

Part 2

Applications to Thermal Reactions

In Chapters 1-3 the theoretical foundations were laid that are needed to understand the energetics of reactions taking place on a single potential energy surface. It would be quite difficult to apply those concepts in a rigorous quantitative fashion to any reaction involving a potential energy surface having more than a few degrees of freedom. The process of walking along the reaction coordinate requires that the potential surface be explored and that the precise nature of the reaction coordinate Q_r be determined. Although such calculations have recently become feasible for systems containing three or four atoms, one almost never knows *exactly* how to walk along Q_r for reactions of more complicated molecules. Therefore, in most applications of symmetry-conservation concepts, a reaction path is *postulated*, and one attempts to explore how the orbital, configuration, and state energies vary along this path. One hopes that, by choosing a path that gives rise to favorable overlap of the important orbitals of the reactant species, the postulated path is close to the true reaction coordinate.

Another problem is that, in addition to being able to know the reaction coordinate precisely, reaction pathways other than those chosen may be available. For example, if the one-step four-center reaction of H_2 with I_2 to produce $2HI$ were examined, a reasonable conclusion would be that the reaction has a high activation energy. However, this conclusion does not eliminate the possibility that HI can be formed by some other mechanism, so it is important to explore all pathways that might yield the desired products. The symmetry methods illustrated in this chapter and those for photochemical reactions in Chapter 7 can be used to analyze any single reaction step that involves breaking old bonds and *simultaneously* forming new product bonds. If a proposed reaction path causes reactants to give rise to products in a single step, the reaction is termed *concerted*. The symmetry rules can be applied to the single step of such concerted reactions to predict directly whether the reaction would have a large activation energy. For stepwise reaction mechanisms, the symmetry

rules must be applied to each step. If any step in the reaction is predicted to have a large activation energy, the overall reaction would not be expected to proceed with great speed.

It is suggested that readers who have not recently made use of point-group symmetry tools such as character tables, direct products, and projection operators read Appendix C before beginning the examples treated in Chapter 4.

Chapter 4

Examples for Analyzing Ground-State Thermal Processes

In this chapter several examples of applications of the symmetry arguments are presented.

4.1. Simple Predictions from Orbital-, Configuration-, and State-Correlation Diagrams

The thermal addition reaction of a nitrogen molecule and a hydrogen molecule to yield *cis*-diimide is a straightforward problem.



We begin by considering only the orbitals directly involved in changing the bonds and assume that C_{2v} symmetry is preserved during the reaction path—this is the guess of the reaction coordinate. The steps for attacking the problem are the following:

1. An orbital-correlation diagram is drawn for the proposed reaction path.
2. A hypothesis is made for the likely (energetically favorable) configurations, and a configuration-correlation diagram is constructed.
3. The state-correlation diagram is made and is then used to determine whether the reaction is thermally allowed along this reaction path.

If we *assume* that the reaction coordinate involves the C_{2v} approach as shown in Figure 4-1, the active orbitals are the bonding and antibonding σ_{HH} and π_{NN} orbitals. Notice that we are not trying to deduce the reaction coordinate but merely proposing a reaction coordinate and observing whether a high barrier to *that* reaction is expected. The basic approach is to try all reaction pathways that we believe to be likely for good bond formation. If we then assume that the potential energy surface can be smoothly interpolated between

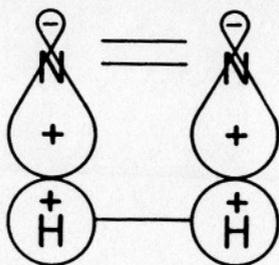


Figure 4-1
Cis addition path.

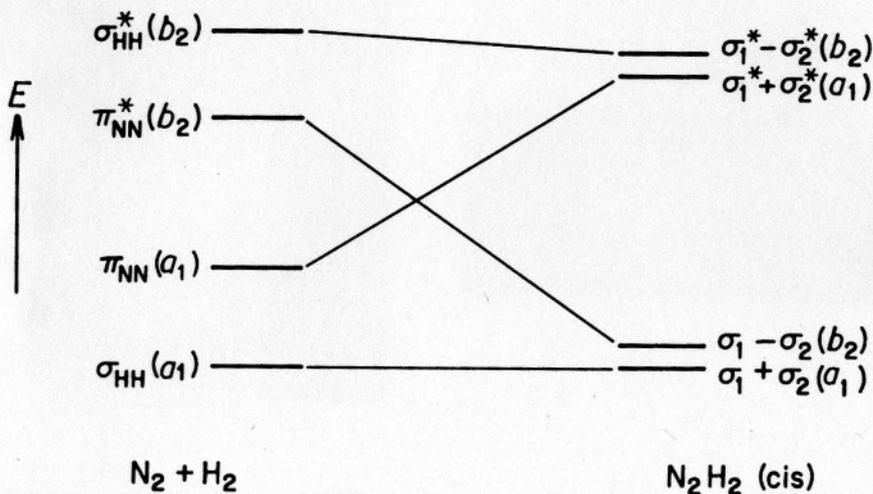


Figure 4-2
Orbital-correlation diagram for cis addition.

these postulated pathways, which have some symmetry, then a qualitative picture of the full surface can be obtained.

