

Intermolecular Orbital Theory of the Interaction between Conjugated Systems. II. Thermal and Photochemical Cycloadditions¹

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Abstract: The expressions of part I allow one to establish the important molecular orbital interactions for both thermal and photochemical cycloadditions between conjugated molecules. It is possible to draw a "theoretical" pathway for a given reaction. Many such reaction paths are drawn. It is also possible to determine the magnitude of the π -electron stabilization energy, and whether the bonds close in a concerted fashion or in two steps. Detailed examples are given for the thermal and photochemical dimerization of butadiene. The existence of a butadiene excimer, in which the two central bonds interact, is predicted. The Diels-Alder addition is also studied in detail; in particular the Woodward-Katz hypothesis on its asymmetric but "concerted" nature is substantiated. The existence of a low, secondary, activation energy, makes for a "retarded one-step" reaction. The Diels-Alder *endo* effect is assessed in a somewhat different manner from that of Hoffmann and Woodward; for Diels-Alder dimerizations, a symmetric transition state is postulated in which the condensation can operate at two distinct, but equally possible, places. The Hoffmann-Woodward selection rules are also substantiated on a quantitative basis. The photodimerization of tropone is treated in connection with these selection rules. Finally a discussion emphasizes the weaknesses and potentialities of the theory. The method is simple enough to allow rapid application to large systems. Its major asset appears to be the possibility of "testing," without elaborate calculations, a reaction between two (not too highly polar) conjugated systems by its π reaction surface and reaction paths.

In this paper we apply the equations of part I² successively to the study of various thermal and photochemical cycloadditions: first the dimerization of butadiene, with one case treated as a detailed example; then the Diels-Alder reaction, together with the *endo-exo* effect; next a mathematical demonstration of the Hoffmann-Woodward rules and a study of the conditions of their validity; and finally a study of tropone photodimerization. In each case we shall calculate the π -electron energy of interaction, realizing full well that this energy can only give an *indication* of whether a reaction is possible or not, because at some point important σ -energy changes in the separate molecules, due to bond extension or bond compression, will come into play.

For photochemical reactions, there are two further important restrictions. (1) We assume that the degradation of the excitation energy does not occur during the first, " π " stage of the reaction. (2) When evaluating whether a given reaction is a *concerted* rather than a *two-step* reaction, we will be thinking of reactions in excited singlet states only. In triplet states, spin requirements generally force the reaction to occur in two steps. Hence the observed dimerization in sensitized reactions often corresponds to a far less favorable pathway (two-step) than that which could hold if the reaction could take place in a concerted fashion.

Thermal and Photochemical Dimerization of Butadiene

Let us consider the four possible cycloadditions I, II, III, and IV of two butadiene molecules as schematized in Figure 1. (The Diels-Alder cycloaddition will be treated in the next section.) The dotted lines indicate pairs of interacting atoms. As an example we shall first give details of the calculation for reaction I.

(1) Research supported in part by National Institutes of Health Grant GM-12343.

(2) L. Salem, *J. Am. Chem. Soc.*, **90**, 543 (1968).

As only starred-starred and unstarred-unstarred interactions occur, the interaction energy in configuration I of two *ground-state* molecules is given by (24a) of part I.² Therefore

$$E_{\text{int}} = -2(\eta_{11'}S_{11'} + \eta_{22'}S_{22'}) + 4 \left\{ \frac{[(0.362)^2\eta_{11'} - (0.602)^2\eta_{22'}]^2}{3.236\beta} + \frac{2[0.362 \times 0.602(\eta_{11'} - \eta_{22'})]^2}{2.236\beta} + \frac{[(0.602)^2\eta_{11'} - (0.362)^2\eta_{22'}]^2}{1.236\beta} \right\} = -2(\eta_{11'}S_{11'} + \eta_{22'}S_{22'}) + \frac{1}{\beta} (0.628\eta_{11'}^2 + 0.404\eta_{22'}^2 - 0.808\eta_{11'}\eta_{22'}) \quad (1)$$

At the outset we see that the second-order effect in η^2/β , which should compensate partially the "closed-shell" repulsive term $-2(\eta_{11'}S_{11'} + \eta_{22'}S_{22'})$, contains a large *repulsive* cross term $-0.808\eta_{11'}\eta_{22'}/\beta$. Hence such a thermal dimerization should be energetically highly unfavorable. If we assume the proportionality relation (6) of part I, E_{int} becomes

$$E_{\text{int}}/\beta = -2(kS_{11'}^2 + kS_{22'}^2) + 0.628k^2S_{11'}^2 + 0.404k^2S_{22'}^2 - 0.808k^2S_{11'}S_{22'} \quad (2)$$

which, for $k \approx 3$ (see part I, eq 32) gives

$$E_{\text{int}}/\beta = -0.35S_{11'}^2 - 2.36S_{22'}^2 - 7.27S_{11'}S_{22'} \quad (2)$$

Whatever the respective values of the two overlaps $S_{11'}$ and $S_{22'}$, the interaction energy is repulsive (β is a negative quantity).

Let us now calculate the energy for a photochemical reaction in which one butadiene molecule is excited, an electron having jumped from the top bonding to lowest

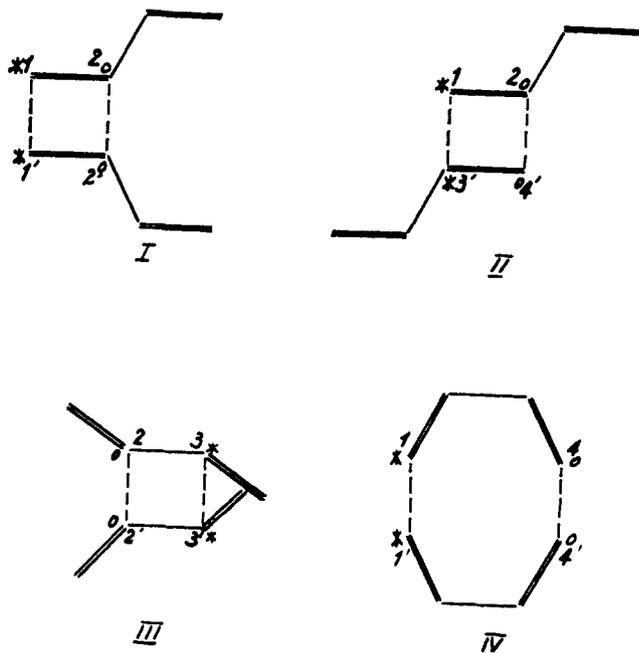


Figure 1. Configurations of interaction for two butadiene molecules.

antibonding orbital (in a molecule like butadiene where these two orbitals are well separated from the rest, this p state is certainly the lowest energy state for each spin multiplicity, singlet or triplet). Using (26a) of part I we obtain a change in interaction energy due to excitation.

$$\Delta E_{\text{int}} = +(0.724\eta_{11'} + 0.276\eta_{22'}) + \frac{1}{\beta} (-0.156\eta_{11'}^2 + 0.025\eta_{22'}^2 + 0.452\eta_{11'}\eta_{22'}) \quad (3)$$

In (3) two major effects are noticeable: a large, attractive first-order term, particularly favorable along the 11' coordinate (the factor of $\eta_{11'}$ is more than twice as large as that of $\eta_{22'}$), and a significant attractive second-order cross-term in $\eta_{11'}\eta_{22'}$ which should compensate part of the corresponding repulsion in the initial interaction energy. With $k = 3$ again (this value will be used henceforth), (3) and (2) give, for the interaction energy E_{int}^* in the photochemical interaction

$$E_{\text{int}}^*/\beta = 2.17S_{11'} + 0.83S_{22'} - 1.75S_{11'}^2 - 2.14S_{22'}^2 - 3.20S_{11'}S_{22'} \quad (4)$$

Equation 4 can be considered as the equation of a "reaction surface" in which the energy would be plotted, not in terms of some normal displacement coordinates, but in terms of the various atomic overlaps, themselves a function of distance. If we assume a unitary overlap increase

$$S = aS_{11'} + \sqrt{1 - a^2}S_{22'} \quad (5)$$

we can calculate the change in energy for any value of a . For reactants of zero relative velocity, the reaction path will coincide with the energy curve of greatest slope

$$\frac{1dE}{Sda} = 0 = \frac{\partial E}{\partial S_{11'}} - \frac{a}{\sqrt{1 - a^2}} \frac{\partial E}{\partial S_{22'}} \quad (6)$$

where we have used the unitary property of the ($S_{11'}$,

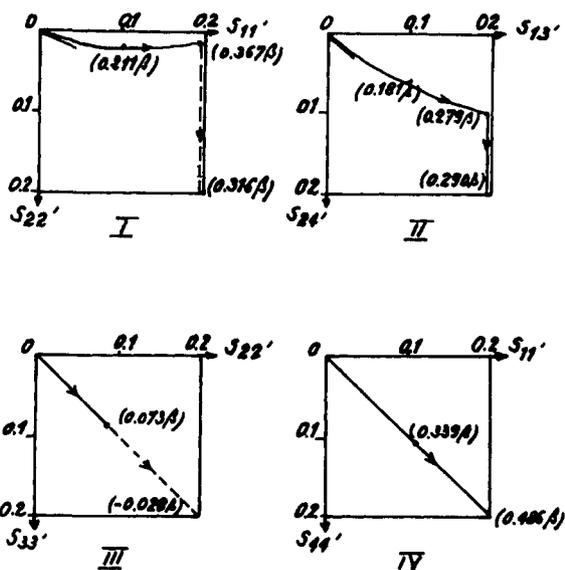


Figure 2. Reaction paths for butadiene photodimerizations. Dotted paths require activation energy.

$S_{22'}$) matrix, whence

$$\frac{a}{\sqrt{1 - a^2}} \left(= \frac{S_{11'}}{S_{22'}} \right) = \frac{\partial E/\partial S_{11'}}{\partial E/\partial S_{22'}}$$

The reaction path, under these assumptions, is given by

$$\frac{S_{11'}}{S_{22'}} = \frac{\partial E/\partial S_{11'}}{\partial E/\partial S_{22'}} \quad (7)$$

Such a path is drawn in Figure 2 for the photochemical reaction (I)

$$\frac{S_{11'}}{S_{22'}} = \frac{2.17 - 3.50S_{11'} - 3.20S_{22'}}{0.83 - 4.28S_{22'} - 3.20S_{11'}} \quad (8)$$

The plot is restricted to values of the overlap from 0 to 0.2. For our purposes a new bond will be considered established when the overlap reaches the value 0.2.

At very large distances, the path is such that the ratio of the overlaps $S_{11'}$ and $S_{22'}$ is equal to the ratio of the coefficients of the linear terms in (4), 2.17/0.83. Then, as the molecules get closer, the second-order effects come into play; here they reinforce the first-order asymmetry: the second-order repulsion is larger for the 22' interaction, just as the first-order attraction was weaker. As a result, the overlap $S_{22'}$ never becomes larger than 0.025. For $S_{11'} = 0.2$, $S_{22'}$ is equal to 0.016. Therefore, the π -electron interaction energy will be lowest if the cycloaddition starts by an almost pure 11' bond closure. The over-all stabilization for $S_{11'} = 0.2$ and $S_{22'} = 0.016$ is $E_{\text{int}}^* = 0.367\beta = -25.6$ kcal/mole ($\beta_{\text{spectroscopic}} = -3$ eV). The reaction is concerted only in a restricted sense; there is a small π activation energy (dotted path) between this intermediate asymmetric configuration and the symmetric configuration ($S_{11'} = 0.2$, $S_{22'} = 0.2$) in which both bonds are "closed" and for which $E_{\text{int}}^*(\text{symmetric}) = 0.316\beta = -22$ kcal/mole. Our prediction that the 11' bond should close first is in agreement, at least for radical reactions, with predictions based on classical chemical structures.⁸

(3) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc. New York, N. Y., 1965, pp 216-217.

