

JOURNAL

OF THE AMERICAN CHEMICAL SOCIETY

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VOLUME 100, NUMBER 2

JANUARY 18, 1978

σ Participation in Electrocyclic Reactions. A Consequence of Symmetry

E. A. Halevi,^{1a} J. Katriel,^{1a} R. Pauncz,^{1a} F. A. Matsen,^{1b} and T. L. Welsher*^{1b}

Contribution from the Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel, and the Departments of Chemistry and Physics,^{1c} The University of Texas, Austin, Texas 78712. Received March 11, 1977

Abstract: It is shown that the n -orbital basis employed in the conventional analysis of n -carbon-atom electrocyclic isomerization is not sufficient for a complete symmetry analysis of the problem. In particular, the allyl-cyclopropyl isomerization requires the use of a five-orbital rather than the conventional three-orbital basis. Selection rules for the variously charged species are obtained using a five-orbital basis in OCAMS (orbital correspondence analysis in maximum symmetry) and Hückel-Hubbard calculations. It is shown that the additional pair of σ orbitals behaves as a closed shell throughout the reaction and thus a sound theoretical foundation is provided for the conventional treatment of σ orbitals in electrocyclic reactions. The predictions of OCAMS and Hückel-Hubbard are mutually supportive and consistent with MINDO/3 and ab initio calculations.

I. Introduction

The conventional orbital symmetry analyses of n -carbon-atom electrocyclic isomerizations^{2a,b} typically consider a set of n molecular orbitals whose form is deduced from Hückel theory. For instance, the analysis of the allyl-cyclopropyl isomerization, which we consider in detail in this paper, involves three orbitals: butadiene-cyclobutene, four-orbitals, etc. The symmetry elements considered are only those which are "conserved" along a reaction path. This analysis is incomplete in several respects: (1) it does not contain an explicit representation of the σ orbitals involved in the isomerization; (2) it does not completely analyze the symmetry changes in the isomerization; (3) it does not include an explicit treatment of electron repulsion and configuration interaction which are particularly important in the prediction of photochemistry and may be simply included by using the Hückel-Hubbard Hamiltonian.^{2c}

In this paper we make the analysis more complete by (1) extending the orbital basis set from n to $n + 2$, the allyl-cyclopropyl isomerization thus becoming a five-orbital problem (section II); (2) extending the symmetry analysis by OCAMS³ (orbital correspondence analysis in maximum symmetry) (section III); (3) performing Hückel-Hubbard calculations using the five-orbital basis (section IV). The results are discussed in section V and conclusions are made in section VI.

II. The Complete Basis Set

That the conventional n -orbital basis employed for electrocyclic reactions is incomplete may be seen by considering symmetries of the various basis elements under C_{2v} , the point group common to both reactants and products. The basis for the open-chain side of the reaction consists of the n Hückel

molecular orbitals of an n -carbon-atom linear polyene. If we label these orbitals 1, 2, . . . , n in order of increasing Hückel orbital energy we find that the orbitals labeled by odd integers have symmetry a_2 while those labeled by even integers have symmetry b_2 . On the other hand, the basis for the cyclic system consists of a pair of σ orbitals (one bonding, one antibonding) which represent the newly formed C-C σ bond plus $n - 2$ Hückel MOs of a linear polyene of length $n - 2$. Again the linear polyene MOs alternate in symmetry (a_2 or b_2) according to their Hückel energies. However, the σ bonding orbital has symmetry a_1 and the antibonding orbital has symmetry b_1 . Thus these σ orbitals cannot correlate directly with orbitals of the open-chain partner and if a complete (maximum) symmetry analysis is to be carried out the basis set must be extended.

We extend the basis set by noting that, in order for the reaction to proceed, σ C-H bonding must play a role. We consider as an example the allyl-cyclopropyl isomerization ($n = 3$). Generalization to arbitrary n is straightforward.

We define a five-orbital basis set

$$\{|A_x\rangle, |B_x\rangle, |A_y\rangle, |B_y\rangle, |C_y\rangle\} \quad (2.1)$$

Here $|C_y\rangle$ is a pure π orbital centered at the methine carbon in both allyl and cyclopropyl. In allyl, $|A_y\rangle$ and $|B_y\rangle$ are part of the π system and $|A_x\rangle$ and $|B_x\rangle$ participate in C-H σ bonding while in cyclopropyl $|A_y\rangle$ and $|B_y\rangle$ participate in C-H bonding and $|A_x\rangle$ and $|B_x\rangle$ form the AB σ bond. The phases chosen for the basis functions and the coordinate system are shown in Figure 1.

From these atomic orbitals we construct molecular orbitals which are exhibited in Figure 2 along with their symmetries with respect to C_{2v} . An ad hoc energy assignment is employed

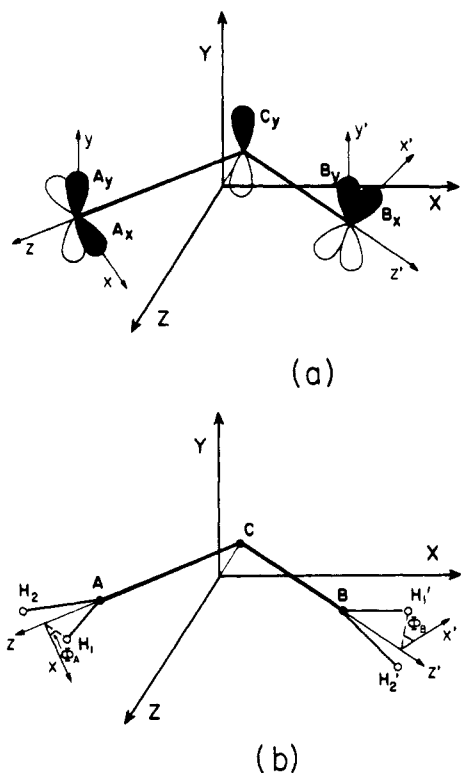


Figure 1. Basis set (a) and coordinate system (b).