Since nitrogen is more electronegative than hydrogen, the expected energy ordering of the N_2 and H_2 orbitals is that shown in Figure 4-2. The spacing between the bonding and antibonding H_2 orbitals is larger than for the N_2 π bond energy. In more complicated situations, one often resorts to using information about valence ionization potentials to provide, via Koopmans' theorem (Pilar, 1961), the ordering of the orbital energies for reactants and products. Figure 4-2 also yields the symmetries of the orbitals of both $N_2 + H_2$ and cis-

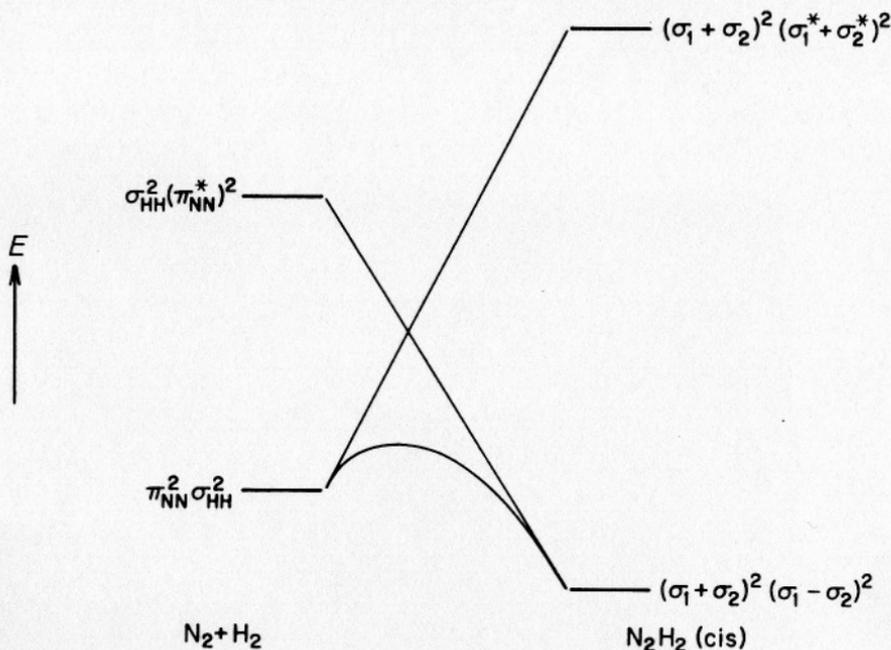


Figure 4-3
Configuration-correlation diagram and state-correlation diagram for cis addition.

reaction $\text{N}_2 + \text{H}_2 \rightarrow \text{HNNH}$ is forbidden (remember that only cis-HNNH is being treated here because we assume C_{2v} symmetry); we still have to look at the configuration-correlation diagram and the state-correlation diagram.

Since the ground electronic states of N_2 and H_2 possess double occupancy of the bonding π_{NN} orbital and the bonding σ_{HH} orbital, the $\pi_{\text{NN}}^2 \sigma_{\text{HH}}^2$ configuration, which has $(a_1^2 a_1^2) = {}^1A_1$ symmetry, should be important. At the other end of the assumed reaction coordinate is cis-HNNH, which should be dominated by the $(\sigma_{\text{NH}_1}^2)(\sigma_{\text{NH}_2}^2) = (a_1^2)(b_2^2) = {}^1A_1$ configuration. The fact that these two configurations do not correlate is shown in Figure 4-3, which also shows the avoided configuration crossing that gives rise to the state-correlation diagram. Notice that configurations are correlated according to the symmetries of the orbitals that are occupied in the configurations rather than by their overall space-spin symmetry. The steepness of the two configuration energy lines shown in Figure 4-3 is determined by the relative energies of the two dominant configurations at the extremes of the reaction coordinate. For example, the $\pi_{\text{NH}}^2 \sigma_{\text{HH}}^2$ configuration, which correlates to $\sigma_{\text{NH}}^2 \sigma_{\text{NH}}^2$, is expected to be very high in energy (since both NH bonds are broken) on the diimide side of the reaction. Based upon the above state-correlation diagram, a substantial

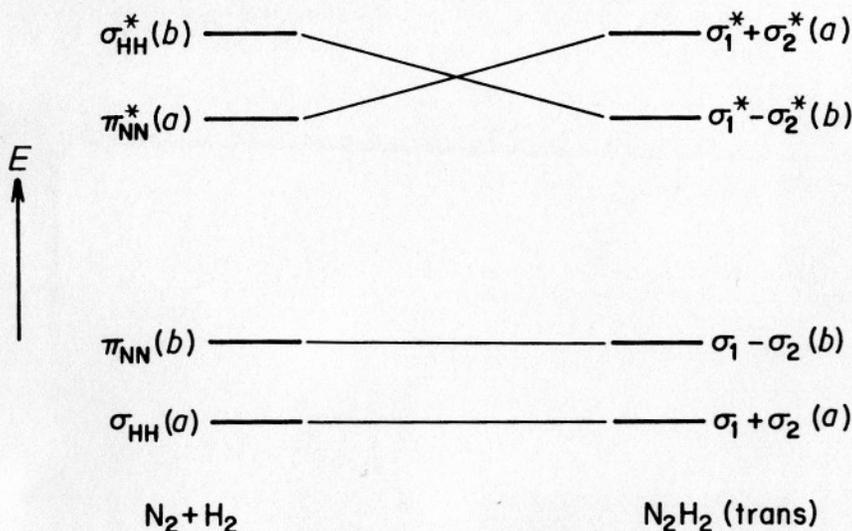


Figure 4-4
Orbital-correlation diagram for trans addition.

We must also consider whether the interaction between the two configurations that cross would be large enough to produce such strongly avoided crossings that the state-correlation diagram would show no barrier. This is not likely because the configuration coupling is caused only by the r_{ij}^{-1} terms in h_c (since the configurations differ by *two* orbitals as discussed in Appendix A), and these electronic interaction terms are usually quite small. Hence, configuration pairs that differ by two orbitals relative to one another should display *weakly* avoided crossings. Notice that the orbital crossing (noncorrelation) leads to the configuration noncorrelation, from which a high barrier is predicted. The above analysis shows that this reaction is thermally forbidden. The word *thermal* is employed because the molecular orbitals are occupied in a way that is appropriate to the ground states of reactants and products, and the system is considered to move on this ground-state surface. The reaction is forbidden only because a large symmetry-imposed activation barrier to this thermal reaction should be present.