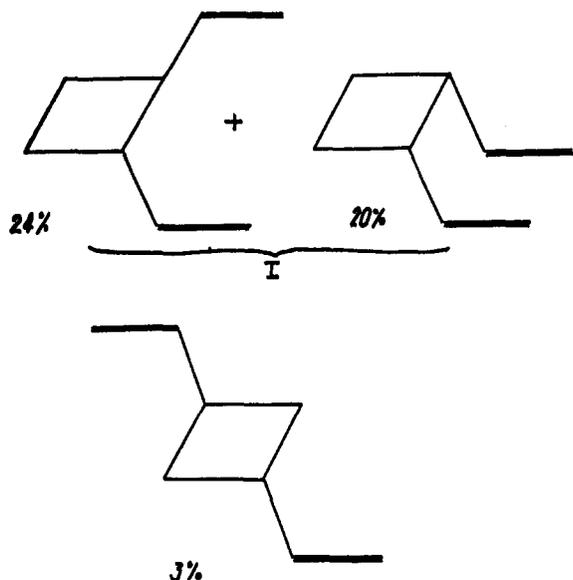


Figure 3.

But here we do not need to invoke the stabilization of some intermediate unit.

Similar calculations can be effected for reactions II, III, and IV. The results are shown in eq 9–11. With

$$\text{II} \left\{ \begin{array}{l} E_{\text{int}} = -2(\eta_{13'}S_{13'} + \eta_{24'}S_{24'}) + \\ \quad \frac{1}{\beta} (0.492\eta_{13'}^2 + 0.492\eta_{24'}^2 - 0.808\eta_{13'}\eta_{24'}) \\ \Delta E_{\text{int}} = 0.448(\eta_{13'} + \eta_{24'}) + \\ \quad \frac{1}{\beta} (0.064\eta_{13'}^2 - 0.060\eta_{24'}^2 + 0.452\eta_{13'}\eta_{24'}) \end{array} \right. \quad \text{(unprimed molecule excited)} \quad (9)$$

$$\text{III} \left\{ \begin{array}{l} E_{\text{int}} = -2(\eta_{22'}S_{22'} + \eta_{33'}S_{33'}) + \\ \quad \frac{1}{\beta} (0.404\eta_{22'}^2 + 0.404\eta_{33'}^2 - 0.088\eta_{22'}\eta_{33'}) \\ \Delta E_{\text{int}} = 0.276(\eta_{22'} + \eta_{33'}) + \\ \quad \frac{1}{\beta} (0.025\eta_{22'}^2 + 0.025\eta_{33'}^2 - 0.498\eta_{22'}\eta_{33'}) \end{array} \right. \quad (10)$$

$$\text{IV} \left\{ \begin{array}{l} E_{\text{int}} = -2(\eta_{11'}S_{11'} + \eta_{44'}S_{44'}) + \\ \quad \frac{1}{\beta} (0.628\eta_{11'}^2 + 0.628\eta_{44'}^2 - 0.536\eta_{11'}\eta_{44'}) \\ \Delta E_{\text{int}} = 0.724(\eta_{11'} + \eta_{44'}) + \\ \quad \frac{1}{\beta} (-0.156\eta_{11'}^2 - 0.156\eta_{44'}^2 - 0.136\eta_{11'}\eta_{44'}) \end{array} \right. \quad (11)$$

$k = 3$, the interaction energies in ground and excited states are then respectively, those shown in eq 12–14.

$$\text{II} \left\{ \begin{array}{l} E_{\text{int}}/\beta = -1.50(S_{13'}^2 + S_{24'}^2) - 7.27S_{13'}S_{24'} \\ E_{\text{int}}^*/\beta = 1.34(S_{13'} + S_{24'}) - \\ \quad 0.92S_{13'}^2 - 2.04S_{24'}^2 - 3.20S_{13'}S_{24'} \end{array} \right. \quad \text{(unprimed molecule excited)} \quad (12)$$

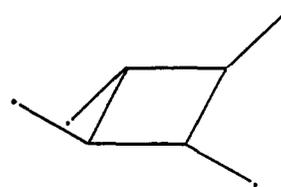


Figure 4.

$$\text{III} \left\{ \begin{array}{l} E_{\text{int}}/\beta = -2.36(S_{22'}^2 + S_{33'}^2) - 0.79S_{22'}S_{33'} \\ E_{\text{int}}^*/\beta = 0.83(S_{22'} + S_{33'}) - \\ \quad 2.14(S_{22'}^2 + S_{33'}^2) - 5.27S_{22'}S_{33'} \end{array} \right. \quad (13)$$

$$\text{IV} \left\{ \begin{array}{l} E_{\text{int}}/\beta = -0.35(S_{11'}^2 + S_{44'}^2) - 4.82S_{11'}S_{44'} \\ E_{\text{int}}^*/\beta = 2.17(S_{11'} + S_{44'}) - \\ \quad 1.75(S_{11'}^2 + S_{44'}^2) - 6.05S_{11'}S_{44'} \end{array} \right. \quad (14)$$

We see that all three reactions are *repulsive* in the ground state, *i.e.*, all three cycloadditions are unfavorable thermally. When one molecule is excited, however, the presence of an attractive term, linear in the overlap, makes the interaction more favorable. The most favorable reaction paths are then shown in Figure 2. Each interaction shows a different behavior.

Interaction II proceeds in a truly concerted, though asymmetric fashion. Both bonds close at the same time, the bond 13' closing faster. When bond 13' is formed, no activation energy is required to terminate the closure of the second bond 24'. The asymmetric bond closure is curious in view of the apparent total symmetry of the configuration (Figure 1). This asymmetry is introduced by the excitation of one molecule. It appears only in the second-order terms so that the cycloaddition starts off symmetrically. The stabilization energy obtained along the reaction path, $E_{\text{int}}^{11*} = 0.279\beta = -19.6$ kcal/mole, is somewhat smaller (6 kcal/mole) than that obtained in the first step of reaction I. This may explain the relative proportions⁴ of I and II in the direct photodimerization of butadiene without sensitizers (Figure 3).

Interaction III proceeds symmetrically but, due to the relatively small attractive terms and large second-order repulsive term, quickly reaches an energy minimum for $S_{22'} = S_{33'} = 0.087$. The corresponding distance (part I, Figure 2), $R = 3.4$ Å, is still large and the molecules are not close enough for any rehybridization to be effective. Hence no cycloaddition will occur, in agreement with "classical" chemistry which shows (Figure 4) that the end product would be a multiradical. However, two butadiene molecules, one of which is excited, may well form a *weakly bound* (stabilization energy, 5 kcal/mole) *excimer* (Figure 5), if they interact through their central bonds.

Interaction IV, finally, leads to a highly favored (symmetric) reaction; the stabilization energy for $S_{11'} = S_{44'} = 0.2$ is $E_{\text{int}}^{1V*} = 0.486\beta = -34$ kcal/mole. Although the low concentration of *cis* relative to *trans* isomers and the difficulty of *trans-cis* isomerization in the excited state make the direct encounter of a *cis*-butadiene with another, excited, *cis*-butadiene rather

(4) N. J. Turro, private communication. The difference in stabilization energies is even larger (0.374β vs. 0.231β) if the reactions occur *via* a triplet state in two totally distinct steps, the first step being a 11' (case I) or 13' (case II) bond closure.

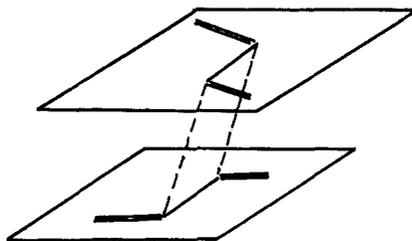


Figure 5. Proposed excimer structure for butadiene.

improbable, sufficient encounters should occur for some cyclooctadiene to be formed. Experimentally, it has not yet been possible to analyze all the products in the *direct* photodimerization of butadiene. Whether cyclooctadiene is present or not will be an important test of the predictive power of the theory. (Cyclooctadienes are obtained in the photodimerization of isoprene^{5a} but the mechanism of their formation is not clear.) Cyclopentadiene in the *singlet* state should also dimerize to a tricyclooctadiene. Unfortunately the lifetime of the singlet state of cyclopentadiene seems limited by intramolecular conversion to the homocyclobutadiene.⁶

Most experiments on the photodimerization of butadienes^{3,5} use *triplet* sensitizers, so the products need not be those predicted from the best one-step mechanism. In fact, the photosensitized dimerization of butadiene yields products corresponding to the two-step mechanisms I and VIa (photochemical Diels–Alder; see next section). Similarly the photosensitized dimerization of cyclopentadiene leads⁷ to the two-step products corresponding to I and VIa.

Diels–Alder Addition

Figure 6 shows four different Diels–Alder interactions: ethylene and butadiene with *cis*-butadiene (V and VI), and acrolein with *cis*-acrolein (two possibilities, VII and VIII). Calculations similar to the previous ones yield the interaction energies shown in eq 15. (For the last two results, (15a) of part I has

$$\begin{aligned}
 E_{\text{int}}^{\text{V}} &= -2(\eta_{11'}S_{11'} + \eta_{42'}S_{42'}) + \\
 &\quad \frac{1}{\beta}(0.554\eta_{11'}^2 + 0.554\eta_{42'}^2 + 0.684\eta_{11'}\eta_{42'}) \\
 E_{\text{int}}^{\text{VI}} &= -2(\eta_{11'}S_{11'} + \eta_{42'}S_{42'}) + \\
 &\quad \frac{1}{\beta}(0.628\eta_{11'}^2 + 0.492\eta_{42'}^2 + 0.628\eta_{11'}\eta_{42'}) \\
 E_{\text{int}}^{\text{VII}} &= -1.542\eta_{11'}S_{11'} - 2.563\eta_{42'}S_{42'} + \\
 &\quad \frac{1}{\beta}(0.574\eta_{11'}^2 + 0.408\eta_{42'}^2 + 0.470\eta_{11'}\eta_{42'}) \\
 E_{\text{int}}^{\text{VIII}} &= -1.805\eta_{12'}S_{12'} - 2.300\eta_{41'}S_{41'} + \\
 &\quad \frac{1}{\beta}(0.506\eta_{12'}^2 + 0.588\eta_{41'}^2 + 0.568\eta_{12'}\eta_{41'}) \quad (15)
 \end{aligned}$$

been used instead of (24a). The Hückel calculations on acrolein use $\Delta\alpha_4 = \beta$ and the results of Coulson and

(5) (a) G. S. Hammond and R. S. H. Liu, *J. Am. Chem. Soc.*, **85**, 477 (1963). No cyclooctadienes are obtained in the solid, where the lattice stereochemistry controls the photodimerization: M. Lahav and G. M. J. Schmidt, "Studies in Topochemistry. XXIII," to be published. (b) G. S. Hammond, N. J. Turro, and A. Fischer, *ibid.*, **83**, 4674 (1961); etc.