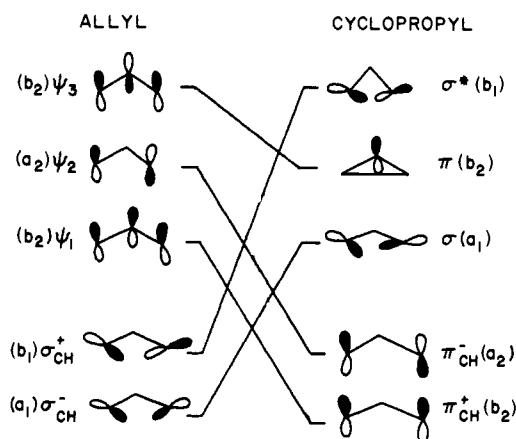


Figure 2. Molecular orbitals of allyl and cyclopropyl and the direct symmetry correlations between them.

so that the top three orbitals are the three employed in the conventional analysis.² Also shown are the symmetry orbital correlations under C_{2v} . We see that all five orbitals are required to obtain full correlation. Furthermore, since the two lower orbitals correlate with highly excited orbitals all reactions in which C_{2v} symmetry is preserved are forbidden at the orbital level and thus any reaction can proceed only by breaking the C_{2v} symmetry.

III. OCAMS⁴

The procedures of Woodward and Hoffmann^{2a} and of Longuet-Higgins and Abrahamson^{2b} (henceforth referred to together as WHLHA) analyze a prespecified reaction path in the symmetry point group appropriate to it, and characterize it as either "allowed" or "forbidden" on the basis of orbital or configuration correlation. In OCAMS the analysis, which is carried out in the higher symmetry point group common to reactant and product, specifies the symmetry properties of "allowed" pathways, if any.^{4a} In effect, the method selects as

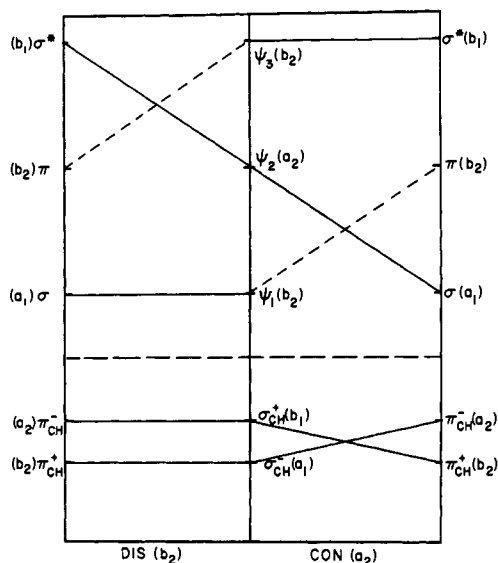


Figure 3. Induced correspondences for the b_2 (disrotatory) and a_2 (conrotatory) paths.

an "allowed" pathway one that, by reducing the symmetry from that of the group to that of one of its subgroups, allows the incursion of terms in the Hamiltonian which facilitate circumvention of the totally symmetric barrier between reactant and product.⁴ The requirements of such a pathway are that the occupied orbitals be either in pairwise *direct correspondence* (i.e., that they correlate in the original group) or in *induced correspondence* (i.e., that they are reduced to a common symmetry species in the subgroup retained after symmetry has been broken by displacement along the pathway).

The direct correspondences are shown in Figure 2 while the induced correspondences are shown in Figure 3 for both the b_2 (disrotatory) and a_2 (conrotatory) paths. We note that not all orbitals can be brought into induced correspondence. Also, we see that in each case there occur correspondences between the two lowest orbitals. This provides a partial justification for the three-orbital treatment since, given the energy ordering of Figure 2, these orbitals are fully occupied in the isomerization reactions considered. For the upper three orbitals we see that the conventional three-orbital correlation diagram is duplicated by all possible induced correspondences plus remaining direct correspondences.

To predict the reaction selection rules the OCAMS procedure is applied as follows:

(1) Construct the appropriate ground and excited state configurations for allyl and cyclopropyl (for the cation, anion, and radical).

(2) Correspond separately the singly and doubly occupied orbitals in the reactant and product configurations of a given species beginning with the direct correspondences. (However, see section V below and ref 4c,e,f).

If one (or more) pair of orbitals is not in direct correspondence but is in induced correspondence for a given reaction path, the reaction is said to be allowed (A) for that path whose symmetry induces the correspondence. Otherwise it is said to be forbidden (F), the degree of forbiddenness being estimated by the number of noncorrespondences.

(4) If for the lowest excited state several nearly isoenergetic configurations are possible two cases may arise: (a) two or more configurations of the same overall state symmetry (here the reaction is classified forbidden only if it is forbidden by the OCAMS rules in both configurations); (b) several configurations of different overall symmetry (here selection rules are inferred separately for each configuration. Ultimately one must

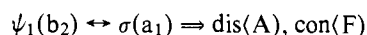
decide, on the basis of experiment or a proper many-body calculation, which, if any, of the several configurations might be involved in the photochemistry.

The OCAMS procedure has some features in common with the approach of Bader,⁵ Pearson,⁶ and Salem and Wright.⁷ It differs from them in according equivalent status to reactants and products, thus allowing the reaction in either direction to be discussed with equal ease.

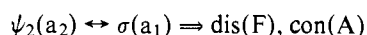
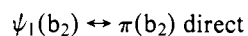
We now apply the OCAMS rules to the allyl-cyclopropyl isomerization using the correspondences in Figures 2 and 3. Since the lowest two orbitals are in correspondence in either possible concerted pathway, they may be ignored in the analysis.