We now consider the reaction $\text{N}_2 + \text{H}_2 \rightarrow \text{HNNH}(\text{trans})$. The relevant point group is now C_2 (where the C_2 rotation axis is perpendicular to the plane of the molecule, and the orbital correlation diagram is given in Figure 4-4. Now the orbital symmetries correlate differently, so that the configuration-correlation diagram (Figure 4-5) does not involve configuration crossing (i.e.,

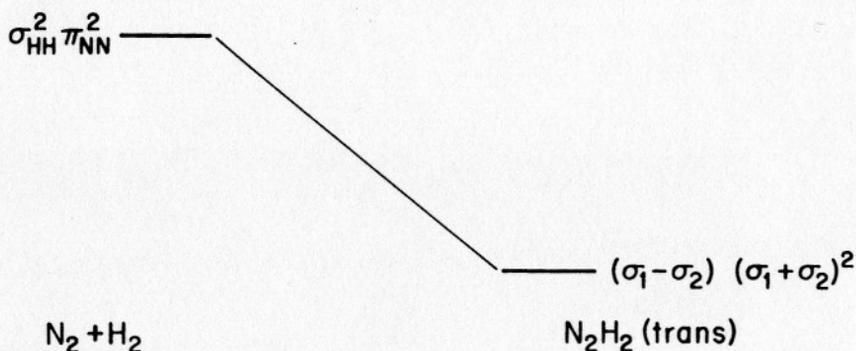


Figure 4-5

Configuration-correlation diagram and state-correlation diagram for trans addition.

$\pi_{\text{NN}}^2 \sigma_{\text{HH}}^2$ correlates directly with $\sigma_{\text{NH}_1}^2 \sigma_{\text{NH}_2}^2$). Hence, the formation of trans-HNNH via a C_2 reaction coordinate should involve no significant symmetry-imposed barrier. Thus, N_2H_4 should thermally fragment via a *trans* reaction coordinate, and H_2 should attack N_2 in a *trans* manner. This latter prediction is based upon symmetry considerations alone, and it does *not* mean that such a *trans* attack would occur easily—for example, in a collision. In fact, such a collision is not likely to be successful, since the bond length of the H_2 molecule is so short that a great deal of energy would be required just to stretch the H_2 sufficiently to make formation of the two new NH bonds feasible.

The above symmetry considerations include nothing about geometrical factors or the overall reaction thermodynamics (such as bond strengths of the reactant and product); symmetry only makes requirements on the nodal patterns of the important orbitals. It is essential to keep this point in mind in all subsequent problems.

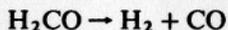
Notice also that, because the C_{2v} point group has no degenerate representations, nowhere (except at infinite separation) along the hypothetical reaction path do any orbitals or states become degenerate. Hence, questions involving first-order Jahn-Teller instability do not occur in this example.

Only two possible reaction paths have been considered, and it is reasonable to wonder whether collisions that are slightly non- C_{2v} can yield *cis*-diimide, because in the C_s point group, which would rigorously pertain to such a collision, the a_1 and b_2 orbitals both have a' symmetry. As a result, the rigorous orbital-correlation diagram would *not* include an orbital crossing and, hence, the configuration-correlation diagram and state-correlation diagram would not predict a forbidden reaction. However, this rigorous analysis is incorrect! The concept of near symmetry also allows us to apply conclusions based upon

C_{2v} symmetry analysis to collisions that involve near- C_{2v} geometries. That is, near the C_{2v} geometry that was analyzed, a symmetry-imposed barrier, whose precise shape and height will vary somewhat as one moves further from C_{2v} geometry, will still be present. As will be seen in later examples, it is not the rigorous symmetry that actually gives rise to orbital symmetry nonconservation but the nodal characteristics of the orbitals. These nodal patterns remain even when rigorous symmetry is lost.

4.2. An Example of Unimolecular Decomposition

This example makes use of more quantitative data on ionization energies to order the molecular orbitals. If such data is available, it is certainly wise to use it, because then one can make more quantitative predictions about the thermal and photochemical behavior of a system. As an example, the thermal decomposition of formaldehyde to carbon monoxide and a hydrogen molecule



is analyzed. A minimum-basis molecular-orbital calculation has been carried out (Cook, 1978; Pilar, 1968; Schaefer, 1971) and has yielded the orbital energies (in eV) given in Table 4-1. We begin by postulating a reaction coordinate, by assuming that C_{2v} symmetry is preserved during the decomposition, and proceed through the following steps:

1. The symmetry of the molecular orbitals of the formaldehyde molecule, the hydrogen molecule, and carbon monoxide are classified according to the point-group symmetry that is preserved during the reaction path.
2. An orbital-correlation diagram for this reaction path is drawn.
3. A configuration-correlation diagram is constructed, and the state-correlation diagram is used to determine whether the thermal decomposition of formaldehyde is allowed.

The irreducible representations of the formaldehyde molecular orbitals given in Table 4-1 determine the coordinate system to be used. The $1a_1$ and $2a_1$ molecular orbitals are the $1s$ orbitals on oxygen and carbon, respectively. All a_1 orbitals have the symmetry of the z coordinate axis. The $1b_1$ orbital is unique among the occupied molecular orbitals and, hence, must represent the π molecular orbitals of the carbonyl group that are aligned along the y axis, lying perpendicular to the plane of the formaldehyde molecule (Figure 4-6). The symmetry labels that can thus be attached to the active molecular orbitals are the following:

The hydrogen molecule. $1\sigma_g(a_1)$, $1\sigma_u(b_2)$

TABLE 4-1
ORBITAL ENERGIES IN eV FOR
FORMALDEHYDE, CARBON MONOXIDE, AND
HYDROGEN

Formaldehyde (C_{2v})	Carbon monoxide ($C_{\infty v}$)	Hydrogen ($D_{\infty h}$)
$1a_1$ -553.4	1σ -553.3	$1\sigma_g$ -17.51
$2a_1$ -302.8	2σ -302.7	$1\sigma_u$ 20.05
$3a_1$ -36.52	3σ -35.82	
$4a_1$ -23.02	4σ -19.92	
$1b_2$ -18.48	1π -15.78	
$5a_1$ -15.09	5σ -13.09	
$1b_1$ -12.22	2π 7.07	
$2b_2$ -10.28	6σ 25.36	
$6a_1$ 3.99		
$2b_1$ 7.10		
$7a_1$ 19.75		
$3b_2$ 23.07		

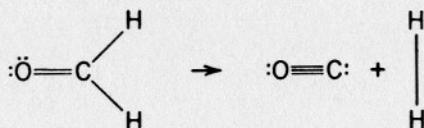


Figure 4-6
Decomposition of formaldehyde.