(6) J. I. Braumen, L. E. Ellis, and E. E. van Tamelen, *ibid.*, **88**, 846 (1966).

(7) N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962).

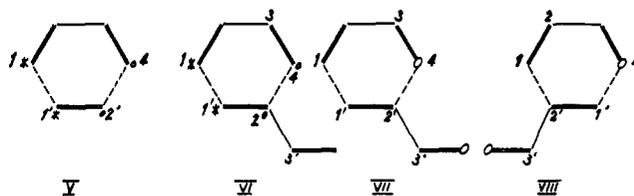


Figure 6. Various Diels–Alder additions.

Streitwieser.⁸) Comparison with the results, eq 1, 9 10, 11, for the thermal reactions I–IV, shows one major change: the cross term involving simultaneously both bond overlaps is now attractive instead of repulsive. This is due to the favorable "second-order" interaction between occupied orbitals on one side and unoccupied orbitals on the other. In consequence, a simultaneous bond closure is now possible thermally. Numerically, with $k = 3$

$$\begin{aligned}
 E_{\text{int}}^{\text{V}}/\beta &= -1.01(S_{11'}^2 + S_{42'}^2) + 6.16S_{11'}S_{42'} \\
 E_{\text{int}}^{\text{VI}}/\beta &= -1.35S_{11'}^2 - 1.50S_{42'}^2 + 5.65S_{11'}S_{42'} \quad (16)
 \end{aligned}$$

$$E_{\text{int}}^{\text{VII}}/\beta = 0.64S_{11'}^2 - 4.02S_{42'}^2 + 4.23S_{11'}S_{42'}$$

$$E_{\text{int}}^{\text{VIII}}/\beta = -0.86S_{12'}^2 - 1.61S_{41'}^2 + 5.20S_{12'}S_{41'}$$

The calculated reaction paths are shown in Figure 7. Their main features are that (1) they are straight lines, indicating that the bonds close in such a manner that the overlaps keep a constant ratio. In all cases the bonds should close at the *same time but not*, except in the highly symmetric reaction V where ethylene is used as the dienophile, *at the same rate*. This asymmetry is most pronounced in configuration VII which leads to the observed dimerization of acrolein. For this very reaction Woodward and Katz made the hypothesis⁹ that the Diels–Alder reaction is *concerted*, but the rate-determining step is the closure of bond 11', while the other bond lags behind. That the reaction occurs asymmetrically is no surprise since configuration VII certainly has no symmetry in it. However, Woodward and Katz' contention that the reaction, although asymmetric, is still *concerted*, is entirely verified in the sense in which they use the word "concerted." (a) The two bonds are being formed *simultaneously*, "even though there may be considerable asymmetry in the rate at which...they are established."¹⁰ (b) "Certainly it is a two-stage mechanism, in that the formation of two bonds takes place in separable, even if overlapping, processes, discretely delineated in structural terms, and displaced in time. *It is entirely possible, indeed likely, that a second, low barrier will be involved in some specific cases, and not in others.*"^{9,11} Reaction paths VII and VI behave according to these rules, one with a slight secondary barrier and the other without.

Purely in terms of definition, there arises the question¹² of whether such a reaction should not be called "two-step" rather than "concerted" or "two-stage." Granted that the behavior of the reaction is precisely that

(8) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π Electron Calculations," Pergamon Press, Oxford, 1965, p 227.

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

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

(11) This author's italics.

(12) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **83**, 4947 (1961).

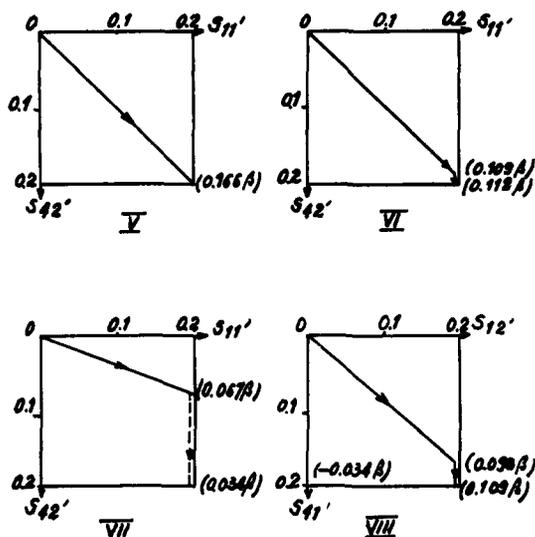


Figure 7. Reaction paths for (*exo*) Diels-Alder additions. Dotted paths require activation energy.

predicted by Woodward and Katz, the question of denomination is itself an important one. Calculated pathways appear to fall into three distinct categories: pathways V, VI, or II (simultaneous, symmetric, or asymmetric bond closure; no secondary activation energy); pathways VII or I (simultaneous, asymmetric bond closure; *small* secondary activation energy of the order of a few kilocalories/mole); pathway VIa. The latter occurs (Figure 8) for the photochemical Diels-Alder dimerization of butadiene, where the interaction energy has the form

$$(E_{\text{int}}^{\text{VI}})^* = -|0.724\eta_{11'} - 0.448\eta_{42'}| - 2(\eta_{11'}S_{11'} + \eta_{42'}S_{42'}) + \frac{1}{\beta}(0.466\eta_{11'}^2 + 0.492\eta_{42'}^2 - 0.104\eta_{11'}\eta_{42'}) \text{ (diene excited)}$$

$$(E_{\text{int}}^{\text{VI}})^*/\beta = |2.17S_{11'} - 1.34S_{42'}| - 1.81S_{11'}^2 - 1.50S_{42'}^2 + 0.936S_{11'}S_{42'} \quad (17)$$

Here the opposite sign in the linear terms should compel the bonds to close one at a time, with a *large* activation energy (~ 20 kcal/mole) for formation of the second bond.¹³ Clearly pathway VII is intermediate in this respect between V or II (true one-step) and VIa (true two-step). A good denomination might be "*retarded one-step*" or "*quasi-concerted*."

(2) The π stabilization energies are rather weak, -7.6 kcal/mole for VI and -4.5 kcal/mole for VII, and do not seem to account for the experimental readiness of these reactions. Furthermore *relative* stabilization energies appear to be in the wrong direction; V is predicted more stable than VI by $0.057\beta = -4$ kcal/mole, whereas the experimental activation energies differ by 3.8 kcal/mole in the opposite direction.¹⁴ Similarly VIII seems to be favored relative to VII, whereas only VII occurs experimentally!

(13) The best pathway would actually correspond to a *negative* overlap for one of the two bonds as the other bond is formed. Note also that, whereas for bond closure of $42'$ (after $11'$ is established) the energy increases continuously until $S_{42'} = 0.2$, for bond closure of $11'$ (if $42'$ is established first) there is a hump at $S_{11'} = 0.123$ after which the energy decreases again. See also footnote 29.

(14) A. Wasserman "Diels-Alder Reactions," Elsevier Publishing Co., New York, N. Y., 1965, Table 13.

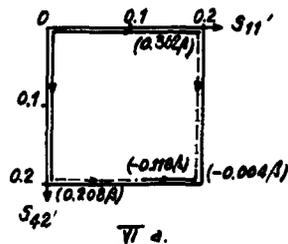


Figure 8. Pathways for photochemical Diels-Alder dimerization of butadiene. Dotted paths require activation energy.

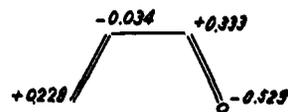


Figure 9. Hückel net charge densities in acrolein.

Most of the discrepancies will be accounted for in the next section in the study of the *endo* effect. However, one point must be made concerning the competition between reactions VII and VIII. Clearly as Woodward and Katz remarked, product VIII would be favored if the reaction occurred in one step and symmetrically. However, a glance at the charge distribution in acrolein (Figure 9) shows that such an approach is extremely unlikely for configuration VIII. The difference in Coulombic interaction between atoms $4,1'$ ($-0.120/R$ au) and $1,2'$ ($-0.008/R$ au) is so enormous (nearly 10 kcal/mole at 4 \AA) that automatically bond $4,1'$ will tend to close first. But this leads to a repulsive π energy, as shown in Figure 7 for pathway VIII ($S_{41'} = 0.2$; $E_{\text{int}} = -0.034\beta$). In configuration VII, on the other hand, the electrostatic effects ($11'$, $0.052/R$ au; $42'$, $0.018/R$ au) are better balanced; at 4 \AA the difference is less than 3 kcal/mole. So it seems possible that the reaction can set out in the manner determined by the best overlap interaction, independently of electrostatic interactions.

The *endo* Mechanism

In the preceding section we pointed out that the second-order energy stabilization due to the mixing of orbitals of different energy rendered the Diels-Alder reaction feasible. More precisely one can draw out the constructive interaction between the bonding orbital $(1/\sqrt{2})(\phi_1 + \phi_2)$ of ethylene and the lowest antibonding orbital $0.602(\phi_1 + \phi_4) - 0.362(\phi_2 + \phi_3)$ of butadiene, on the one hand, and between the bonding orbital $0.602\phi_1 - \phi_4) + 0.362(\phi_2 - \phi_3)$ of butadiene and the antibonding orbital $(1/\sqrt{2})(\phi_1 - \phi_2)$ on the other hand. For nonalternants the size effect (part I,² last section), due to the mixing between occupied orbitals, can also help the reaction (witness the low coefficient of $\eta_{11'}S_{11'}$ in $E_{\text{VII}}^{\text{int}}$, eq 15). But the second-order mixing between occupied and unoccupied levels seems to be the predominant factor in explaining the behavior of the Diels-Alder reaction. This was first pointed out, it seems, by Fukui.¹⁵

(15) K. Fukui in "Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p 513 (in particular Figure 8).

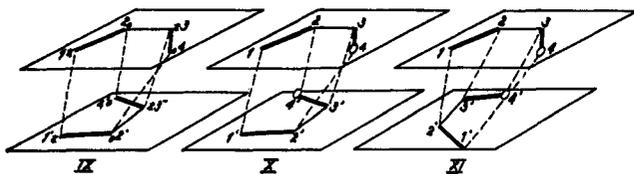


Figure 10. Configurations for Diels-Alder *endo* additions ("diene" is above; cf. Figure 6).

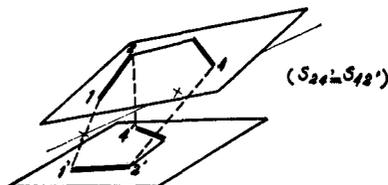


Figure 11. Postulated *endo* transition state for Diels-Alder condensation of butadiene (light axis is axis of symmetry).

Hoffmann and Woodward have suggested¹⁶ that these second-order interactions are also responsible for the preference in Diels-Alder reactions for *endo*, rather than *exo*, additions. More precisely, the interaction between the " β " atom adjacent to the olefinic group of the dienophile (atom 3' in reactions VI, VII, and VIII) and a " β " atom of the diene (atom 3 in VI, VII; atom 2 in VIII) would be responsible for a large additional energy stabilization. This hypothesis was substantiated by extended Hückel calculations with maleic anhydride and *p*-benzoquinone as dienophiles.