A. Cation

1. Thermal: $[\psi_1(b_2)]^2 \rightleftharpoons [\sigma(a_1)]^2$

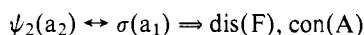
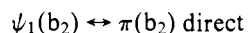


2. Photochemical: $\psi_1(b_2)\psi_2(a_2) \rightleftharpoons \sigma(a_1)\pi(b_2)$



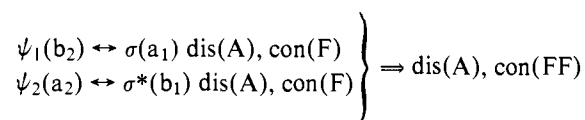
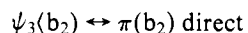
B. Anion

1. Thermal: $[\psi_1(b_2)]^2[\psi_2(a_2)]^2 \rightleftharpoons [\sigma(a_1)]^2[\pi(b_2)]^2$



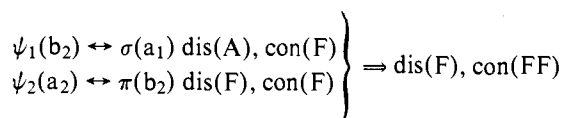
2. Photochemical:

$$[\psi_1(b_2)]^2\psi_2(a_2)\psi_3(b_2) \rightleftharpoons [\sigma(a_1)]^2\pi(b_2)\sigma^*(b_1)$$



C. Radical

1. Thermal: $[\psi_1(b_2)]^2\psi_2(a_2) \rightleftharpoons [\sigma(a_1)]^2\pi(b_2)$

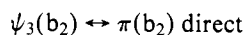
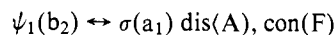


2. Photochemical

a. Allyl (excited state) cyclopropyl (ground state)

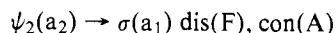
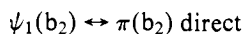
i. $[\psi_1(b_2)]^2\psi_3(b_2) \rightleftharpoons [\sigma(a_1)]^2\pi(b_2)$

(state symmetry = $B_2 \rightarrow B_2$)



ii. $\psi_1(b_2)[\psi_2(a_2)]^2 \rightleftharpoons [\sigma(a_1)]^2\pi(b_2)$

(state symmetry = $B_2 \rightarrow B_2$)

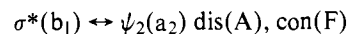
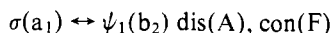


Both excited state configurations of allyl (i and ii) have the same overall symmetry and thus can be expected to mix so that both paths can be followed. Thus, dis(A), con(A).

b. Cyclopropyl (excited state) allyl (ground state)

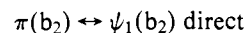
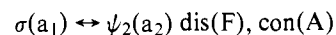
i. $[\sigma(a_1)]^2\sigma^*(b_1) \rightleftharpoons [\psi_1(b_2)]^2\psi_2(a_2)$

(state symmetry = $B_1 \rightarrow A_2$)



ii. $\sigma(a_1)[\pi(b_2)]^2 \rightleftharpoons [\psi_1(b_2)]^2\psi_2(a_2)$

(state symmetry, $A_1 \rightarrow A_2$)



To make a firm prediction here we need the ordering of the first few excited states (section V).

Finally, we note that we have not considered distortions of symmetry b_1 , since any such rotation of the methylene groups destroys symmetry with respect to reflection in the molecular plane. Note, however, that a superposition of conrotatory (a_2) and disrotatory (b_2) rotations contains a b_1 component.^{4b} We shall discuss composite displacements such as this only briefly in section V.

IV. The Hueckel-Hubbard Theory^{2c,8}

The Hueckel-Hubbard theory^{2c,8} is a proper many-electron theory which employs an atomic-orbital product basis and a Hamiltonian of the form

$$H \equiv H_h + H_I \quad (4.1)$$

Here

$$H_h \equiv \sum_i h_i \quad (4.2)$$

where h_i is a Hueckel Hamiltonian for the i th electron and

$$H_I \equiv I \mathbf{d} \quad (4.3)$$

where \mathbf{d} is an operator which counts the number of doubly occupied atomic orbitals in each configuration and I is the Hubbard repulsion parameter.⁹

The Hueckel-Hubbard Hamiltonian can be used to generate reaction surfaces by employing the Hueckel parameters as reaction coordinates. In this section we treat the allyl-cyclopropyl isomerization in two stages: (a) a one-electron Hueckel-like treatment; (b) a proper many-electron treatment using an n -electron product basis constructed from the five-orbital basis set (2.1).

A. The One-Electron Hamiltonian. We first construct the one-electron Hueckel Hamiltonian of the form

$$\mathbf{h} \equiv \sum_{rs} h_{rs} [r:s] \quad (4.4)$$

where

$$[r:s] \equiv \frac{1}{1 + \delta_{rs}} (|r\rangle \langle s| + |s\rangle \langle r|) \quad (4.5)$$

and the h_{rs} are the Hueckel parameters.

Now the five-orbital basis may be symmetry adapted to C_{2v} to obtain

$$\begin{aligned} |a_1\rangle &= \frac{1}{\sqrt{2}} (|A_x\rangle - |B_x\rangle) \\ |b_1\rangle &= \frac{1}{\sqrt{2}} (|A_x\rangle + |B_x\rangle) \\ |a_2\rangle &= \frac{1}{\sqrt{2}} (|A_y\rangle - |B_y\rangle) \\ |1b_2\rangle &= \frac{1}{\sqrt{2}} (|A_y\rangle + |B_y\rangle) \\ |2b_2\rangle &= |C_y\rangle \end{aligned} \quad (4.6)$$

The one-electron operators (4.5) may also be symmetry adapted. They are shown in Table I, sorted according to their irreducible representations.