Carbon monoxide. All of the σ and lone-pair orbitals transform as a_1 ; the π orbitals transform as b_1 and b_2 ; the π^* orbitals also transform as b_1 and b_2 .

Formaldehyde. The CO σ and one of the CH σ bonds transform as a_1 , the other CH σ bond as b_2 , the nonbonding orbitals on oxygen as a_1 and b_2 , and the CO π and π^* orbitals as b_1 .

The orbital-correlation diagram that results from simply connecting the orbital lists of H_2CO and $H_2 + CO$ is given in Figure 4-7. Notice that several orbital crossings are present, so the possibility exists that an activation barrier will be predicted. By using the 16 electrons to occupy the lowest 8 molecular orbitals of H_2CO (since we are considering the thermal or ground-state reaction)

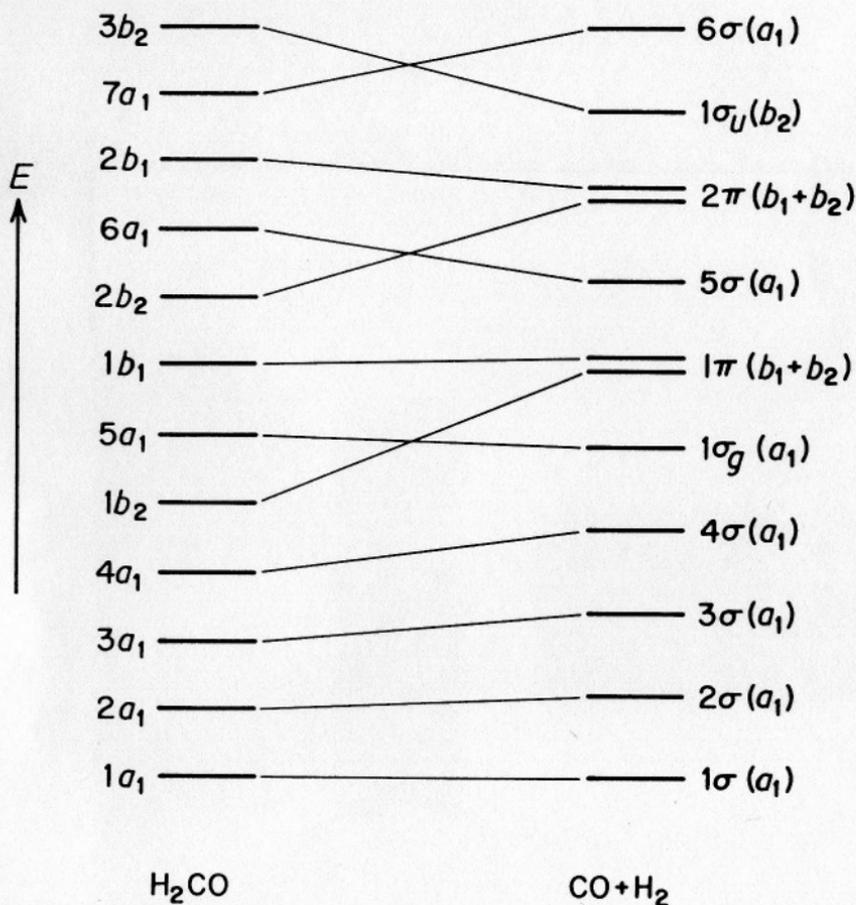


Figure 4-7
Orbital-correlation diagram for decomposition of formaldehyde.

the $2b_2^2$ part of the resulting configuration correlates with a $2\pi^2$ occupancy of CO (i.e., double occupancy of an antibonding π_{CO}^* orbital). The 2π orbital of the ground state of CO is not doubly occupied. The crossing of the $5a_1$ and $1b_2$ orbital energies is not relevant, for both of these orbitals are doubly occupied in the ground states of both the reactant and the product.

The configuration-correlation diagram shown in Figure 4-8 results when the lowest 8 orbitals of CO + H₂ and of H₂CO are occupied by the 16 electrons. The two configurations that cross do have the same overall symmetry (1A_1), so they can mix to give the state-correlation diagram also shown in Figure 4-8 by the dashed lines. However, the existence of the orbital