In Figure 10 we show potential *endo* configurations of approach IX, X, XI for the Diels-Alder condensations of butadiene and acrolein considered previously. These configurations, in which the molecules lie on top of each other in roughly parallel planes orthogonal to the direction of the bonds to be formed, require the dienophile to have a bond *cis* to its reacting double bond (This is the case for familiar dienophiles like maleic anhydride or *p*-benzoquinone, but will require a little additional energy for butadiene or acrolein. Configuration X is similar to one proposed by Woodward and Katz for the acrolein condensation.⁹) In each configuration *two* additional atom-atom interactions operate: that postulated by Hoffmann and Woodward, and also the interaction between the atom next-nearest neighbor to the olefinic group and the remaining atom of the diene (interaction 24' in IX and X, 34' in XI).

The energy of each configuration now depends on *four* overlaps between pairs of p atomic orbitals. The calculation proceeds just as in the previous section, with the use of eq 15a and 24a of part I, but is somewhat lengthier in view of the greater number of interactions. With a certain amount of practice the calculation of the energy of interaction of a configuration such as X takes about 2 hr on a desk machine. As the number of π energy levels of the interacting systems increases, so does the computing time. The results are given in eq 18, where $E_{\text{int}}^{\text{VI}}$, $E_{\text{int}}^{\text{VII}}$, and $E_{\text{int}}^{\text{VIII}}$ are given by (15).

(16) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 4388 (1965).

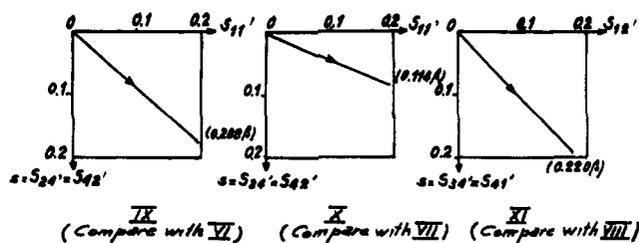


Figure 12. Reaction paths for Diels-Alder *endo* additions.

$$E_{\text{int}}^{\text{IX}} = E_{\text{int}}^{\text{VI}} - 2(\eta_{24'}S_{24'} + \eta_{33'}S_{33'}) + \frac{1}{\beta}(0.404\eta_{33'}^2 + 0.492\eta_{24'}^2 + \frac{0.628\eta_{11'}\eta_{24'}}{0.226\beta}) + 0.092\eta_{11'}\eta_{33'} + 0.092\eta_{24'}\eta_{42'} - 0.180\eta_{24'}\eta_{33'} - 0.180\eta_{33'}\eta_{42'}$$

$$E_{\text{int}}^{\text{X}} = E_{\text{int}}^{\text{VII}} - 1.334\eta_{33'}S_{33'} - 2.563\eta_{24'}S_{24'} + \frac{1}{\beta}(0.264\eta_{33'}^2 + 0.408\eta_{24'}^2 + \frac{0.470\eta_{11'}\eta_{24'}}{0.226\beta}) - 0.102\eta_{11'}\eta_{33'} + 0.036\eta_{24'}\eta_{42'} - 0.226\eta_{24'}\eta_{33'} - 0.226\eta_{33'}\eta_{42'}$$

$$E_{\text{int}}^{\text{XI}} = E_{\text{int}}^{\text{VIII}} - 1.701\eta_{23'}S_{23'} - 2.196\eta_{34'}S_{34'} + \frac{1}{\beta}(0.442\eta_{23'}^2 + 0.530\eta_{34'}^2 - 0.236\eta_{12'}\eta_{23'} + 0.190\eta_{12'}\eta_{34'} + \frac{0.372\eta_{34'}\eta_{41'}}{0.226\beta}) - 0.226\eta_{23'}\eta_{34'} + 0.134\eta_{23'}\eta_{41'} \quad (18)$$

A close examination of the energies $E_{\text{int}}^{\text{IX}}$ and $E_{\text{int}}^{\text{X}}$ shows that the terms due to the additional interactions are of two kinds: (1) square terms involving the new interactions 33' or 24' alone, a repulsive size effect, and an attractive second-order effect (the corresponding energy is always slightly repulsive; for instance, $-2 \cdot (\eta_{24'}S_{24'}) + 0.492(\eta_{24'}^2/\beta) = -1.50\beta S_{24'}^2$, for $k = 3\beta$); (2) cross terms involving simultaneously a new interaction (33' or 24') and one of the primary interactions (11' or 42') postulated in the simple configurations VI and VII. Among these, the cross terms involving bond 33' are *repulsive*, or negligible, and the *only large attractive cross term is that involving the secondary interaction 24'*; apparently, therefore, any additional stabilization proceeds from the novel interaction 24' rather than 33'.

Furthermore, the numerical terms involving the interactions 42' and 24' are *identical* in the expressions for $E_{\text{int}}^{\text{IX}}$ and $E_{\text{int}}^{\text{X}}$ (see (15) and (18)). Hence these interactions play identical roles, and it is possible to draw out a *symmetrical endo* configuration (Figure 11, with an axis of symmetry passing through the middle of "bonds" 11' and 33', in which "bonds" 24' and 42' are entirely equivalent. We therefore assume that, at least in the butadiene and acrolein condensations, the *endo* configuration involves the following three atom-atom interactions: 11' (between two terminal atoms) and 42' and 24' (equivalent interactions between second terminal atom on each molecule and atom adjacent to first terminal atom on the other molecule). The interaction 33', however, which Hoffmann and Woodward considered to be important, should be weak.

If we assume, then, that the overlaps $S_{24'}$ and $S_{42'}$ are equal to a common value s during the initial ap-

proach of the molecules, the interaction energies for IX and X become ($k = 3$)

$$E_{\text{int}}^{\text{IX}}/\beta = -1.35S_{11'}^2 - 2.10s^2 + 11.30S_{11'}s \quad (19)$$

$$E_{\text{int}}^{\text{X}}/\beta = 0.64S_{11'}^2 - 7.72s^2 + 8.46S_{11'}s$$

(compare with (16)). The calculated reaction paths are shown in Figure 12. Again, for configuration XI, the only new favorable cross terms involve the interaction 34' with the terminal atom of the "dienophile," rather than 23' which would correspond to the Hoffmann-Woodward hypothesis. Although no symmetry is present here, let us assume $S_{41'} = S_{34'} = s$ for simplicity. Then

$$E_{\text{int}}^{\text{XI}}/\beta = -0.86 S_{12'}^2 - 0.08s^2 + 6.91S_{12'}s \quad (19a)$$

The hypothetical reaction path (Figure 12) is still highly symmetrical.

The principal feature shown by the new pathways is the increase in stabilization energy. For two butadiene molecules, this stabilization energy is now

$$0.288\beta = -20.2 \text{ kcal/mole} \quad (20)$$

instead of $0.109\beta = -7.6$ kcal/mole. It is of the same order of magnitude as the π -stabilization energies computed by Herndon and Hall¹⁷ for various Diels-Alder reactions using Hoffmann's method. In the previous section we found a stabilization energy of

$$0.166\beta = -11.6 \text{ kcal/mole} \quad (21)$$

for the Diels-Alder condensation of butadiene with ethylene. The relative stabilization energies of these two reactions are now in the right order. Their difference of -8.6 kcal/mole compares nicely with the experimental difference in activation energies,¹⁴ -3.8 kcal/mole, once the ~ 2 -kcal/mole loss in the butadiene dimerization due to an additional *trans-cis* isomerization is included.

For the condensation of acrolein, reaction X, like reaction VII, is highly asymmetrical. Although the reaction path, once bond 11' is closed, cannot be described simply on our diagram (one overlap $S_{42'}$ or $S_{24'}$ will continue to increase while the other decreases), the reaction probably proceeds *via* a retarded one-step mechanism with a small secondary activation energy. However, we still cannot explain, other than by the electrostatic argument of the previous section, why reaction X (VII) is preferred to XI (VIII): the calculated stabilization energy for XI remains much larger than that for X.

Our main conclusion is that the *endo* preference in Diels-Alder condensations is generally due to the secondary interaction 24' between the next nearest atom to the olefinic site of the dienophile (atom α' in the Hoffmann-Woodward notation) and a central atom (β) of the diene. This should hold for the dimerization of butadiene, acrolein, cyclopentadiene,¹⁸ etc. For these basic reactions the interaction 33' ($\beta\beta'$) postulated by Hoffmann and Woodward does not seem to be important although it is true that the basic mecha-

(17) W. C. Herndon and L. H. Hall, *Theoret. Chim. Acta*, 7, 4 (1967).

(18) In the case of cyclopentadiene, Wasserman has drawn (ref 14, Figure 3) various "valence" structures for the transition state; our result corresponds to giving a large weight to his structures (B) and (E).

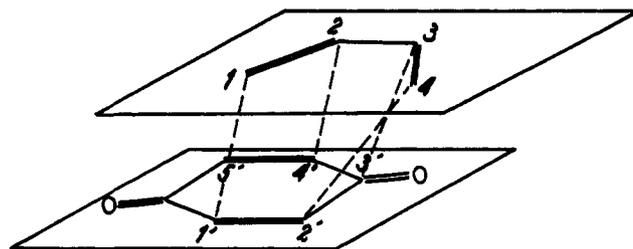


Figure 13. Butadiene + *p*-benzoquinone system.

nism which they suggested (mixing of occupied with unoccupied orbitals) seems correct. However, the important secondary interaction may well vary from one reaction to another. We have performed a calculation on the butadiene-*p*-benzoquinone system, which Hoffmann and Woodward used to establish their theory (XII, Figure 13). The total interaction energy is found to be

$$\begin{aligned} E_{\text{int}}^{\text{XII}} = & -2.083\eta_{11'}S_{11'} - 2.083\eta_{42'}S_{42'} - \\ & 1.993\eta_{33'}S_{33'} - 2.083\eta_{24'}S_{24'} + \frac{1}{\beta}(0.614\eta_{11'}^2 + \\ & 0.614\eta_{42'}^2 + 0.364\eta_{11'}\eta_{42'}) + \frac{1}{\beta}[0.450\eta_{33'}^2 + \\ & 0.454\eta_{24'}^2 + 0.180\eta_{33'}\eta_{11'} + 0.058\eta_{24'}\eta_{11'} - \\ & 0.012\eta_{33'}\eta_{42'} - 0.095\eta_{24'}\eta_{42'} - 0.124\eta_{33'}\eta_{24'}] \quad (22) \end{aligned}$$

where the terms in square brackets exist only in the *endo* configuration. Here the only significant favorable cross terms is that between $\eta_{11'}$ and $\eta_{33'}$, so that any *endo* stability must arise from the 33' rather than 24' interaction, in agreement with Hoffmann and Woodward's calculation. However, the size of the cross term ($0.180/\beta$) is significantly smaller than those operating in the previous *endo* interactions (eq 18, underlined terms) and the additional stabilization will also be smaller.¹⁹

The proposed *endo* configuration (Figure 11) has an interesting feature when diene and dienophile are indistinguishable. The configuration has an axis of symmetry and the condensation can operate at two distinct, but equally possible, places. Hence the cycloaddition can take place just as well in 11', 42' (our initial assumption when no *endo* interactions were assumed) as in 11', 24'. The molecules are thus in a position to "choose" between two equally probable cycloadditions. As shown in Figure 12 (X), bond 11' closes first, while bonds 24' and 42' are established partially, after which either bond 42' or bond 24' closes completely (while the third bond opens up again). Hence, in opposition to the entropy loss due to the highly ordered and rigid configuration of the *endo* transition state, there arises a statistical entropy gain, $S = R \log 2$. This entropy is small relative to the configurational entropy loss, but $-T\Delta S$ is almost enough to make up for the enthalpy of the additional *cis* isomerization required for the dienophile.