Table I. The Symmetry-Adapted One-Particle Operators

A_1	B_1
$[A_x:A_x] + [B_x:B_x]$	$[A_x:A_x] - [B_x:B_x]$
$[A_y:A_y] + [B_y:B_y]$	$[A_y:A_y] - [B_y:B_y]$
$[A_x:B_x]$	
$[A_y:C_y] + [B_y:C_y]$	$[A_y:C_y] - [B_y:C_y]$
$[C_y:C_y]$	
$[A_y:B_y]$	
A_2	B_2
$[A_x:A_y] + [B_x:B_y]$	$[A_x:A_y] - [B_x:B_y]$
$[A_x:B_y] + [B_x:A_y]$	$[A_x:B_y] - [B_x:A_y]$
$[A_x:C_y] + [B_x:C_y]$	$[A_x:C_y] - [B_x:C_y]$

The allyl and cyclopropyl Hamiltonians, being totally symmetric with respect to C_{2v} , can only contain the six terms of A_1 type. Out of these terms ($[A_x:A_x] + [B_x:B_x]$) and ($[A_y:A_y] + [B_y:B_y]$) simulate the bonds of atoms A and B to the hydrogens of allyl and cyclopropyl, respectively, $[A_x:B_x]$ relates to the σ bond between the carbons A and B in cyclopropyl, and ($[A_y:C_y] + [B_y:C_y]$) describes the π interactions. We can dispose of $[C_y:C_y]$ by fixing the zero of energy at that of the single-center p orbital. The π interaction between the terminal atoms, $[A_y:B_y]$, is of secondary significance, and, for consistency with most Hückel treatments, is neglected.

A conrotation can be represented by the three A_2 terms and a disrotation by the three B_2 ones. The one-center terms $[A_x:A_y] \pm [B_x:B_y]$ are likely to be the most significant ones; they are most directly associated with the rotation of the methylene groups which gives rise to the breakdown of the symmetry of the nuclear framework.

The remaining B_1 terms, ($[A_y:C_y] - [B_y:C_y]$), for example, would reflect the effect of an asymmetric in-plane distortion. In the immediate context, such a displacement is not considered, so terms of this symmetry species do not appear. Thus, the terms important in allyl are $[A_x:A_x] + [B_x:B_x]$; $[A_y:C_y] + [B_y:C_y]$; those important in cyclopropyl are $[A_y:A_y] + [B_y:B_y]$; $[A_x:B_x]$. The distortions are given by $[A_x:A_y] \pm [B_x:B_y]$, in which the positive and negative combinations refer to conrotation and disrotation, respectively.

The one-electron Hamiltonian for the reacting system may be written as a function of the methylene rotation angles ϕ_A and ϕ_B . That is,

$$\mathbf{h}(\phi_A, \phi_B) \equiv \mathbf{h}_a(\phi_A, \phi_B) + \mathbf{h}_c(\phi_A, \phi_B) + \mathbf{h}_d(\phi_A, \phi_B) \quad (4.7)$$

where \mathbf{h}_a is the allyl Hamiltonian, \mathbf{h}_c is the cyclopropyl Hamiltonian, and \mathbf{h}_d is the symmetry-breaking term. Clearly, the following boundary conditions must be met:

$$\begin{aligned} \mathbf{h}_a\left(\frac{\pi}{2}, \frac{\pi}{2}\right) &= 0 \\ \mathbf{h}_c(0,0) &= 0 \end{aligned} \quad (4.8)$$

$$\mathbf{h}_d(0,0) = \mathbf{h}_d\left(\frac{\pi}{2}, \frac{\pi}{2}\right) = 0$$

Also, the reacting system is, at any stage, invariant under a 180° local rotation of each of the methylene groups. Hence, the angular dependence must have a period of π .

The restrictions discussed above are met if we write

$$\begin{aligned} \mathbf{h}_a \equiv & -T\{[A_y:C_y]\cos^2\phi_A + [B_y:C_y]\cos^2\phi_B\} \\ & - \tau\{[A_x:A_x]\cos^2\phi_A + [B_x:B_x]\cos^2\phi_B\} \\ & + (\epsilon/2)\{[A_x:B_x](\cos^2\phi_A + \cos^2\phi_B)\} \end{aligned} \quad (4.9)$$

$$\begin{aligned} \mathbf{h}_c = & -T^*\{[A_x:B_x](\sin^2\phi_A + \sin^2\phi_B)/2\} \\ & - \tau\{[A_y:A_y]\sin^2\phi_A + [B_y:B_y]\sin^2\phi_B\} \\ & - (\epsilon/2)\{[A_y:B_y](\sin^2\phi_A + \sin^2\phi_B)\} \end{aligned} \quad (4.10)$$

$$\mathbf{h}_d = -(\tau/2)\{[A_x:A_y]\sin(2\phi_A) + [B_x:B_y]\sin(2\phi_B)\} \quad (4.11)$$

Here T^* is the relative energy of the AB σ bond and T is that of the allylic π bonds. The parameter values chosen in order to obtain approximate agreement with spectral and thermochemical data are $T = 3.0$ eV and $T^* = 1.25T$.² In addition, τ is a strength parameter, simulating the CH bonding orbital energies. It is deliberately chosen to be large enough, i.e., $4T$, so as to induce separation of the CH orbitals from the remaining orbitals. Also the arbitrary parameter $\epsilon = 0.2T$ is introduced in order to split the nearly degenerate CH bonding orbitals for convenience in making the orbital correlations, but it does not affect the many-electron predictions. While this Hamiltonian was developed in a somewhat heuristic manner, its angular dependence is rigorously prescribed by the actual structure of the complete Born-Oppenheimer Hamiltonian, as developed in the Appendix.

