

The Electronic Mechanism of Electrocyclic Reactions

Sir:

In a recent communication¹ Woodward and Hoffmann have offered a theoretical interpretation of the stereospecificity of "electrocyclic reactions," such as the conversion of cyclobutene to butadiene or the cyclization of hexatrienes to cyclohexadienes. Such reactions may be induced by either heat or light, and both the thermal and the photochemical reactions are highly stereospecific. In the ring opening of cyclobutenes the thermal reaction is "conrotatory" (see Figure 1a) while the photochemical reaction is "disrotatory" (Figure 1b); by contrast the photochemical cyclization of hexatrienes is a conrotatory process. Woodward and Hoffmann point out that the stereochemical course of an electrocyclic ring closure is determined by the symmetry of the highest occupied molecular orbital of the open-chain reactant; their calculations based on the extended Hückel theory support this generalization and show that it also applies to the ring-opening reactions.

In a sense the work of Woodward and Hoffmann disposes of the problem, but two questions might remain in the mind of the physical chemist. First, why should the ring-opening reactions be guided by the electronic structure of the product rather than the reactant, and second, why should the extended Hückel theory lead to the same predictions as a rule based on the symmetry of only one molecular orbital? Perhaps in this note we may be allowed to recommend a point of view from which these questions are more easily answered.

Let us begin by considering the electrocyclic conversion of cyclobutene to butadiene. In this process four molecular orbitals undergo a radical change; namely, σ , σ^* , π , and π^* , where the first two are the bonding and antibonding orbitals of the bond which is to be broken, and the last two refer to the carbon-carbon double bond in the cyclobutene ring. Eventually these four orbitals become the molecular π -orbitals of butadiene, namely, ψ_1 , ψ_2 , ψ_3 , and ψ_4 in order of increasing energy. Each of the first set of orbitals passes adiabatically into one of the second set, and we now ask: how are the orbitals of the two sets correlated?

The answer depends upon whether the isomerization proceeds in a conrotatory or a disrotatory manner. In the conrotatory mode the system preserves a twofold axis of symmetry throughout the reaction, so that each orbital may be rigorously classified as A or B according as it is symmetric or antisymmetric about that axis. In the disrotatory mode a symmetry plane is maintained, and each orbital remains either symmetric (A') or antisymmetric (A'') about this plane. The situation is illustrated in Figure 1, and Table I gives the symmetries of the orbitals in the two cases. Thus in the conrotatory mode σ correlates with ψ_2 , π with ψ_1 , etc., but in the disrotatory mode the correlations are different, σ correlating with ψ_1 and π^* with ψ_2 , etc.

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

Table I

	Symmetry	Cyclobutene	<i>s-cis</i> -Butadiene
Conrotatory mode	{ A B	σ , π^*	ψ_2 , ψ_4
		π , σ^*	ψ_1 , ψ_3
Disrotatory mode	{ A' A''	σ , π	ψ_1 , ψ_3
		π^* , σ^*	ψ_2 , ψ_4

Having correlated the orbitals of cyclobutene with those of butadiene *via* the conrotatory and disrotatory modes, we can now correlate the electron configurations of the two molecules, with reference to the same alternative modes. The result is given in Figure 2. Here the straight lines indicate what would happen to a given electron configuration if there were no configurational interaction; the full lines represent a more realistic

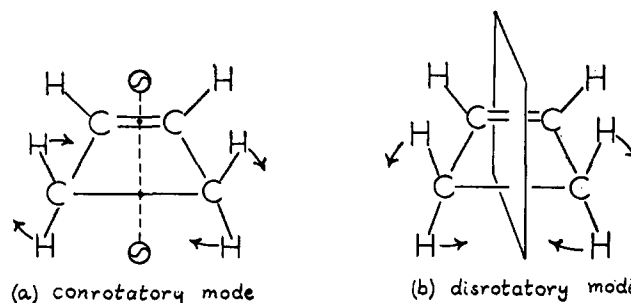


Figure 1. Alternative modes for the conversion of cyclobutene to *s-cis*-butadiene.

view of the correlations between states since electron repulsion prevents states of the same symmetry from crossing. It is immediately clear why both the forward and the reverse reactions should be conrotatory in the ground state and disrotatory in the first excited state, as indicated by the quantitative computations of Woodward and Hoffmann. An analogous treatment of the C_6 systems to an exactly converse result, again in agreement with their analysis.

Besides studying the even-membered rings and chains, Woodward and Hoffmann examined the C_3 and C_5 systems and made predictions about the stereochemical courses of their electrocyclic transformations. We think it may be of interest to give the orbital and state correlations for the interconversion of cyclopropyl and allyl, to bring out a point which was not mentioned in their paper. Table II gives the orbital correlations for the two species in the conrotatory and disrotatory modes; π stands for the 2p-orbital of the trivalent carbon atom.

