlet $\pi \rightarrow \pi^*$ state at least seems improbable as the active entity since the molecules were irradiated by high-pressure mercury lamps[20,21] at essentially $\lambda > 3000$ Å.

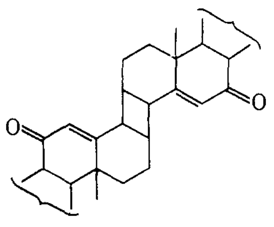
In the present study we have assumed that the $\pi \rightarrow \pi^*$ triplet is responsible for the photodimerization, and have performed our calculations accordingly. We will however discuss briefly the possibility of cycloaddition in an n → π^* state. It might be objected that a reaction in a triplet state cannot be governed by favorable paths calculated as if the addition were concerted, since there must be *two* steps. However it now seems well established[29] that addition in a triplet state can be governed stereospecifically by orbital interactions,[30] the product being already predetermined at the (late) time when intersystem crossing occurs back to the singlet manifold. We should note further that in V and VI the excited state of the relatively long conjugated system will probably retain the planar geometry of the ground state, because of the highly delocalized character of the excitation and of the steric constraints due to the rings.

Under these conditions the interaction energy between two linear β,δ-hexadienone systems, one of which is excited ($\pi \rightarrow \pi^*$), has been calculated by the method of the first section. Five configurations of approach were selected. They alone correspond either to a favorable interaction energy for V or VI, or to a sterically feasible dimer. Steric forbiddenness is assumed to occur when nonbonded H–H distances, as calculated from actual Dreiding stereomodels, happen to be smaller than 1.5 Å.[31] All additions were assumed to occur *cis* relative to both active double bonds, with formation of *cis,-anti-cis* or *cis,syn-cis* dimers; the latter, however, are sterically forbidden. Table II shows the changes ${}^3\Delta E$ upon excitation in overlap, polar, and "cross" interaction energies for the triplet $\pi \rightarrow \pi^*$ state. We also give the total interaction energy ${}^3E$ together with that (${}^1E$) for the singlet $\pi \rightarrow \pi^*$ state and that (E_0) for the ground state of the dimer. In all cases the energies correspond to $R = 5$ au for both incipient bonds. We also indicate whether the dimer appears to be sterically permissible.

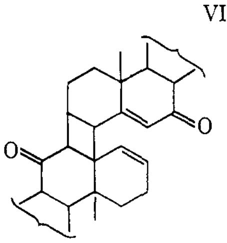
Let us consider first the photodimerization of V. The only sterically allowed dimers are the 11′,22′ (VIIa) and 12′,21′ (VIIb) adducts. An adduct such as 14′,23′ (VIIc) yields the lowest interaction energy but is sterically forbidden. Figures 4 and 5 show photographs of stereomodels of VIIa and VIIc. The



VIIa



VIIb



VIIc

absence of close hydrogen contacts in the first dimer, and their presence in the second one, is evident. The choice then lies between VIIa and VIIb. The calculations indicate unambiguously that VIIa is more stable, due to a more favorable overlap energy as shown

(28) (a) P. de Mayo, J.-P. Pete, and M. Tchir, *J. Am. Chem. Soc.*, **89**, 5712 (1967) (a reaction from an upper triplet state); (b) R. S. H. Liu and J. R. Edman, *ibid.*, 90, 213 (1968) (another such reaction). (c) The photoisomerization of benzene to Dewar benzene seems to occur from the ${}^1B_{1u}$ state (rather than the ${}^3B_{1u}$ state): D. Bryce-Smith, *Pure Appl. Chem.*, **16**, 47 (1968); H. R. Ward and J. S. Wishnok, *J. Am. Chem. Soc.*, 90, 1085 (1968). The photochemical reaction is therefore competitive with radiationless deactivation to the lowest singlet state. It is true, however, that no molecular collision is required in the process.

(29) (a) S. Kende, private communication to the authors, 1968; (b) D. Bryce-Smith, private communication to the authors, 1968; (c) R. Hoffmann, private communication to the authors, 1968; (d) P. de Mayo, J.-P. Pete, and M. Tchir, *Can. J. Chem.*, **46**, 2535 (1968).