Now for a conrotation $\phi_A = \phi_B$ and for a disrotation $\phi_A = -\phi_B$. Hence

$$\begin{aligned} \mathbf{h}^\pm = & -T([A_y:C_y] + [B_y:C_y])\cos^2\phi \\ & + T^*[A_x:B_x]\sin^2\phi - \tau\left\{([A_x:A_x] \right. \\ & + [B_x:B_x])\cos^2\phi + ([A_y:A_y] + [B_y:B_y])\sin^2\phi \\ & + ([A_x:A_y] \pm [B_x:B_y])\frac{\sin^2\phi}{2}\left. \right\} \\ & + \epsilon([A_x:B_x]\cos^2\phi - [A_y:B_y]\sin^2\phi) \end{aligned} \quad (4.12)$$

where $\phi \equiv \phi_A = \phi_B$ and plus and minus refer to a conrotation and disrotation, respectively. The orbital energies corresponding to (4.12) are plotted as a function of the reaction coordinate ϕ in Figure 4.

B. The Hückel-Hubbard Procedure. The full Hückel-Hubbard Hamiltonian (4.1) is now given by

$$\mathbf{H}^\pm = \mathbf{H}_h^\pm + \mathbf{H}_I \quad (4.13)$$

where (4.2) becomes

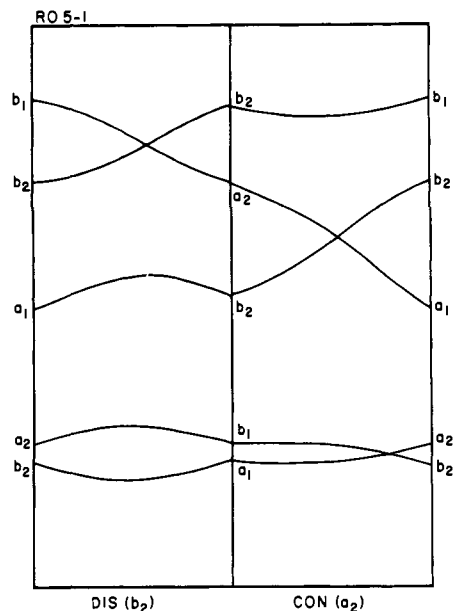
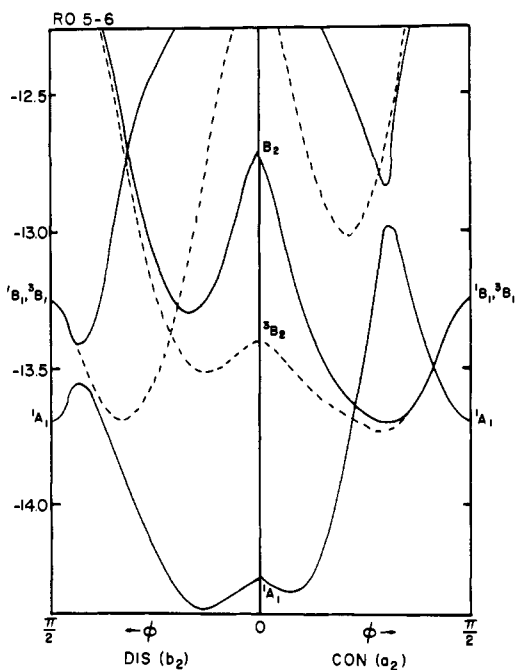
$$\mathbf{H}_h^\pm = \sum_i \mathbf{h}_i^\pm \quad (4.14)$$

with \mathbf{h}_i^\pm given by (4.12). The remaining unspecified parameter, I , is chosen to be equal to $2T = 6.0$ eV. This value reproduces the unpaired electron density of allyl radical.¹⁰

The matrix representations of (4.13) on the full configuration spaces are especially easy to compute by methods discussed elsewhere.^{11,12} The dimensions of these spaces are 50 and 45 for the singlet and triplet cation ($n = 6$), respectively, 40 and 10 for the doublet and quartet radical ($n = 7$), and 15 and 10 for the singlet and triplet anion ($n = 8$). The eigenvalues of (4.13) may then be obtained for various values of the reaction coordinate, ϕ . The resulting plots are given in Figures 5-7. Finally, we note that nonconcerted paths may be considered if we allow independent variation of ϕ_A and ϕ_B .

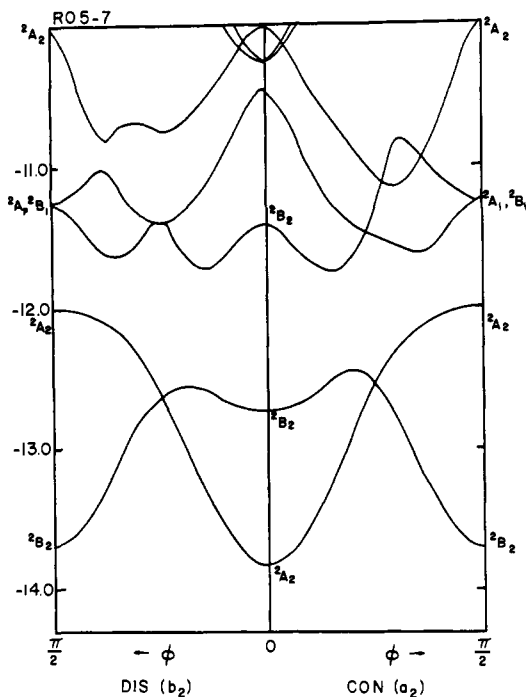
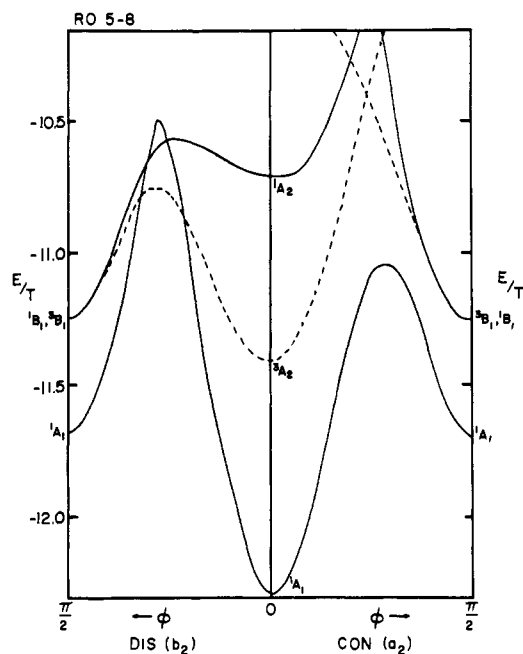
V. Discussion