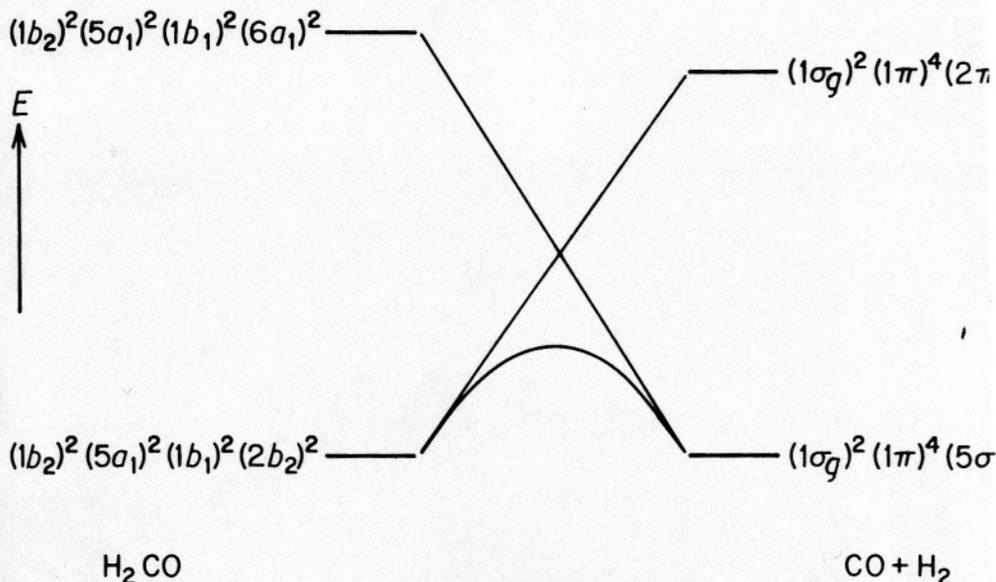


Figure 4-8

Configuration-correlation diagram and state-correlation diagram for decomposition of formaldehyde.

thermal reaction. Since the two configurations that cross differ with respect to one another by two electron occupancies, only the electron-electron interaction terms (r_{ij}^{-1}) in h_c couple them together. Hence, the barrier predicted by the configuration crossing should not be substantially lowered in going to the state-correlation diagram.

Because of the low point-group symmetry (C_{2v}), degenerate representations are not possible; therefore, first-order Jahn-Teller effects do not come into play. Notice also that if the reaction were to occur along a path that preserves only the one plane of symmetry (C_s point group), then both b_2 and a_1 orbitals become a' . Consequently, the reaction becomes orbitally allowed (since now the orbitals of reactants and products correlate) and, hence, allowed in the configuration- and state-correlation diagrams. Thus, the high barrier predicted for the C_{2v} path will probably be reduced when moving away from the C_{2v} path. However, the barrier should not *suddenly* disappear when moving slightly away from the C_{2v} symmetry because approximate symmetry is still present. In contrast, if we imagine distortions of H_2CO that make the molecule nonplanar but preserve the plane of symmetry bisecting the HCH bond angle, the crossing of the $2b_2$ and $6a_1$ orbitals would still occur, since these two orbitals have dif-

4.3. A Degenerate Case with Jahn-Teller Effects

In this section a case in which degenerate orbitals can occur is examined. We ask whether the π orbital structure of the cyclopropenyl radical (C_3H_3) favors an equilateral triangular structure. The $(C_3H_3)^+$ or $(C_3H_3)^-$ forms will also be considered. At the equilateral-triangle geometry, the p_π orbitals on the three carbon atoms can be combined to yield one orbital having a_1 symmetry (C_{3v} point group)

$$a_1 = P_A + P_B + P_C$$

and two degenerate orbitals of e symmetry

$$e = \left[\frac{P_A - P_C}{2P_B - P_A - P_C} \right]$$

These symmetry-adapted orbitals can be generated by applying the projectors (see Appendix C or Cotton, 1963)

$$P_i = \frac{1}{g} \sum_R \chi_i(R) R$$

to the individual atomic basis orbitals (P_A, P_B, P_C), in which $\chi_i(R)$ is the character of irreducible representation i . The two degenerate e orbitals that would be obtained are not orthogonal. After orthogonalization the two e orbitals given above are obtained. The a_1 orbital is bonding between all three carbon atoms, whereas the e orbitals are antibonding. Because only the effects of the π orbitals are examined here, all of the factors that determine the shape of C_3H_3 are not considered. If the σ -bonding effects are sufficiently strong (i.e., if the σ force constants are large enough), the π -orbital effects treated here will be negligible. However, they are still interesting and instructive to study.

What predictions can be made within these limitations? First, $(C_3H_3)^+$ should be stable at the equilateral-triangle geometry, since it would have both of its π electrons in the bonding a_1 orbital; thus, ψ_0 would be nondegenerate. Second, C_3H_3 should be first-order Jahn-Teller unstable, since the configuration $(a_1)^2 e$ is degenerate. The kind of vibration that will distort the equilateral-triangle geometry is predicted (by forming the direct product of $\psi_0^* \psi_0$ (Cotton, 1963) from the first-order Jahn-Teller matrix element $\langle \psi_0 | \partial h_e / \partial Q | \psi_0 \rangle$ to have $(e \times e = a_1 + e + a_2)$ or e symmetry (for this point group, a_2 is a rotation and e a symmetric ring distortion that would not break the degeneracy of ψ_0).

groups away from the other two. Consequently, equilateral triangle C_3H_3 is unstable and cannot even be a true transition state (since it has a nonzero value of slope). Third, $(C_3H_3)^-$ should not be stable at the equilateral-triangle geometry for two possible reasons: (1) it has two electrons in the antibonding e orbitals that would "cancel" any π bonding due to the two a_1 electrons (but the σ bonds would remain intact). (2) The configuration $(e)^2$ might be Jahn-Teller unstable. The $(e)^2$ configuration has symmetry components ${}^1A_1 + {}^3A_2 + {}^1E$, of which, by Hund's rules, the 3A_2 would be the lowest energy state. This triplet state is not spatially degenerate and is therefore not first-order Jahn-Teller unstable.

The above symmetry- and spin-term symbols for $C_3H_3^-$ are obtained by forming, for the singlet states (which have antisymmetric two-electron spin functions), the symmetric direct product $(e \times e)_+$; for the triplet (which has an even spin function), one forms the antisymmetric direct product $(e \times e)_-$. The characters (χ_{\pm}) for these two kinds of direct products are given in terms of the characters (χ) of the e representation of the individual orbitals appearing in the e^2 configuration as

$$\chi_{\pm}(R) = \frac{1}{2}[\chi^2(R) \pm \chi(R^2)].$$

Within the C_{3v} point group,

	E	$2C_3$	$3\sigma_v$
χ_+	3	0	1
χ_-	1	1	-1

Then, the χ_{\pm} are decomposed into their individual representations using the projections (Cotton, 1963)

$$n_i = \frac{1}{g} \sum_R \chi_i(R) \chi_{\pm}(R)$$

(g is the group order 6, and the χ_i are the characters of irreducible representations), which indicate the number of times (n_i) representation i occurs in χ_{\pm} . It is important to use these symmetric and antisymmetric direct products when dealing with two *equivalent* electrons. If the electrons were in different sets of degenerate orbitals ($1e, 2e$), then they are nonequivalent and you can use the usual direct product (Cotton, 1963).