(30) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

(31) This distance was chosen somewhat arbitrarily, but represents the limit between nonbonded distances of 1.6 Å in the observed dimers and the apparently intolerable nonbonded distance of 1.4 Å in all "sterically forbidden" dimers. Professor J. D. Dunitz (private communication) has pointed out that 1.8 Å seems to be the minimum nonbonded H–H distance in crystals. In the dimers for which 1.6-Å distances appear in the models, distortions will probably allow relaxation of 0.2 Å to about that value. It seems difficult at the present stage to evaluate these van der Waals interactions between CH σ cores explicitly.

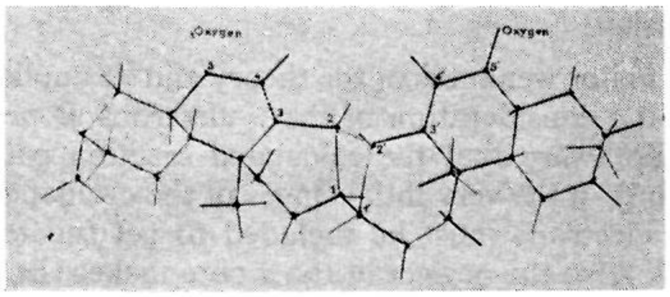


Figure 4.

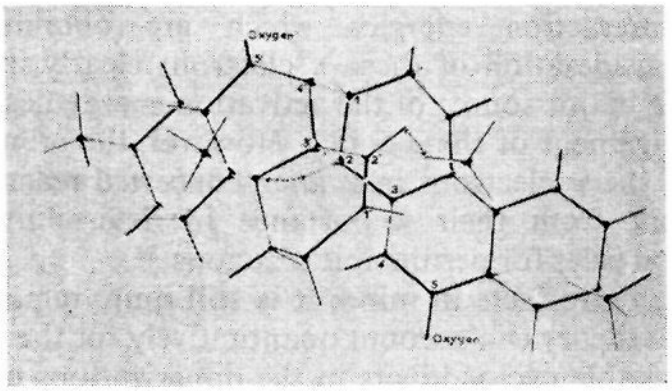
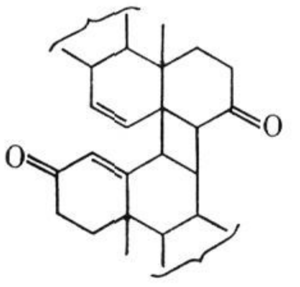
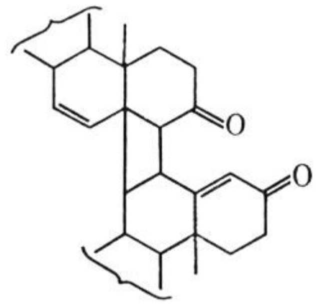


Figure 5.

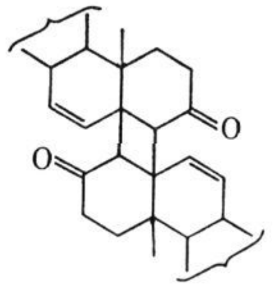
by relative values of $^3\Delta E$ overlap. The result is similar to that obtained[3b] in the photodimerization of butadiene, and arises from the same effect (more favorable interaction between the orbital of the excited electron and its opposite partner of equal energy). We therefore expect the head-to-head dimer VIIa to be the stable photoproduct, in agreement with experiment,[20] and also predict that the external (11′) bond closes faster than the 22′ bond.



VIIIc



VIIId



VIIIe

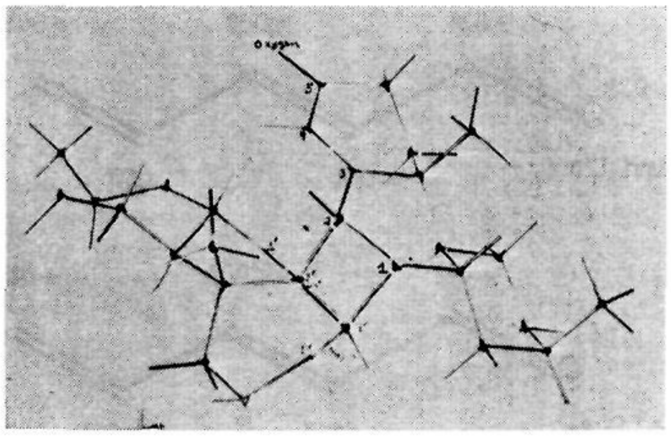


Figure 6.