The results of the Hückel-Hubbard calculations for $n = 1$ (which reduce to Hückel-like orbital correlations), $n = 6$ (cation), $n = 7$ (radical), and $n = 8$ (anion) are plotted in Figures 4-7. We note that for $n = 1$, the results are consistent with the OCAMS correspondence diagram (Figure 3). This establishes that the correspondence diagram has a sound quantum mechanical basis and also that the Hückel-Hubbard Hamiltonian (4.13) incorporates all the information contained in the OCAMS procedure. It is particularly pleasing that, since the two σ -CH orbitals are in correspondence for both the disrotatory and conrotatory paths, they remain filled orbitals throughout the reactions and so provide a formal justification for the three-orbital analysis. The remaining three orbitals then mimic the conventional three-orbital correlation diagram.^{1,2}


 Figure 4. Computed orbital energies as functions of the rotation angle ϕ .

 Figure 5. Computed Hueckel-Hubbard state energies as functions of ϕ for the cationic ($n = 6$) system.

The activation energies from the cation, anion, and radical surfaces are listed in Table II together with the OCAMS predictions. We see that, even with full configuration interaction, there is strong qualitative agreement. In particular, we note that the thermal reactions are in agreement for all species, including the difference in the two paths predicted for the radical.

For the photochemical reactions, the two theories are in agreement with two exceptions: (1) OCAMS predicts that disrotatory isomerization of the cation should be less forbidden than the conrotatory isomerization of the cation should be less forbidden than the conrotatory isomerization of the anion. This disagreement may rest in the fact that small barriers which result from multiple noncorrespondences may not be observed in a many-body calculation where the energy separations between correlating states is large. (2) The Hueckel-Hubbard calculations, with the present set of parameters, indicate that


 Figure 6. Computed Hueckel-Hubbard state energies as functions of ϕ for the radical ($n = 7$) system.

 Figure 7. Computed Hueckel-Hubbard state energies as functions of ϕ for the anionic ($n = 8$) system.

the first excited state of cyclopropyl radical is neither of the two configurations considered. Instead, it is a third configuration, $\sigma(a_1)\pi(b_2)\sigma^*(b_1)$ with overall state symmetry, A_2 , which consequently correlates with the A_2 ground state of allyl. This correlation is also expected on the basis of valence bond arguments.¹³ This is in fact a general problem with purely MO considerations. This point will be discussed in detail elsewhere. Although the order of these states could only be resolved by experiment or by a more complete calculation which maintains adequate configuration interaction, it is nonetheless of interest to note that the above correlation can be effected by the OCAMS procedure, but only if rule 2 of section III is relaxed

Table II. Hueckel-Hubbard Barrier Heights (Ring Opening, eV) and OCAMS Selection Rules

	Dis		Con	
	Thermal			
Cation	0.36 (A)		2.13 (F)	
Anion	3.12 (F)		1.95 (A)	
Radical ^a	3.12 (F)		3.69 (FF)	
Photochemical				
Cation	5.13 (F)		1.56 (A)	
Anion	1.80 (A)		5.13 (FF)	
Radical (ring opening)				
B ₁ : $[\sigma(a_1)]^2\sigma^*(b_1) \rightarrow$ allyl	0.00 (A)		1.34 (FF)	
A ₁ : $\sigma(a_1)[\pi(b_2)]^2 \rightarrow$ allyl	0.79 (F)		0.00 (A)	
A ₂ : $\sigma(a_1)\pi(b_2)\sigma^*(b_1) \rightarrow$ allyl	0.00 (A)		0.00 (A)	
Radical (ring closure)	0.51 (A)		0.84 (A)	

^a Here EA defined as height of crossing.

and if orbitals are brought into correspondence electron by electron.^{4c}

$$\sigma(a_1)\pi(b_2)\sigma^*(b_1) \leftrightarrow \psi_1(b_2)\psi_1(b_2)\psi_2(a_2)$$

$$\pi(b_2) \leftrightarrow \psi_1(b_2) \text{ direct}$$

$$\sigma(a_1) \leftrightarrow \psi_2(a_2) \text{ con(A), dis(F)}$$

$$\sigma^*(b_1) \leftrightarrow \psi_1(b_2) \text{ con(A), dis(F)}$$

or

$$\pi(b_2) \leftrightarrow \psi_1(b_2) \text{ direct}$$

$$\sigma(a_1) \leftrightarrow \psi_1(b_2) \text{ dis(A), con(F)}$$

$$\sigma^*(b_1) \leftrightarrow \psi_2(a_2) \text{ dis(A), con(F)}$$

The previous Hueckel-Hubbard calculations on this reaction using a three-orbital basis obeyed a particle-hole theorem which exactly reversed the predictions of the cation and anion and required the radical reaction to be totally nonstereospecific.^{2c} The extension of the treatment to five orbitals removes the restriction due to the particle-hole theorem as can be seen immediately from Figures 5-7.