The lowest energy state of $(e)^2({}^3A_2)$ is nondegenerate; thus, $(C_3H_3)^-$ is *not* unstable by a first-order Jahn-Teller distortion. Its unstable nature is an

did not have different spin symmetry from the 3A_2 ground state, then quadratic terms in the Jahn-Teller theory should come into play through the $\langle \psi_0 | \partial h_e / \partial Q | \psi_k \rangle$ factors. The distortion that should contribute would have either $A_2 \times A_1 = A_2$ or $A_2 \times E = E$ symmetry. The C_{3v} -character table shows that the molecule has no A_2 vibration, though it does have an E vibration. Hence, an E distortion should occur. Of course, this analysis is nothing but an exercise in futility because the different spin symmetries of the 3A_2 and (${}^1A_1, {}^1E$) states would make the $\langle \psi_0 | \partial h_e / \partial Q | \psi_k \rangle$ integrals vanish—unless spin orbit effects were very large—and this is not likely for $(C_3H_3)^-$.

4.4. The Bond-Symmetry Rule—Another Jahn-Teller Case

In this section we consider whether two ethylene molecules will combine to give cyclobutane if they collide in a D_{2h} -symmetry manner (in a head-on fashion such that their π orbitals bump into one another directly) and then examine the analogous exchange reaction $H_2 + D_2 \rightarrow 2HD$.

The orbital-correlation diagram for both of these reactions is shown in Figure 4-9, in which each orbital is labeled according to its D_{2h} symmetry (and according to the D_{4h} symmetry that appears once the four hydrogen atoms are equivalently located in the latter reaction). Notice, for $H_2 + D_2$, that the b_{2u} and b_{3u} orbitals cross at D_{4h} symmetry where they are symmetry-degenerate (e_u). These orbitals also cross in the case of ethylene, but not at D_{4h} symmetry. As a result of these orbital crossings, the ethylene $\pi^2 \pi^2 (a_g^2 b_{2u}^2)$ and $\sigma^2 \sigma^2 (a_g^2 b_{3u}^2)$ configurations also cross one another—they do not correlate (Figure 4-10). The corresponding configurations also cross in the case of H_2 and D_2 . Since both of these configurations have 1A_g symmetry, the state-correlation diagram will show an avoided crossing once they mix to give rise to two 1A_g state wave functions. A substantial barrier (an avoided crossing) to both of these reactions should be present, but it should be weakly avoided because the two participating configurations differ by two orbitals, so only the r_{ij}^{-1} can couple them.

If the D_{4h} geometry were proposed as a possible transition state for the hydrogen-exchange reaction, several kinds of motion that might be important in distorting this geometry must be considered. At D_{4h} , the configuration $a_{1g}^2 e_u^2$ —through the symmetric direct product for this singlet reaction—gives rise to ${}^1A_{1g} + {}^1B_{1g} + {}^1B_{2g}$ electronic states. Quantum chemical calculations indicated that the ${}^1B_{1g}$ state is the lowest singlet state. Thus, this $D_{4h} {}^1B_{1g}$ state is not first-order Jahn-Teller unstable, and we cannot conclude that the slope of the surface is nonzero along any nonsymmetric direction. Hence, it is possible that the square geometry is a transition state. Furthermore, quadratic Jahn-Teller effects involving $\langle {}^1B_{1g} | \partial h_e / \partial Q | {}^1A_{1g} \rangle$ could give rise to a $B_1 \times A_{1g} = B_1$ distortion of the molecule.