(19) The one large term coming from the interaction between top occupied diene orbital and lowest unoccupied dienophile orbital—the sole interaction considered by Hoffmann and Woodward—is partially cancelled out when all occupied orbital-unoccupied orbital interactions are included.

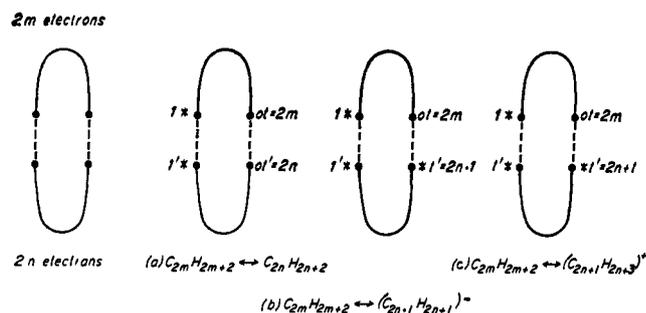


Figure 14. Interaction between two closed-shell linear conjugated systems.

Just recently Dewar has postulated²⁰ an *endo* configuration for Diels–Alder condensations similar to ours. He suggests that such a transition state would be highly favored because of its “aromatic character,” due to the presence of two “six-membered rings” (12’3’4’21 and 12342’1’). Our calculations lead independently to the same conclusion and further they provide information on the relative strengths of the bonds being formed.

The Hoffmann–Woodward Rules

By qualitative consideration of the mixing of the various π molecular orbitals of conjugated reactants in simple cycloadditions, cleverly guided by the relative position of the final π and σ orbitals in the products, Hoffman and Woodward established^{10,21} correlation diagrams showing the orbital energy variation as the reaction proceeded. These diagrams allowed them to demonstrate general rules, valid for concerted (*i.e.*, *one-step*, or *retarded one-step*) cycloadditions. In particular the condensation of two conjugated systems, one with $2m$ electrons and the other with $2n$ electrons, should occur thermally if $2m + 2n = 4q + 2$, and photochemically if $2m + 2n = 4q$. (We use the notation $2m$ and $2n$ rather than m and n like Woodward and Hoffmann, in order to keep with the notation of part I where ψ_m is the top bonding orbital.) They insisted that the rules did not “exclude multistep alternative mechanisms involving discrete intermediates” and that cycloadditions which apparently violated their rules “must proceed through multistep mechanisms.”

We shall now seek to establish these rules on a more quantitative basis. Thanks to the expressions for the interaction energy, it will not be necessary to consider the orbitals of the product or postulate any particular symmetric configuration of approach. On the contrary it will be easy to see what assumptions are involved and what possible exceptions might arise. Consider then two interacting *closed-shell* molecules, one with $2m$ electrons and the other with $2n$ electrons (Figure

(20) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1967); see also B. Eisler and A. Wasserman, *J. Chem. Soc.*, 979 (1953), who also propose such a transition state on the basis of kinetic studies.^{20a}

(20a) NOTE ADDED IN PROOF. The classical valence structure which resembles most our postulated *endo* transition state with two *cis*-butadienes and a strong 11’ bond is that of the *cis,cis*-octadiene-1,7,diyl 3,6-biradical. This biradical has precisely been proposed as the Diels–Alder addition intermediate by S. W. Benson, *J. Chem. Phys.*, **46**, 4920 (1967), on the basis of kinetic evidence.

(21) The alternative correlation diagram proposed by P. Millie, *Bull. Soc. Chim. France*, 4031 (1966), appears to be incorrect since it raises the lowest orbital of butadiene ($E = 1.618\beta$) and lowers the bonding orbital of ethylene ($E = \beta$) in their interaction, whereas precisely the opposite is expected from perturbation theory.

14). For the sake of simplicity we shall take alternant hydrocarbons; for systems with heteroatoms or non-alternants the results will be valid as long as the heteroatoms do not perturb the nodal properties of the various molecular orbitals. We will distinguish three cases, which are illustrated in Figure 14a–c.

Consider first (case a) the thermal addition of two neutral molecules with $2m$ and $2n$ atoms, respectively, to which we apply eq 24a of part I. The “second-order” contribution is a sum of many terms, but we may assume that the major contribution comes from the term with the smallest energy denominator²²

$$\frac{(b_1^* b_{1'}^* \eta_{11'} - b_1^{\circ} b_{1'}^{\circ} \eta_{11'})^2}{\epsilon_m + \epsilon_n} \quad (23)$$

where we have used the fact that if atom 1 is starred, atom t must be unstarred. The coefficients b have been defined in eq 25, part I. The numerator will be large, and the reaction favored, if the products $b_1 b_{1'}$ and $b_1^{\circ} b_{1'}^{\circ}$ have opposite signs. In linear polyenes atomic orbital coefficients on the end atoms are either equal or opposite, so that favorable possibilities are

$$\begin{cases} b_1 = b_{1'} \\ b_{1'} = -b_1 \end{cases} \quad \text{or} \quad \begin{cases} b_1 = -b_{1'} \\ b_{1'} = b_1 \end{cases} \quad (24)$$

The first possibility requires $2m$ to be equal to $4p + 2$ (p integer; *viz.*, ethylene, hexatriene) and $2n = 4p'$ (p' integer; *viz.*, butadiene), the second possibility $2m = 4p$, $2n = 4p' + 2$. Whence

$$2m + 2n = 4q + 2$$

Under this condition the presence of large, favorable cross terms between $\eta_{11'}$ and $\eta_{11''}$ allows the reaction to proceed in one step (direct or retarded). On the contrary, if $2m + 2n = 4q$, the numerator vanishes and no stabilization occurs.

Consider next (case b) the interaction between a neutral alternant and an odd polyene negative ion with $2n$ electrons but $2n - 1$ atoms. Such interactions occur in 1,3 dipolar cycloadditions. The ion has a nonbonding orbital, and expressions for even alternants are not valid here. One must return to eq 15a of part I and seek out the most important term.

The term with the smallest energy denominator is that which links the filled nonbonding orbital of the ion with the lowest antibonding orbital of the neutral molecule

$$-2 \frac{(b_1^* c_{1'}^* - b_1^{\circ} c_{1'}^{\circ})^2}{\epsilon_{m+1} - 0} \quad (25)$$

Here $c_{1'}$ and $c_{1'}^{\circ}$ denote the terminal coefficients of the nonbonding orbital. Favorable possibilities are then

$$\begin{cases} b_1 = b_{1'} \\ c_{1'} = -c_{1'}^{\circ} \end{cases} \quad \text{or} \quad \begin{cases} b_1 = -b_{1'} \\ c_{1'}^{\circ} = c_{1'} \end{cases} \quad (26)$$

Therefore $2m = 4p + 2$ and $2n = 4p'$ (*viz.*, allyl anion), or $2m = 4p$ and $2n = 4p' + 2$. Hence the condition $2m + 2n = 4q + 2$ still holds for the total number of electrons.

(22) Since this term comes from interactions between top occupied and bottom unoccupied orbitals, the procedure is entirely equivalent to Fukui’s frontier theory.

The calculation is quite similar for the interaction between a neutral alternant with $2m$ atoms and a positive ion with $2n + 1$ atoms (case c). Here the term with the smallest energy denominator involves the interaction between the top occupied orbital of the neutral species and the empty nonbonding orbital of the ion

$$\frac{(b_1^* c_{1'}^* + b_i^{\circ} c_{i'}^*)^2}{0 - \epsilon_m} \quad (27)$$

This term reaches large values if

$$\begin{cases} b_1 = b_i \\ c_{1'} = c_{i'} \end{cases} \quad \text{or} \quad \begin{cases} b_1 = -b_i \\ c_{1'} = -c_{i'} \end{cases} \quad (28)$$

Conditions 28 lead to $2m = 4p + 2$ and $2n = 4p'$ (viz., pentadienyl cation) or $2m = 4p$ and $2n = 4p' + 2$ (allyl cation). Again $2m + 2n = 4q + 2$.

Clearly then, *thermal reactions are strongly favored and occur in one step if the total number of electrons is $4q + 2$, forbidden if it is $4q$* . These conclusions agree with those of Hoffmann and Woodward and show that the total number of electrons, rather than atoms, is the important factor.

Let us now turn to photochemical reactions. For small molecules the lowest excited state corresponds generally to the transition from top occupied to lowest unoccupied orbital (the lowest singlet states of certain aromatics, like benzene and naphthalene, are exceptions). Equations 26 and 26a, part I, are therefore adequate for our purposes. Here it is important to distinguish whether or not the interacting molecules are identical.

For identical neutral molecules (Figure 14a) the behavior of the interaction energy when one molecule is excited is determined essentially by the linear term arising from the energy change due to the excitation (part I, eq 18 and Figure 4). If this linear term

$$-2 \left| \sum_{rr'} b_r^* b_{r'}^* \eta_{rr'} + \sum_{ss'} b_s^{\circ} b_{s'}^{\circ} \eta_{ss'} \right| \quad (29)$$

is large, a significant stabilization occurs, which more than compensates for the repulsion due to the mixing of occupied orbitals, and the reaction is favored. This requires $|b_1^* b_{1'}^* \eta_{11'} + b_i^{\circ} b_{i'}^{\circ} \eta_{ii'}|$ to be large; hence

$$\begin{cases} b_1 = b_i \\ b_{1'} = b_{i'} \end{cases} \quad \text{or} \quad \begin{cases} b_1 = -b_i \\ b_{1'} = b_{i'} \end{cases} \quad (30)$$

$$-2 \sum_{j'}^{\text{occ}} \frac{\left(\sum_{rr'} b_r^* c_{j'r'}^* \eta_{rr'} + \sum_{ss'} b_s^{\circ} c_{j's'}^{\circ} \eta_{ss'} \right)^2 + \left(\sum_{rs} b_r^* c_{j's}^{\circ} \eta_{rs'} + \sum_{s'r'} b_s^{\circ} c_{j'r'}^* \eta_{sr'} \right)^2}{\epsilon_m - \epsilon_{j'}} \quad (31)$$

These conditions lead to $2m + 2n = 4q$ ($m = n$). Under this condition the reaction will occur in one step (retarded or not) similarly to reactions I, II, and IV. At the start of the reaction the overlaps will be in the ratio $(\partial E / \partial S_{11'}) / (\partial E / \partial S_{ii'}) = b_1^* b_{1'}^* / b_i^{\circ} b_{i'}^{\circ}$. If $2m + 2n = 4q + 2$, the linear term vanishes, and chances are the reaction will not occur. To make sure, however, it is necessary to consider the second-order terms; the treatment is then similar to that for different molecules.