In Table III, the Hueckel-Hubbard barrier heights are compared to the MINDO/3 calculations of Dewar et al.¹⁴ Again we see strong qualitative agreement. Of special interest are the barriers to the thermal isomerization of the radical. The OCAMS predicts that the disrotatory path should be less forbidden than the conrotatory path. The Hueckel-Hubbard calculations then specify that the difference in barrier heights be small. The MINDO/3 calculations bear this out. We also see that the conrotatory thermal reactions of the anion are less allowed than the disrotatory reaction of the cation as predicted by MINDO/3. (Hueckel-Hubbard theory probably overestimates this effect.)

We have considered only reactions in which the a_2 or b_2 symmetry is strictly conserved along the reaction path. However, Figures 5-7 provide information about processes in which a small nonsymmetric distortion would allow "funneling" from one surface to another thus reducing the effective barriers to reactions. For instance, the barrier to the thermal conrotatory transformation of the cation would be greatly reduced by such a distortion. Also the singlet excited state of the reactant may transform directly to the ground state of the product by a similar mechanism, whereas the triplet state would be expected to remain on the excited state surface and correlate with the triplet excited state of the product. In the radical, similar considerations are implicit in regarding the crossing-point to be the barrier of the reaction (Figure 6). A full nonconcerted reaction surface exhibiting these effects has previously been obtained for the three-orbital Hueckel-Hubbard model of the radical.^{2c}

Table III. Hueckel-Hubbard Barrier Heights (eV)

		HH		MINDO/3	
		Dis	Con	Dis-con	dis-con
Thermal					
Cation	(A→C)	2.13	3.90	-1.77	
	(C→A)	0.36	2.13	-1.77	-1.29
Anion	(A→C)	4.89	3.72	1.17	
	(C→A)	3.12	1.95	1.17	1.79
Radical	(A→C)	3.51	4.08	-0.57	
	(C→A)	3.12	3.69	-0.57	-0.35
Photochemical					
Cation	(A→C)	5.94	0	5.94	
	(C→A)	5.13	1.56	3.57	
Anion	(A→C)	0.63	5.94	-5.31	
	(C→A)	1.80	5.13	-3.33	
Radical	(A→C)	0.51	0.84	-0.33	
	(C→A)	0	0	0	

VI. Conclusion

We have shown that for a complete symmetry analysis, the minimum basis set for an n -carbon-atom electrocyclic reaction must contain $n + 2$ orbitals. In particular, we have extended the conventional three-orbital analysis of the allyl-cyclopropyl isomerization by employing OCAMS and Hueckel-Hubbard calculations on a five-orbital basis. The analysis shows that the low-lying σ bonding orbitals correlate with each other, thus shoring up the foundation of and supporting the use of the three-orbital analysis.

The OCAMS suggests and the Hueckel-Hubbard calculations confirm that many details of the reaction paths missing from the three-orbital analysis are picked up if one employs the expanded basis set. It is also seen that the effects of configuration interaction in the Hueckel-Hubbard results are important in considering possible photochemical pathways. The numerical results for the thermal reactions compare qualitatively with the MINDO/3 results and also those of Pople et al.¹⁵ and Farnell and Richards.¹⁶ It appears therefore that OCAMS and/or Hueckel-Hubbard theory isolate important qualitative features of the problem, thereby providing useful substitutes to higher calculations. They also identify areas of interest where more extensive calculations should be performed.

Appendix

The Schroedinger-Born-Oppenheimer Hamiltonian. We use the Neumann expansion in real form

$$\frac{1}{|\bar{r} - \bar{R}|} = \sum_{l=0}^{\infty} \sum_{r>l+1} \frac{r<l}{r>l+1} \frac{4\pi}{2l+1} \sum_{m=-l}^l \Theta_{l|m|}(\theta)\Theta_{l|m|}(\theta) \times [\cos(m\Phi)\cos(m\phi) + \sin(m\Phi)\sin(m\phi)] \quad (\text{A1})$$

in which (r, θ, ϕ) and (R, Θ, Φ) are the spherical polar coordinates of an electron at \bar{r} and a nucleus at \bar{R} , respectively. Changing the summation order we get

$$\frac{1}{|\bar{r} - \bar{R}|} = \frac{1}{4} \sum_{m=-\infty}^{\infty} [\cos(m\Phi)\cos(m\phi) + \sin(m\Phi)\sin(m\phi)] Z_m(r, \theta; R, \Theta) \quad (\text{A2})$$

where

$$Z_m(r, \theta; R, \Theta) = \sum_{l=|m|}^{\infty} \frac{16\pi}{2l+1} \cdot \frac{r<l}{r>l+1} \Theta_{l|m|}(\theta)\Theta_{l|m|}(\theta)$$

Local coordinate axes (x, y, z) and (x', y', z') are introduced on carbons A and B, respectively (Figure 1b); 1, 2 and 1', 2' are the hydrogens which rotate in circles of radius $\rho \sin \theta$ about carbons A and B in the planes (x, y) and (x', y') respectively, ρ being the bond length and 2θ the HCH angle.