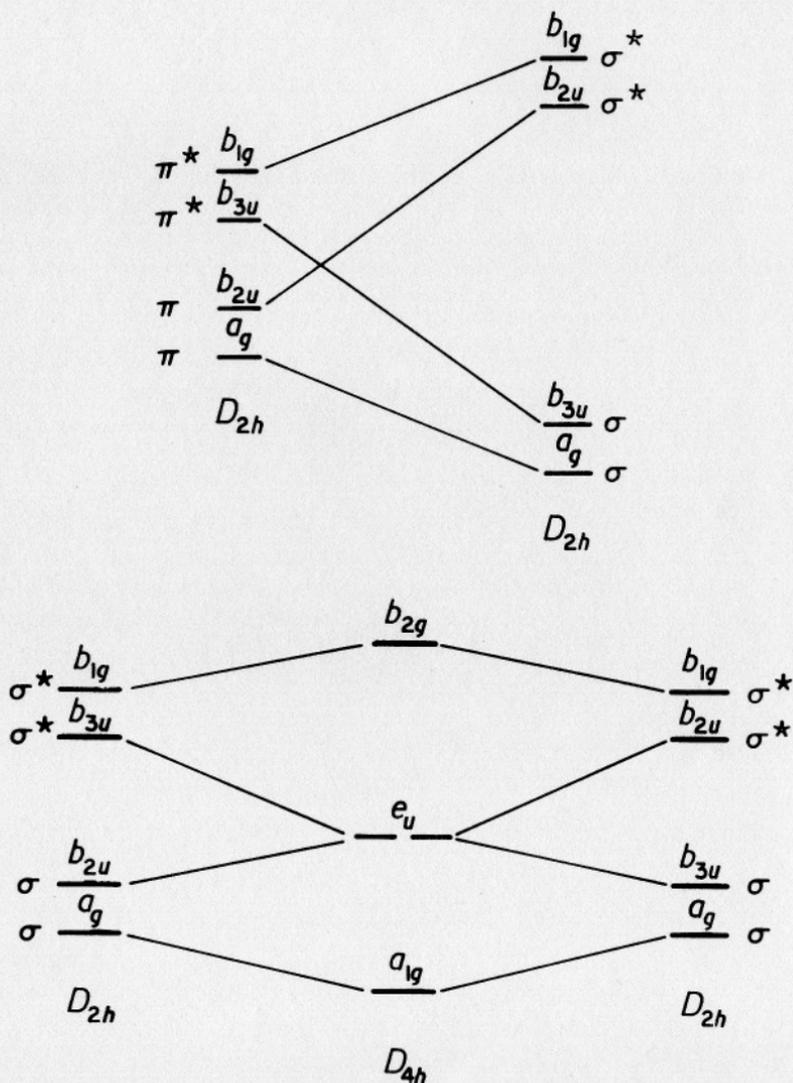


Figure 4-9

Orbital-correlation diagrams for (a) dimerization of ethylene and (b) H_2 - D_2 exchange.

The other distortion $B_{1g} \times B_{2g} = A_{2g}$ cannot occur because the D_{4h} point group has no A_{2g} vibration (Cotton, 1963). Thus a $D_{4h}H_4$ transition state

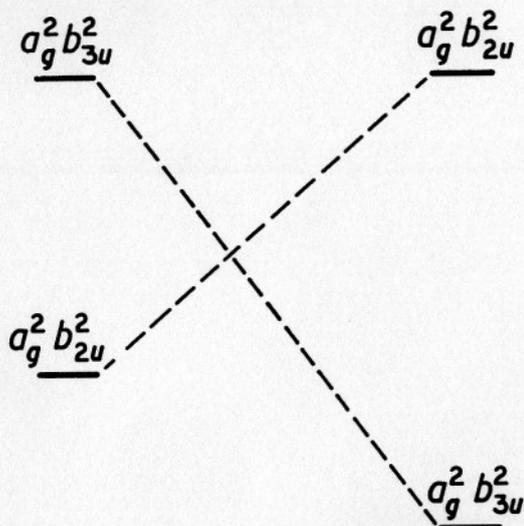


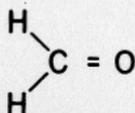
Figure 4-10
Configuration-correlation diagram for dimerization of ethylene.

vibration. The term *pseudo*-Jahn-Teller is used rather than second-order Jahn-Teller, because the excited state ($\psi_k = {}^1A_{1g}$) arises by electron rearrangement between the two degenerate e_u orbitals (analogous to the atomic orbital configuration p^2 giving rise to 3P , 1D , and 1S states) and not from electron promotion into an excited orbital. One cannot conclude that the square geometry is definitely pseudo-Jahn-Teller unstable because, from what has been said, it is not clear whether the negative-curvature terms caused by coupling of the ${}^1B_{1g}$ and ${}^1A_{1g}$ states are larger in magnitude than the positive-curvature terms described in equation 2.20—more quantitative information about these coupling matrix elements is needed to make this prediction.

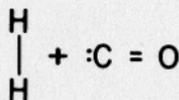
This example—two ethylenes combining to give cyclobutane—illustrates the concept called the *bond-symmetry rule* (Pearson, 1976). This rule states that a reaction will be orbitally forbidden—that is, involve orbital crossing problems—unless the symmetries of the bonds plus lone pairs broken in the reactants match the symmetries of bonds plus lone pairs formed in the products. For example, the rearrangement of benzene—which has one occupied a_1b_1 and $b_2\pi$ orbital (see Cotton, 1963, and section 7.5)—to give dewarbenzene



(which has two occupied a_1 orbitals and one occupied b_2 orbital) is forbidden. Also the C_{2v} decomposition of



to give



is forbidden, since the reactant has two a_1 and two b_2 orbitals (CH bonds and oxygen lone pairs), whereas the products have one b_2 orbital (the CO π bond) and three a_1 orbitals (HH and the :CO: lone pairs).

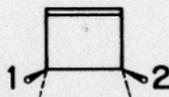
The addition of a halogen to the 1 position of dewarbenzene



reduces the symmetry from C_{2v} to C_s . As a result, the reactant has two a' and one a'' orbitals, as does the halobenzene. Thus, the reaction becomes allowed, though the reaction rate is still very low (Pearson, 1976, p. 90). The reason is that the halogen does not have a strong influence on the active orbitals, so C_{2v} symmetry (in which the reaction is forbidden) is approximately valid.

The bond-symmetry rule is, or course, nothing but a short cut for recognizing when nonconservation of occupied-orbital symmetry will occur. Whenever the symmetries of the occupied orbitals of reactants and products do not match, the orbital-correlation diagram will display a crossing of occupied and unoccupied orbitals, which then causes nonconservation of symmetries.

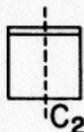
Use of this (or any other) symmetry rule requires that only symmetry elements that are preserved along the full reaction path are used to label the orbitals. Only for these symmetry elements is the reaction coordinate Q_r symmetric, and this is necessary if the orbital, configuration, and state symmetries are to remain constant (i.e., be correlated by symmetry) along the reaction path. For example, in considering the opening of



to give

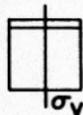


two possible "reaction paths" are commonly examined (Woodward and Hoffmann, 1970). Two kinds of ring opening—*conrotatory* and *disrotatory*—must be considered. In conrotatory opening, both CH_2 groups are twisted in the same direction (e.g., clockwise). When this motion is used as a reaction coordinate, the only symmetry element preserved throughout the reaction is a C_2 axis



The occupied σ and π orbitals of the reactant and the two occupied π orbitals in the 1,3-butadiene product are even and odd, respectively, with respect to this C_2 axis. Hence, the bond-symmetry rule indicates that conrotatory ring opening is orbitally allowed.