For different molecules, any significant energy stabilization comes from the term illustrated in (31) (see also part I, eq 26, and subsequent discussion). In part I

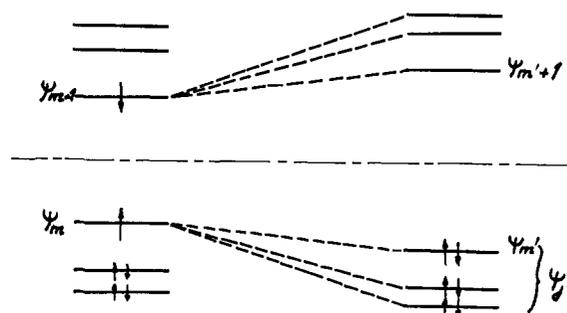


Figure 15. Orbital interactions leading to large energy stabilization for (excited molecule) \leftrightarrow (molecule) reactions.

we pointed out that this term arises from the mixing between ψ_m , the orbital having lost the excited electron, and the occupied orbitals on the other molecule, together with the mixing between ψ_{m+1} , the orbital with the excited electron and the unoccupied orbitals of the second molecule (Figure 15). Only occupied orbital indices occur in the summation because of the pairing property. It was also emphasized that the validity of this expression is strictly restricted to ψ_m (and ψ_{m+1}) being *well separated*²³ from the corresponding orbitals on the other molecule. Now the major contribution to (31) should come from the term $j' = m'$ (with coefficients $b_{r'}$). Indeed the top bonding orbital of the unexcited molecule interacts best with ψ_m to raise the energy of the hole, while an identical contribution comes from the mixing of $\psi_{m'+1}$ with ψ_{m+1} to lower the energy of the excited electron. For two neutral alternants (Figure 14a), a large stabilization requires therefore

$$|b_1^* b_{1'}^* \eta_{11'} + b_i^{\circ} b_{i'}^{\circ} \eta_{ii'}|$$

to be large. The required conditions are given again by (30) and the relation $2m + 2n = 4q$ still holds.

Consider next the photochemical cycloaddition of an excited negative ion and a neutral molecule (Figure 14b). (If the neutral molecule is excited, the excitation energy will probably decay rapidly onto the odd ion which, thanks to its nonbonding orbital, is the species with the lowest excitation energy.) The transition is from nonbonding orbital $\psi_{n'}$ to lowest antibonding orbital $\psi_{n'+1}$. Equation 21a of part I, in which we reverse prime and unprimed notations, gives the rele-

vant change in interaction energy

$$-\sum_{rr'} (c_{n'r'}^2 - c_{n'+1,r'}^2) \eta_{rr'} S_{rr'} + \sum_j \frac{\left(\sum_{rr'} c_{jr} c_{n'r'} \eta_{rr'} \right)^2}{\epsilon_j - 0} - \sum_j \frac{\left(\sum_{rr'} c_{jr} c_{n'+1,r'} \eta_{rr'} \right)^2}{\epsilon_j - \epsilon_{n'+1}}$$

The largest terms are difficult to select but are probably those for the interaction of the "hole" with the top

(23) By "well separated" we mean that $\epsilon_m - \epsilon_{j'}$ is large compared with the matrix element in the numerator (part I,² ref 20). It is difficult to give a definite lower limit for $|\epsilon_m - \epsilon_{j'}|$ but one should be wary of energy differences smaller than 0.3β .

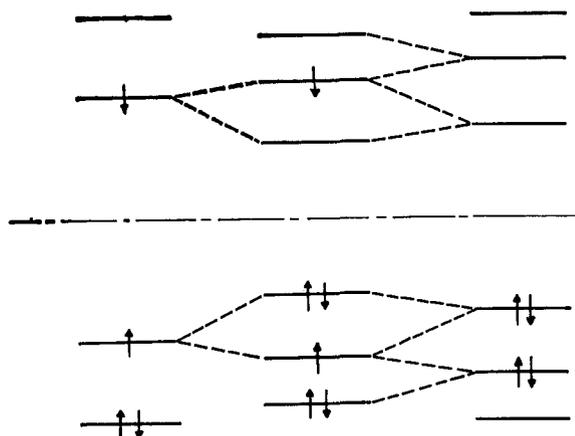


Figure 16. Unusual case where excitation is trapped in shorter chain.

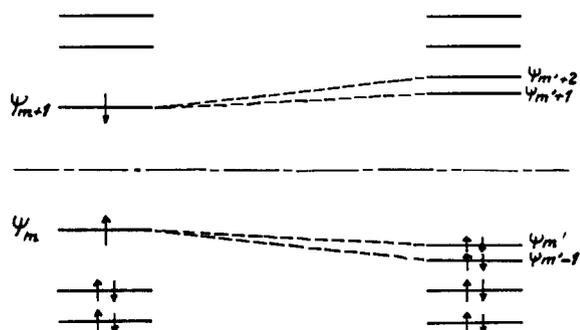


Figure 17. Unusual case where $4q$ and $(4q + 2)$ processes compete in photochemical cycloaddition.

bonding orbital ψ_m and lowest antibonding orbital ψ_{m+1} of the neutral alternant

$$\frac{(b_1^* c_{11}^* \eta_{11} + b_i^{\circ} c_{i1}^* \eta_{i1})^2}{\epsilon_m} - \frac{(b_1^* c_{11}^* \eta_{11} - b_i^{\circ} c_{i1}^* \eta_{i1})^2}{\epsilon_{m-1}} \quad (\epsilon_m < 0) \quad (32)$$

The first, negative term will be largest and the positive term will vanish if conditions (28) are satisfied. For an ion with $2n - 1$ atoms this gives $2m + 2n = 4q$ again. A similar result occurs for neutral plus excited positive ion. In both cases the selection rule may not be very stringent. These results should hold for nonalternants and systems with heteroatoms if the relevant orbitals have the same qualitative aspects (number of nodes, etc.). However the relative importance of the interactions $\psi_m \leftrightarrow \psi_{m'}$, and $\psi_{m+1} \leftrightarrow \psi_{m'+1}$ will now depend on which couple lies closer in energy.

The selection rules for photochemical cycloadditions are thus as follows. *Photochemical reactions are strongly favored and occur in one step if the total number of electrons is $4q$, forbidden if it is $4q + 2$.* Again the result coincides with the Hoffmann-Woodward rules.

For photochemical reactions there exists two particular situations for which the selection rules may be modified. (1) The excited system has a higher excitation energy than the molecule it interacts with. In our study of the interaction between different molecules, we assumed (Figure 5) that the excited molecule is that with the lowest excitation energy, *i.e.*, the longest chain. Generally this will be true be-

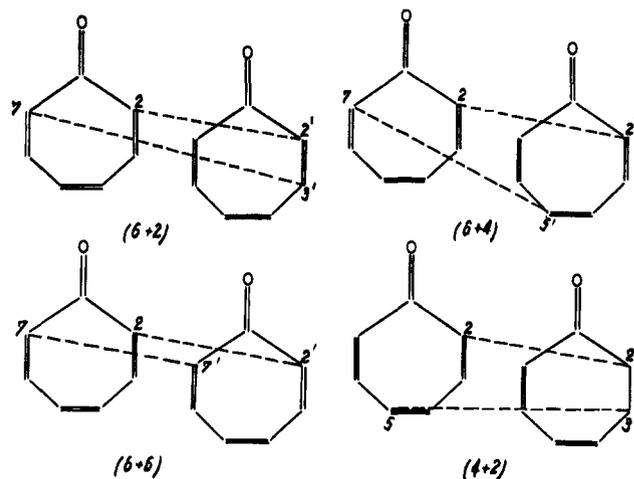


Figure 18. Photodimers of tropones.

cause excitation energy in the shorter chain can always be transferred, in principal, to the longer one. However, sometimes for singlets and *generally for triplets*, this transfer occurs *via* electron exchange and requires orbital overlap between acceptor and donor, but this same overlap also brings on the reaction. It is thus conceivable that the excitation can stay trapped long enough in the shorter chain for the reaction to start while the shorter chain is still excited. This is equivalent to saying that internal conversion in the newly forming adduct does not occur immediately, but only after the reaction is "well on its way." This is shown in Figure 16. Similar reasons have been invoked, for the absence of quenching by triplet acceptors in triplet reactions.²⁴ A look at (31) shows that in this case a large, constructive interaction between ψ_m and $\psi_{m'}$ now leads to a *repulsive* term, since the energy denominator is negative. Therefore $4q$ cycloadditions will be forbidden. If the second bonding orbital, $\psi_{m'-1}$, of the longer chain lies below ψ_m , the reaction will occur for $2m + 2n = 4q + 2$.

(2) Another slightly unusual behavior occurs if there are *two* neighboring orbitals which both interact with the orbital of the excited electron or that of the hole. The case is pictured in Figure 17 for alternants: $\psi_{m'}$ and $\psi_{m'-1}$ both interact with ψ_m ; $\psi_{m'+1}$ and $\psi_{m'+2}$ both interact with ψ_{m+1} . Then two terms of (31) are important

$$\frac{(b_1^* b'_{11} \eta_{11} + b_i^{\circ} b'_{i1} \eta_{i1})^2}{\epsilon_m - \epsilon_{m'}} \quad \text{and} \quad \frac{(b_1^* a'_{11} \eta_{11} + b_i^{\circ} a'_{i1} \eta_{i1})^2}{\epsilon_m - \epsilon_{m'-1}} \quad (33)$$

where the $a'_{i'}$'s are the atomic orbital coefficients of $\psi_{m'-1}$. The first term is large, we have seen, if $2m + 2n = 4q$. But the second term is large if

$$\begin{cases} b_1^* = b_i^{\circ} \\ a'_{11} = a'_{i1} \end{cases} \quad \text{or} \quad \begin{cases} b_1^* = -b_i^{\circ} \\ a'_{11} = -a'_{i1} \end{cases} \quad (34)$$

The first possibility requires $2m = 4p + 2$ and $2n = 4p'$ (*viz.*, next-to-top bonding orbital in butadiene: $a_1 = a_4 = 0.372$); the second possibility requires $2m =$

(24) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **86**, 1436 (1964).

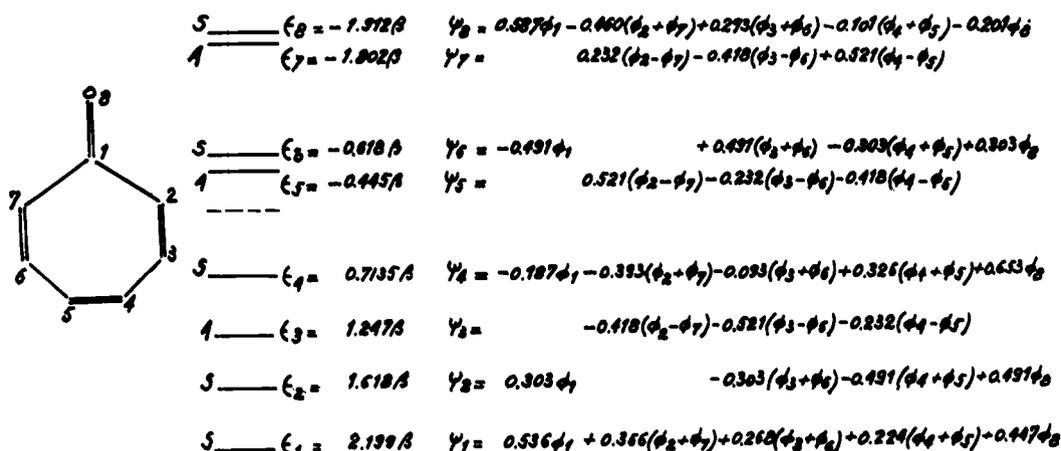


Figure 19. Hückel molecular orbitals and energy pattern for tropone.