The attraction of an electron at r_A, θ, ϕ (with respect to

carbon atom A) to the hydrogens 1 and 2 is given by

$$\begin{aligned} \frac{1}{r_1} + \frac{1}{r_2} &= \frac{1}{4} \sum_{m=-\infty}^{\infty} Z_m(r_A, \theta) [\cos(m\Phi_A) \cos(m\phi) \\ &+ \sin(m\Phi_A) \sin(m\phi)] + [\cos(m(\Phi_A + \pi)) \cos m\phi \\ &+ \sin(m(\Phi_A + \pi)) \sin(m\phi)] \\ &= \frac{1}{2} \sum_{m=-\infty}^{\infty} Z_m(r_A, \theta) [\cos(m\Phi_A) \cos(m\phi) \\ &+ \sin(m\Phi_A) \sin(m\phi)] \frac{(1 + (-1)^m)}{2} \quad (\text{A3}) \end{aligned}$$

where $Z_m(r_A, \theta) \equiv Z_m(r_A, \theta; \rho, \theta)$. One straightforwardly obtains

$$\begin{aligned} \frac{1}{r_1} + \frac{1}{r_2} &= \frac{1}{2} Z_0(r_A, \theta) \\ &+ \sum_{m=1}^{\infty} Z_{2m}(r_A, \theta) [\cos(2m\Phi_A) \cos(2m\phi) \\ &+ \sin(2m\Phi_A) \sin(2m\phi)] \quad (\text{A4}) \end{aligned}$$

The complete one-electron Hamiltonian can now be written in the form

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0 + \left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \left(\frac{1}{r_1'} + \frac{1}{r_2'}\right) \\ &= \mathcal{H}_0' + \sum_{m=1}^{\infty} \{Z_{2m}(r_A, \theta_A) [\cos(2m\Phi_A) \cos(2m\phi_A) \\ &+ \sin(2m\Phi_A) \sin(2m\phi_A)] + Z_{2m}(r_B, \theta_B) [\cos(2m\Phi_B) \\ &\times \cos(2m\phi_B) + \sin(2m\Phi_B) \sin(2m\phi_B)]\} \quad (\text{A5}) \end{aligned}$$

where

$$\mathcal{H}_0' = \mathcal{H}_0 + \frac{1}{2} [Z_0(r_A, \theta_A) + Z_0(r_B, \theta_B)]$$

is totally symmetric with respect to the common C_{2v} group of the allyl and cyclopropyl systems.

From the form of the one-electron Hamiltonian, eq A5, it follows that the one-electron matrix elements will depend on the reaction coordinates Φ_A and Φ_B through symmetric sums of the form $\cos(2m\Phi_A) + \cos(2m\Phi_B)$ and $\sin(2m\Phi_A) + \sin(2m\Phi_B)$. The periodicity of 180° in these coordinates is, of course, explicit in these terms.

The representation of the Hamiltonian, eq A5, in the one-electron basis set A_x, A_y, B_x, B_y, C_y , consisting of p_x and p_y type orbitals on the three carbon atoms, is given by

$$\mathcal{H}_{\text{rep}} = |A_x\rangle \langle A_x | \mathcal{H} | A_x\rangle \langle A_x| + |A_x\rangle \langle A_x | \mathcal{H} | A_y\rangle \langle A_y| + \dots \quad (\text{A6})$$

The relevant matrix elements will now be evaluated:

$$\begin{aligned} \langle A_x | \mathcal{H} | A_x\rangle &= \langle A_x | \mathcal{H}_0' | A_x\rangle + \sum_{m=1}^{\infty} \left\{ \langle A | | Z_{2m}(A) | | A \rangle \right. \\ &\times \frac{2}{\pi} \left[\cos(2m\Phi_A) \int_0^{2\pi} \cos^2 \phi_A \cos(2m\phi_A) d\phi_A \right. \\ &+ \left. \sin(2m\Phi_A) \int_0^{2\pi} \cos^2 \phi_A \sin(2m\phi_A) d\phi_A \right] \\ &\left. + \langle A | | Z_{2m}(B) | | A \rangle \cdot [\dots] \right\} \end{aligned}$$

Here $\langle A | | Z_{2m}(A) | | A \rangle$, etc., are reduced matrix elements. Neglecting the two-center term $\langle A | | Z_{2m}(B) | | A \rangle$ and evaluating the elementary integrals we get

$$\langle A_x | \mathcal{H} | A_x\rangle = \langle A | | \mathcal{H}_0' | | A \rangle + \langle A | | Z_2(A) | | A \rangle \cos(2\Phi_A) \quad (\text{A7})$$

Similarly

$$\langle A_x | \mathcal{H} | A_y\rangle = \langle A | | Z_2(A) | | A \rangle \sin(2\Phi_A) \quad (\text{A8})$$

because, \mathcal{H}_0' being totally symmetric, $\langle A_x | \mathcal{H}_0' | A_y\rangle = 0$. Also,

$$\langle A_y | \mathcal{H} | A_y\rangle = \langle A | | \mathcal{H}_0' | | A \rangle - \langle A | | Z_2(A) | | A \rangle \cos(2\Phi_A) \quad (\text{A9})$$

Typical two-center terms are

$$\langle A_x | \mathcal{H} | C_y\rangle = \langle A | | Z_2(A) | | C \rangle \sin(2\Phi_A) \quad (\text{A10})$$

$$\langle A_y | \mathcal{H} | C_y\rangle = \langle A_y | \mathcal{H}_0' | C_y\rangle - \langle A | | Z_2(A) | | C \rangle \cos(2\Phi_A) \quad (\text{A11})$$

$$\begin{aligned} \langle A_x | \mathcal{H} | B_x\rangle &= \langle A_x | \mathcal{H}_0' | B_x\rangle + \langle A_x | | Z_2(A) | | B_x\rangle \\ &\times (\cos(2\Phi_A) + \cos(2\Phi_B)) + \dots \quad (\text{A12}) \end{aligned}$$

The dependence on Φ_A and Φ_B is easily shown to agree with that established in a heuristic manner in the construction of eq 4.9, 4.10, and 4.11.

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