Figures 3-5 represent the correlations between the ground states and first excited states of the cations, the neutral radicals, and the anions in the two modes. For the ions the stereochemical predictions are clear-cut and agree precisely with those given by Woodward and

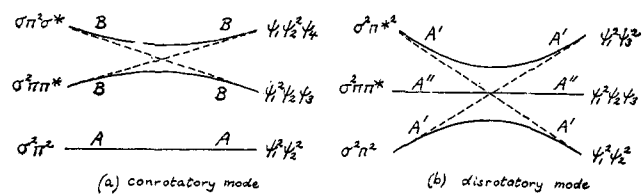


Figure 2. Correlation diagrams for the interconversion of cyclobutene and butadiene.

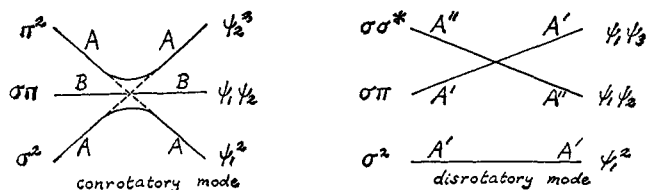


Figure 3. Interconversion of cyclopropyl cation and allyl cation.

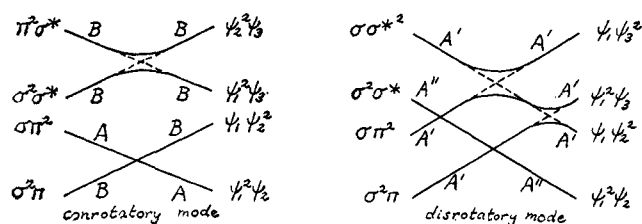


Figure 4. Interconversion of cyclopropyl radical and allyl radical.

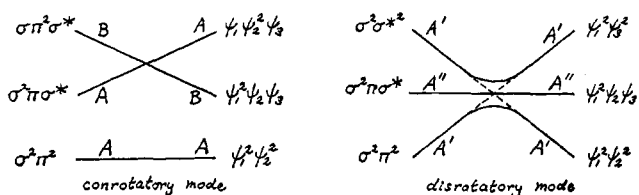


Figure 5. Interconversion of cyclopropyl anion and allyl anion.

Hoffmann. But for the radicals the situation is more complex. In both the conrotatory and disrotatory modes the ground state of each radical is correlated

Table II

	Cyclopropyl	Allyl
Conrotatory mode	$\begin{cases} A \\ B \end{cases}$	$\begin{cases} \sigma \\ \pi, \sigma^* \end{cases}$
Disrotatory mode	$\begin{cases} A' \\ A'' \end{cases}$	$\begin{cases} \psi_2 \\ \psi_1, \psi_3 \end{cases}$

with an excited state of the other. If the excited states occur in the order shown (as one would suppose), the thermal reaction should be slightly less hindered in the conrotatory than in the disrotatory mode, but should show a much larger activation energy than the thermal transformation of the ions. One would therefore expect the thermal isomerization of the cyclopropyl radical to be much slower and probably much less stereospecific than for either the positive or the negative ion.

As to the photochemical transformations, the first excited state of either radical should also isomerize by the conrotatory mode, but in the second excited state, which lies very close above the first, disrotatory transformations are to be expected.

We have thought it worthwhile to supplement the discussion of Woodward and Hoffmann in this way because orbital and state correlation diagrams enable one to follow a reaction along its entire course and draw qualitative conclusions without necessarily engaging in numerical computations.

(2) E. W. A., at present on leave from the Case Institute, Cleveland, Ohio, wishes to thank the National Institute of Neurological Diseases and Blindness for a Fellowship.

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Selection Rules for Concerted Cycloaddition Reactions

Sir:

Recently we characterized orbital symmetry relationships as stereochemical determinants in electrocyclic reactions, which may be regarded as intramolecular cycloadditions, involving net interconversions of one π -bond and one σ -bond.¹ We now examine the general problem of concerted *intermolecular* cycloaddition reactions from a similar point of view.

Our procedure consists in the construction of correlation diagrams for the molecular orbitals involved in reaction, classifying the levels with respect to the symmetry elements of the transition state.² The method is illustrated first in the case of the addition of two ethylenes to form cyclobutane. The assumed geometry of approach places the two ethylene molecules in parallel planes directly above each other, as in Figure 1. The

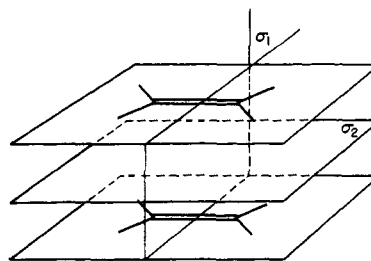


Figure 1.

four reactant π -levels and the four corresponding σ -levels in the product are shown in Figure 2, classified as symmetric (S) or antisymmetric (A) with respect to σ_1 , a plane bisecting the ethylenes, and σ_2 , a plane parallel to and midway between the planes of the approaching molecules. The form of the molecular orbitals, projected upon the plane passing through the four carbon atoms, is shown in Figure 3. The original

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(2) This method has been independently and elegantly used in a discussion of electrocyclic reactions by Professor H. C. Longuet-Higgins (Cambridge), who very kindly communicated his results to us privately prior to publication.