$4p$ and $2n = 4p' + 2$. Hence $2m + 2n = 4q + 2$. The $4q$ and $4q + 2$ processes will then *compete* and either can occur.

To summarize, we have proved rigorously the selection rules for cycloadditions between closed-shell alternant hydrocarbons. The major conclusions agree entirely with those of Hoffmann and Woodward. It is assumed that these rules hold also for nonalternant systems or even for portions of conjugated chains (particularly if the conjugation between the portion which reacts and the rest of the chain is weak). Ultimately the rules depend on the *nodal properties* of the relevant orbitals. The nodal properties determine the relative sign of terminal atomic orbital coefficients in the interacting orbitals (eq 26, 28, and 30). So the calculations simply confirm the qualitative behavior inherent in the molecular orbitals. Finally two important restrictions are brought to light for photochemical cycloadditions: $4q + 2$ closures are possible (1) if the excitation is trapped in the shorter chain, or (2) if the orbital of the hole or that of the excited electron interacts simultaneously with two neighboring orbitals on the other molecule. An example of the latter case is studied in the next section.

There remains the question of whether cycloadditions which do not follow the Hoffmann-Woodward rules are indeed two-step reactions, as they asserted. This seems to be true whenever the reaction really violates the selection rules established here: the pathway of the photochemical Diels-Alder reaction (VIa) is two-step, as would be the pathways for the thermal $2 + 2$ additions studied in the first section. However, photochemical $4q + 2$ cycloadditions occurring in the exceptional situations just quoted and which appear to violate the Hoffman-Woodward rules may well be one-step reactions.

Organic chemists may find it worthwhile to attempt to create such special circumstances in order to obtain particularly difficult $4q + 2$ cycloadditions.

The Photodimerization of Tropone

Recently Kende has obtained,²⁵ by exposing a solution of tropone in acetonitrile to a mercury source, three dimers in approximately equal yields. These dimers correspond, respectively, to $(6 + 4)$, $(6 + 2)$, and

(25) A. S. Kende, *J. Am. Chem. Soc.*, **88**, 5026 (1966).

$(4 + 2)$ modes of addition (Figure 18). At the same time the $(6 + 6)$ dimer was obtained in acidic medium.²⁶ The $(6 + 2)$ and $(6 + 6)$ dimers "obey" the Hoffmann-Woodward rules, whereas the $(6 + 4)$ and $(4 + 2)$ compounds violate the rules and should therefore, according to Hoffmann and Woodward, proceed through multistep mechanisms. Indeed, Kende has very recently obtained²⁷ experimental evidence that all three dimers which he observes arise by way of one or more intermediates of triplet multiplicity. A brief investigation shows that the $(4 + 2)$ compound might also be expected to form under concerted conditions and that it has a large π stabilization energy. This large stabilization for a $(4q + 2)$ photoadduct serves to illustrate potential exceptions to the usual selection rules.

Figure 19 shows the Hückel π molecular orbitals and orbital energies of tropone, calculated with a modified Coulomb integral on the oxygen atom, $\Delta\alpha_8 = \beta$. The orbitals are either symmetric (S) or antisymmetric (A) with respect to the axis of symmetry. Using these orbitals we can discuss the interaction energy between a ground-state tropone molecule and another molecule in an excited state. The reaction should occur in the lowest singlet or triplet excited state, which can have *either* $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ character. (We do not know which *a priori*, but the lowest $n \rightarrow \pi^*$ state, $n \rightarrow \psi_5$, should have a particularly long lifetime for spatial symmetry reasons alone, since the π orbital has a node on the oxygen). The expressions for ΔE_{int} in the case of $n \rightarrow \pi^*$ transitions will account simply for the additional electron appearing in the π system in some antibonding orbital ψ_k ; they are similar to (15a) and (21a), part I, with the simplification that all terms involving ψ_j and c_{jr} drop out.

A quick look at the relevant first-order terms shows that the interaction energy between a tropone molecule in its ground state and another in the excited state $\psi_4 \rightarrow \psi_5$ or $n \rightarrow \psi_5$ favors the $(6 + 6)$ and $(6 + 2)$ additions but inhibits the $(6 + 4)$ and $(4 + 2)$ additions, as shown in eq 35, where the terms in brackets are to be left out in the $n \rightarrow \psi_5$ case. Clearly in the second and last expressions the linear terms are of opposite sign,

(26) (a) T. Mukai, T. Tezuka, and Y. Asasaki, *ibid.*, **88**, 5025 (1966); (b) T. Tezuka, Y. Akasaki, and T. Mukai, *Tetrahedron Letters*, 1397 (1967).

(27) A. S. Kende, private communication (1967); A. S. Kende and J. E. Lancaster, *J. Am. Chem. Soc.*, **89**, 5283 (1967).

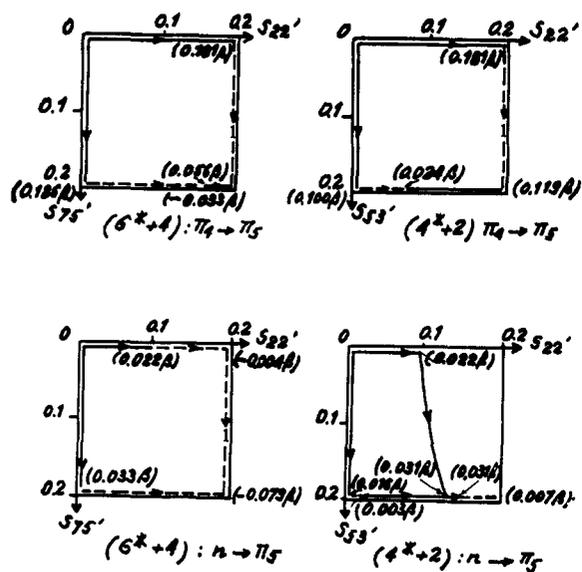


Figure 20. Reaction pathways for troponone photodimerizations. Dotted paths require activation energy.

so that the simultaneous formation of two bonds will be less favorable than the closure of only one bond (compare with eq 17 for the photochemical Diels-Alder reaction). On the other hand, in the (6 + 6) and (6 + 2) cycloadditions the linear terms reinforce each other and the pathways should be one step.

$$\begin{cases}
 (6 + 6) \quad \Delta E_{\text{int}} = [-|0.271\eta_{22'} + 0.271\eta_{77'}| - \\
 \quad |0.154\eta_{22'} + 0.154\eta_{77'}|, \text{ etc.} \\
 (6 + 4) \quad \Delta E_{\text{int}} = [-|0.271\eta_{22'} - 0.218\eta_{57'}| - \\
 \quad |0.154\eta_{22'} - 0.128\eta_{57'}|, \text{ etc.} \\
 (6 + 2) \quad \Delta E_{\text{int}} = [-|0.271\eta_{22'} + 0.121\eta_{37'}| - \\
 \quad |0.154\eta_{22'} + 0.036\eta_{37'}|, \text{ etc.} \\
 (4 + 2) \quad \Delta E_{\text{int}} = [-|0.271\eta_{22'} - 0.097\eta_{35'}| - \\
 \quad |0.154\eta_{22'} - 0.030\eta_{35'}|, \text{ etc.} \quad (35)
 \end{cases}$$

However, there are still two mechanisms which could eventually lead to concerted pathways for the (6 + 4) and (4 + 2) dimers. The first possibility which comes to mind is that two excited states of different spatial symmetry but of nearly equal energy may be involved. For instance, the excited state corresponding to the $\psi_4 \rightarrow \psi_5$ transition has A symmetry, with a Hückel transition energy $|1.158\beta|$. The lowest $\pi \rightarrow \pi^*$ excited state of S symmetry ($\psi_4 \rightarrow \psi_6$) has an excitation energy $|1.331\beta|$, and could well be lowered²⁸ by configuration interaction with the neighboring $\psi_3 \rightarrow \psi_5$ state (transition energy $|1.692\beta|$). For the interaction energy between a molecule in this excited S state and a ground-state molecule, the linear terms are

$$\begin{aligned}
 (6 + 4) \quad \Delta E_{\text{int}} &= -|0.154\eta_{22'} - 0.128\eta_{57'}| \text{ etc.} \\
 (4 + 2) \quad \Delta E_{\text{int}} &= -|0.149\eta_{35'}| - \\
 &\quad |0.154\eta_{22'} - 0.030\eta_{35'}|, \text{ etc.} \quad (36)
 \end{aligned}$$

We see that the (6 + 4) cycloaddition is still strongly

(28) A recently published self-consistent field calculation, [H. Kuroda and T. Kuniti, *Theoret. Chim. Acta*, 7, 220 (1967)] gives the lowest A state (essentially $\psi_4 \rightarrow \psi_5$) at 3.73 eV and the lowest S state (roughly the mixture $0.86\psi_4 \rightarrow \psi_6 - 0.50\psi_3 \rightarrow \psi_5$) at 4.20 eV. (Note how well these values agree with the Hückel estimates for $\beta = -3$ eV.) The lowest triplet state is also of A symmetry. These results indicate that photo-reaction in an excited S state is improbable.

forbidden, whereas the (4 + 2) cycloaddition might possibly occur in a concerted fashion. If the bonds 22' and 35' are being formed at roughly the same rate

$$\Delta E_{\text{int}} = 0.119\eta_{35'} + 0.154\eta_{22'} \quad (37)$$

The linear terms are small but are both favorable; together with the stabilizing second-order terms coming from E_{int} (which favor this Diels-Alder type condensation), they render this mechanism possible. The (4 + 2) addition could conceivably occur in a concerted fashion if one molecule were in the $\psi_4 \rightarrow \psi_6$ state. Reaction in the $n \rightarrow \psi_6$ state seems ruled out, however, since the term $-|0.149\eta_{35'}|$ in the last expression of (36) drops out.

A second potential mechanism arises from the peculiar orbital energy pattern of troponone, in particular, the existence of two nearly degenerate low-lying antibonding orbitals. In consequence, the excited electron (in ψ_5 when the molecules are separate) sees its energy lowered, not only by mixing of ψ_5 with ψ_5' , and formation of the corresponding intermolecular orbital, but also by a strong interaction between ψ_5 and the orbital ψ_6 . This is true whether the excited state is $n \rightarrow \psi_5$ or $\psi_4 \rightarrow \psi_5$. The corresponding stabilization energy is $-(\sum_{rr'} C_{5r} C_{6r'} \eta_{rr'})^2 / (E_6 - E_5)$ (see I, eq 21a) and is found to be very large, $0.243\eta_{53'}^2 / \beta$ in the case (4* + 2) (where the excited molecule contributes the longer chain of the cycloadduct).

Interaction energies have been calculated for the (6* + 4) and (4* + 2) additions for both $n \rightarrow \psi_5$ and $\psi_4 \rightarrow \psi_5$ excitations. The reaction pathways, calculated for $k = 3$, are drawn in Figure 20. All reactions require two steps; however, there is a sharp difference between the energetics of the (6* + 4) and (4* + 2) reactions. For the former either there is no substantial stabilization when either bond closes ($n \rightarrow \psi_5$ case), or a substantial stabilization energy exists but the activation energy required to close the second bond is very large, $-0.219\beta = 15$ kcal/mole ($\psi_4 \rightarrow \psi_5$ case). In either case the over-all π energy when both bonds are closed is repulsive (compare with the photochemical Diels-Alder reaction, Figure 8). No concerted pathway can be found and the reaction must proceed in two steps.