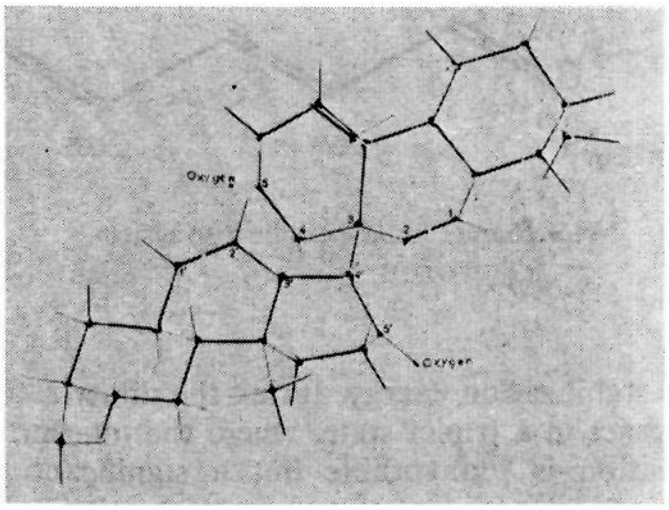


Figure 7.

We now turn to the photodimerization of VI. Here two of the three energetically most favorable dimers, VIIIc and VIIIe, are sterically allowed. The third ranking dimer, VIIId, is forbidden. Dimers VIIIc and VIIIe are shown in Figures 6 and 7. The theory favors VIIIc over VIIIe by 7.5 kcal/mol in the $^3\pi \rightarrow \pi^*$ state. Again this agrees with the experimental observations,[21] although there is some hesitation[22] between VIIIc and VIIId. (That ambiguity is lifted here both on steric and electronic grounds.) The interpretation of the preference for 14′,23′ (c) addition rather than 34′,43′ (e) addition seems to involve the complicated cross terms ΔE_{cross} and is not amenable to a simple physical interpretation. It is noticeable, however, that in the dienic part of the dienone system, the largest positive net charge in the ground state is carried by atom 3 ($\Delta q_r = 0.07$), while in the $\pi \rightarrow \pi^*$ excited state it is carried by atom 4 ($\Delta q = 0.13$; Figure 8). From this simple-minded viewpoint formation of a 34′ bond should be hindered.

It is interesting to consider how those results may be modified if the dimerization were to occur with one molecule in an excited $n \rightarrow \pi^*$ state. The interactions due to p-orbital overlap should vary in the same direction as for the $\pi \rightarrow \pi^*$ state, but they should be weaker because the stabilization of the excited π electron is not accompanied any more by a corresponding destabilization of the π hole. The polar interactions may however be significantly different. The over-all positive charge on the oxygen in the excited molecule should lead to head-to-head structures because of the favorable zwitterionic interaction with the molecule in its ground state. Consideration of the net π charges alone (Figure 8) is less revealing. The large negative π charge ($\Delta q = -0.17$) on atom 4 might, however, favor *a 34′ bond closure (adduct VIIIe) whereas the 14′,23′* closure (adduct VIIIc) would not seem to profit as well from a favorable polar energy. These considerations may be considered as very meagre theoretical evidence in favor of a $\pi \rightarrow \pi^*$ photodimerization.

It is a general feature of Table II that although the results for the $^1\pi \rightarrow \pi^*$ states parallel those for the $^3\pi \rightarrow \pi^*$ states, and although the terms $^3\Delta E$ and $^1\Delta E$—changes in energy upon excitation—are negative, the total interaction energy ^3E for triplets is almost always *positive*. On the other hand ^1E is *negative*, the difference being of the order of 1 eV. We are unable to answer the question whether the molecules prefer (a) to react in a singlet state (most probably $^1n \rightarrow \pi^*$, with a behavior similar to $^1\pi \rightarrow \pi^*$), thereby obtaining

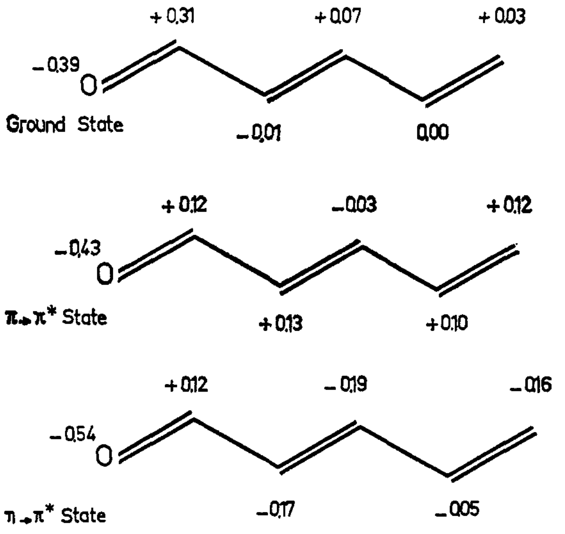


Figure 8. Net π charges in β,δ-hexadienone system.

a large stabilization energy during the dimerization, or (b) to react in a triplet state, where the intermolecular stabilization is unfavorable but a significant energy compensation (again of the order of 1 eV) is received prior to the reaction *via* intersystem crossing from singlet to triplet manifold.

Conclusion

The major weakness of the theory and its applications lies in the consideration of the π electrons alone. We are fully aware that the calculated reaction paths are valid only in the very intial stages of the cycloadditions. The σ electrons must be included to get full reaction paths. Also the neglect of the σ core makes the theory unreliable for the study of photodimerizations such as that of cyclopentenone,[32] where n → π* states could be involved. Again the low, often negative, interaction energies which are obtained by sole consideration of these π electrons clearly indicate that the major source of the activation energy lies in the rearrangement of the σ core. However, the primordial role of the π electrons in *guiding* concerted reactions is apparent from their importance in determining the selection rules for permissible reactions.[33]

With these facts in mind, it is still quite remarkable that the theory can account quantitatively for the nature of the stable cycloadducts in the dimerizations of such complicated systems as unsaturated keto steroids.

Acknowledgments. The authors wish to thank Mr. C. Deniau for kind help with the photographs, and the Quantum Chemistry Program Exchange for providing the molecular SCF program.

---

(32) (a) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962); (b) P. E. Eaton and W. S. Hurst, *ibid.*, **88**, 5038 (1966).

(33) (a) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (b) G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

The Cyclotrimerization of 2-Butyne-1,1,1-d_3 by Transition Metal Catalysts[1]

George M. Whitesides and William J. Ehmann[2]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received November 27, 1968

Abstract: The observation that 1,2,3-trimethyl-4,5,6-tri(methyl-d_3)benzene (**6**) is not a product of the cyclotrimerization of 2-butyne-1,1,1-d_3 (**4**) using a metallic catalyst is sufficient evidence to establish that the activity of the catalyst does not depend on the generation of free or metal-complexed tetramethylcyclobutadiene-d_6 as a reaction intermediate. The relative yield of **6** in the mixtures of the three hexamethylbenzene-d_9 isomers, **6**, 1,2,4-trimethyl-3,5,6-tri(methyl-d_3)benzene (**7**), and 1,3,5-trimethyl-2,4,6-tri(methyl-d_3)benzene (**8**), obtained on catalytic cyclotrimerization of **4** is conveniently established by degradation of the mixture of deuterated 3-methylpentane-2,4-diones (**12**), using a reaction sequence which does not interchange methyl groups, followed by mass spectrometric examination of the deuterium distribution in these materials. Application of this degradation to the hexamethylbenzene-d_9 isomers obtained on cyclotrimerization of **4** using triphenyltris(tetrahydrofuran)chromium(III), dimesitylcobalt(II), dicobalt octacarbonyl, bis(acrylonitrile)nickel(0), and a titanium tetrachloride–triisobutylaluminum Ziegler catalyst has demonstrated that **6** is not a product of these reactions, and consequently that these cyclizations do *not* take place through tetramethylcyclobutadiene intermediates. The relative yield of **6** produced from **4** using aluminum trichloride as catalyst (~12%) is consistent with the intervention of an intermediate of cyclobutadiene-like symmetry during the cyclization. The yield of **6** produced using dichlorobis(benzonitrile)palladium(II) (~9.5%) is intermediate between these two extremes.

The cyclotrimerization of disubstituted acetylenes to derivatives of benzene by transition metal catalysts is one of the simplest of a number of important organic syntheses that utilize metallic reagents to polymerize or cyclooligomerize olefins and acetylenes.[3,4] As such,

---

(1) Supported in part by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G691, and by Eli Lilly and Co.

(2) National Science Foundation Trainee, 1965–1966; National Institutes of Health Predoctoral Fellow, 1966–1969.

(3) Reviews: F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, *A*, 3 227 (1968); P. M. Maitlis, *Advan. Organometal. Chem.*, **4**,