The energetics of the (4* + 2) cycloaddition are quite different, however. Take, for instance, the case of the $\psi_4 \rightarrow \psi_5$ excited state. Here the 22' closure probably occurs first because it gives a much larger initial stabilization. But once 22' is closed, the barrier opposing the establishment of bond 53' is small,²⁹ $-0.062\beta = 4.3$ kcal/mole, and the over-all stabilization when both bonds are closed remains appreciable, $0.119\beta = -8.4$ kcal/mole, of the same order of magnitude as in Diels-Alder *exo* additions. Hence, although one bond closes after another, this may occur in a near-simultaneous fashion since the second barrier is low, and the calculated reaction path resembles much more the retarded one-step thermal Diels-Alder reaction path than the true two-step reaction path of the photochemical Diels-Alder addition.

Note that the (4* + 2) addition in the $n \rightarrow \psi_5$ excited state also gives a (rather peculiar) concerted re-

(29) If bond 53' were to close first, there would also be a small secondary activation energy for the closure of 22'. The energy peak for closure of the second bond occurs at $S_{22'} = 0.072$ for $S_{53'} = 0.2$.

action path. For $k = 3$ the interaction energy has the form

$$E_{\text{int}}^*/\beta = |0.462S_{22'} - 0.090S_{53'}| - 2.40S_{22'}^2 - 0.045S_{53'}^2 + 1.17S_{53'}S_{22'} \quad (38)$$

The reaction path given by (7)

$$\frac{S_{53'}}{S_{22'}} = \frac{-0.090 - 0.090S_{53'} + 1.17S_{22'}}{0.462 - 4.80S_{22'} + 1.17S_{53'}}$$

corresponds initially to closure of bond 22' ($S_{53'} = 0$). But, when $S_{22'}$ reaches the value 0.098, $S_{53'}$ suddenly increases very rapidly, until it reaches 0.2 for $S_{22'} = 0.137$. The pathway crosses the diagram sharply as bond 53' "catches up" with bond 22' and finally terminates first. The bond which starts closing first should terminate last! The calculated reaction path corresponds again to a concerted mechanism.

Admittedly our discussion of tropone photodimerizations is rather crude: electrostatic interactions may play an important role, particularly in the $n \rightarrow \psi_5$ excited dimer. For the $\psi_4 \rightarrow \psi_5$ excited state, however, both Hückel and SCF calculations²⁸ indicate that the ring is positively charged (and the oxygen atom negatively charged) both in the ground and excited ($\psi_4 \rightarrow \psi_5$) molecules. For this state, therefore, electrostatic interactions, although they have been invoked,^{26b} should not determine the reaction pathway.

To summarize we have shown that a ($4^* + 2$) quasi-concerted cycloaddition is allowed and possesses a favorable electronic energy path. Although the actual ($4 + 2$) dimerization occurs *via* a triplet intermediate,²⁷ the ready formation of this ($4q + 2$) cycloadduct is easily understood in terms of the large stabilization energy which we have calculated. It is also in line with the more general selection rules given in the previous section.

Discussion

We would like to summarize briefly what appear to be the major strengths and weaknesses of this theory. A major flaw, inherent to all molecular orbital theories, is the lack of correlation between the order of the orbitals and the order of states. Care must be exercised when considering patterns of electrons in one-electron orbitals. The situation of lowest total energy may not be that with the lowest total *one-electron* energy (example: the lowest singlet excited state of naphthalene). Other weaknesses are the following.

(a) **Neglect of Explicit Intermolecular Coulomb Interactions.** This neglect may cause erroneous prediction of reaction paths, particularly when large net charges force a pathway different from that favored purely from the overlap viewpoint. Thus we failed to explain, without invoking Coulomb effects, the formation of VII, rather than VIII, in the condensation of acrolein. Although the theory is successful with neutral alternants, it is particularly weak in predicting the course of reactions governed by net charge interactions, and further improvement of the theory is required to obviate for this.³⁰

(30) A. Devaquet and L. Salem, "Intermolecular Orbital Theory of the Interaction between Conjugated Systems. III," to be submitted for publication.^{30a}

(30a) NOTE ADDED IN PROOF. The competing role of ionic interac-

(b) **Neglect of Explicit Interaction with the σ Electrons (in certain cases).** We assumed that the σ bonds create a repulsive wall in the region of distances 2–2.5 Å, where the overlap of the p orbitals is about 0.2. Specific cases will occur where this wall may be highly directional or extend to larger distances. In these cases the extended Hückel theory should be more useful than the present approach. However, cases of (σ) steric hindrance, which could modify the preferred reaction path, can often be detected with molecular models.

Professor Coulson has remarked³¹ that the σ electrons would be expected to play an important role (let alone because the total σ density in an aromatic molecule exceeds the total π density almost everywhere) and that yet the theory is reasonably successful in dealing only with the π electrons. Perhaps what counts is that the π density "sticks out" more³² toward the other molecule, but certainly the fact that reaction paths and reaction products seem to be predictable by consideration of the reactants alone is a strong indication that in these cycloadditions the *transition state is much nearer the separate conjugated systems than the final condensed product*. A similar situation seems to obtain for electrocyclic ring openings (or closures) of cyclobutenes and cyclohexadienes.³³

(c) **Existence of the Parameter k .** Calculations here were all effected, with $k = 3$ (and $\beta = -3$ eV), a value which is approximate. However variations of k within reasonable limits should not modify the qualitative behavior of the reactions, which depends on the molecular orbitals and their nodal properties.

In spite of these weaknesses, the theory seems to carry some potentiality for a few major reasons. One is the ease with which one obtains an expression for the interaction energy, for thermal or photochemical reactions, and the consequent ability to draw out a "theoretical" reaction pathway or, even if one wishes, draw energy contours. One can distinguish readily between "concerted" additions, whether one-step or retarded one-step like the Diels–Alder reaction, and two-step additions. For the former one calculates π electron stabilization energies; for the latter one can estimate the π barrier inhibiting the second step. Admittedly the π energy changes are only *indicative* and ultimately σ energy changes will have to be computed to obtain accurate activation energies. But the organic chemist may find it useful to possess a tool which he can use quickly in his laboratory and which enables him to test on paper, with some measure of reliability, all the possible pathways of the reaction he is attempting. Of course, a good knowledge of the states of the separate systems is required. Furthermore, one should always keep in mind that a reaction which *can* occur, according to the reaction diagram, in a concerted fashion, may yet occur in two steps *via* a triplet

tions and orbital interactions has recently been emphasized by G. Klopman and R. F. Hudson, *Theoret. Chim. Acta*, **8**, 165 (1967), and *Tetrahedron Letters*, 1103 (1967).

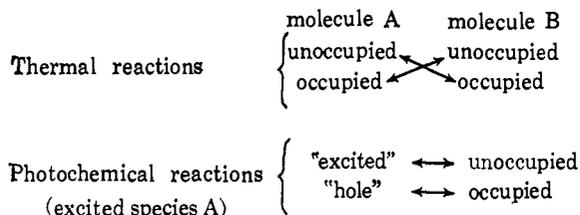
(31) C. A. Coulson, private communication.

(32) See for instance, M. D. Newton, F. P. Boer, and N. W. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2367 (1966). A careful look at their Table VI shows that already at a distance of 2 au (1 Å) from the plane of the benzene ring, the π density exceeds the σ density everywhere.

(33) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395 (1965); see also A. Streitwieser, Jr., R. J. Jagow, R. C. Fahey, and S. Suzuki, *ibid.*, **80**, 2326 (1958), where an early transition state is proposed on the basis of studies of secondary isotope effects.

intermediate. The reaction path may then be useful only in determining the *first* step.

Another reason is the achievement of a certain degree of physical insight into the electronic mechanism of the reaction. Just as molecular orbitals have become important in understanding the stability of a given conjugated molecule, the specific interaction of molecular orbitals in a reaction, and their combination to form intermolecular orbitals are crucial factors in determining the readiness of a reaction. There have been many pioneers in this field.^{15,16,20,34} The purpose of these papers has been to establish more rigorously the role of each molecular orbital interaction. The impor-



(34) See also H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965); H. E. Zimmerman, *Science*, **153**, 837 (1966).

tant orbital interactions may be summarized in the scheme shown where "excited" and "hole" refer to the orbital of the excited electron and the orbital with the hole, respectively. This scheme emphasizes which orbital interactions must be favorable for a given reaction to be allowed. The relevant orbitals are generally the top occupied and lowest unoccupied on each molecule. This scheme is strictly valid only for closed-shell molecules.

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Anomalous Fluorescence Characteristics of Fluoranthene and Some of Its Derivatives¹

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Abstract: The fluorescence characteristics of fluoranthene and three of its derivatives, 3-phenylfluoranthene, 3,3'-bifluoranthenyl, and 3-aminofluoranthene, are reported. For fluoranthene in particular, the natural lifetime, Stokes shift, and relative immunity to concentration and oxygen quenching are found to be anomalous. The first two of these characteristics, long lifetime and large Stokes shift, are interpreted as supporting evidence that fluorescence takes place from a partially hidden level. For the most intense absorption band associated with this transition (¹L_b), ε_{max} is estimated to be 270 ± 40. The anomalous immunity to quenching has not been explained as yet. Depending on the type and position of the substituents, derivatives of fluoranthene also possess some or all of the above anomalies. The synthesis and purification of the above derivatives of fluoranthene are also reported.

Fluoranthene (II in Table I) is a nonalternate conjugated hydrocarbon and therefore has been of interest in theoretical and experimental studies.^{2,3} We have studied the fluorescence characteristics of fluoranthene and several of its derivatives (III-V in Table I) in a dilute cyclohexane solution and have found that most of these compounds have many anomalous characteristics. In particular, II has four anomalous fluorescence characteristics: (1) the value of the fluorescence lifetime τ_{0m} obtained from measuring the decay time, τ, and the quantum yield, QY, is many times greater than a calculated value, τ_{0c} (Table I), obtained by integrating over its long-wavelength band; (2) its Stokes

shift is very large; (3) it appears to be immune to concentration quenching and excimer formation; and (4) it is relatively resistant to oxygen quenching. It is our belief that the last two anomalies are unrelated to the first two.

Fluorescence measurements were made with equipment and according to procedures described elsewhere.⁴ All measurements were made on dilute cyclohexane solutions in the concentration region of about 0.2 g/l., and the solute was excited directly by monochromatic radiation. The following data were obtained: the absorption spectrum, the fluorescence spectrum, the fluorescence decay time, τ, and the relative intensities of the fluorescence spectra of a nitrogenated and an aerated solution, L₀/L. They are shown in Figure 1 in part. From the data, calculations were made of (1) the

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) J. Koutecky, P. Hockman, and J. Michl, *J. Chem. Phys.*, **40**, 2439 (1964); (b) E. Heilbronner, J. P. Weber, J. Michl, and R. Zahradnik, *Theoret. Chim. Acta*, **6**, 141 (1966).

(3) B. L. Van Duuran, *Anal. Chem.*, **32**, 1436 (1960).

(4) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press Inc., New York, N. Y., 1965.