In disrotatory opening, the two CH_2 groups move in opposite directions. Such motion preserves a reflection plane σ , that runs down the middle of the molecule



Under this symmetry element the σ and π orbitals of the reactant are both even, whereas the π orbitals of the product are even and odd. Hence, disrotatory ring opening is orbitally forbidden.

The two different reaction paths (conrotatory and disrotatory) preserve different symmetry elements and therefore lead to different symmetry predictions.

4.5. Breaking of Single Homonuclear and Heteronuclear Bonds

Before considering more sophisticated examples, we return for a moment to the most elementary reactions—those in which only a single bond is fragmented, as in the dissociation of H_2 and HCl . These simple bond-breaking reactions serve as an excellent test of our concepts, for if these ideas are valid, they must certainly apply for these reactions. In these cases, only one active

correlation diagram are the bonding and antibonding orbital pairs (σ_g and σ_u for H_2 , σ and σ^* for HCl). These pairs of orbitals never cross, so such bond breaking cannot be orbitally forbidden. It is important to note that not being forbidden does not mean that the bond breaking costs no energy but instead that symmetry constraints do not impose an *additional* energy barrier to such reactions beyond simple thermochemical energy requirements. In general, the meaning of the symmetry rules forbidding or not forbidding a reaction is only the presence or absence, respectively, of an *additional* energy barrier. The overall thermodynamic stability of reactants and products, which has nothing to do with symmetry, must always be included when one attempts to guess *total* reaction activation barriers.

So far, we have concluded that for breaking (or forming) simple bonds, an orbital-symmetry-related activation barrier will not exist, because the bonding and antibonding orbitals do not cross. We now consider the configuration-correlation diagram for such a reaction, treating the homonuclear and heteronuclear molecules separately. For H_2 , the available orbitals (σ_g and σ_u) can be occupied in several different ways— σ_g^2 and σ_u^2 give ${}^1\Sigma_g$ configurations, and $\sigma_g\sigma_u$ can give ${}^{1,3}\Sigma_u$. Since the ground state of H_2 has ${}^1\Sigma_g$ symmetry, only the σ_g^2 and σ_u^2 configurations can play a role. The energies of these two configurations differ greatly for internuclear distances (R) near equilibrium, but they become degenerate when $R \rightarrow \infty$. Therefore, a strong configuration interaction should exist between σ_g^2 and σ_u^2 for large values of R .

We now analyze the behavior of the σ_g^2 and σ_u^2 configurations at large R to see why they become degenerate. Using the facts that the unnormalized molecular orbitals can be expressed in terms of the $1S$ atomic orbitals as

$$\sigma_g \cong 1S_A + 1S_B$$

$$\sigma_u \cong 1S_A - 1S_B$$

for large R , the two relevant Slater-determinant wavefunctions can be written as (Pilar, 1968)

$$\begin{aligned} |\sigma_g^2| &= \sigma_g(1)\sigma_g(2)(\alpha\beta - \beta\alpha)2^{-1/2} \\ &= [1S_A1S_A + 1S_B1S_B + 1S_A1S_B + 1S_B1S_A](\alpha\beta - \beta\alpha)2^{-1/2} \end{aligned}$$

and

$$|\sigma_u^2| = [1S_A1S_A + 1S_B1S_B - 1S_A1S_B - 1S_B1S_A](\alpha\beta - \beta\alpha)2^{-1/2}.$$

Notice that, at large R , both of these configurations contain equal mixtures of

properly describes $2H$ at $R \rightarrow \infty$; they both attempt to describe $\frac{1}{2}[2H + H^+, H^-]$, whose energy lies above that of $2H$ by one-half the ionization potential of H minus the electron affinity of H. However, at large R the configuration-interaction function $(1/\sqrt{2})[|\sigma_g^2\rangle - |\sigma_u^2\rangle]$ would contain only covalent ($2H$) terms and its orthogonal partner $(1/\sqrt{2})[|\sigma_g^2\rangle + |\sigma_u^2\rangle]$ would describe (H^-, H^+) . Recall that $\sigma_g\sigma_u$ could not contribute because it has the wrong symmetry. Thus, the breaking of a single *homonuclear* bond has no symmetry-caused activation energy and requires mixing of σ^2 and $(\sigma^*)^2$ configurations that are doubly excited relative to one another and that mix very strongly because the σ and σ^* orbitals are degenerate for large R .

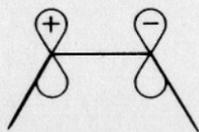
For *heteronuclear* bonds the situation is somewhat different. For example, in HCl the bonding (σ) and antibonding (σ^*) orbitals do not cross, and at large R they do not become degenerate. However, the σ^2 configuration and the $\sigma\sigma^*$ (singlet) configurations do cross as R varies. Near the equilibrium value of R , σ^2 represents the σ bond of HCl, whereas $\sigma\sigma^*$ describes a dissociative excited state. At large values of R the σ orbital becomes $3p$ Cl and σ^* becomes $1s$ H, so σ^2 describes (H^+, Cl^-) and $\sigma\sigma^*$ represents (Cl, H) . Therefore, a configuration interaction should be important in describing breakage of the HCl bond. Notice that, in contrast with the homonuclear case, *singly excited* configurations play the dominant role. As a result, the operator $\partial h_e/\partial Q$ can effectively couple the σ^2 and $\sigma\sigma^*$ configurations and thereby produce a smooth (barrier-free) transition from HCl to $H + Cl$ as the reaction coordinate varies. In *both* cases, a *strong* configuration interaction (σ_g^2 and σ_u^2 for H_2 and σ^2 , $\sigma\sigma^*$ for HCl) yields a smooth potential energy curve that displays *no* symmetry-imposed barriers. Symmetry barriers arise only when more than one electron pair undergoes changes in a reaction, since it is only in this more complicated case that orbital crossings (which then produce avoided configuration crossings) can exist along the reaction coordinate.

4.6. The Use of Bonding-Antibonding Orbital Mixing to Predict the Reaction Coordinate

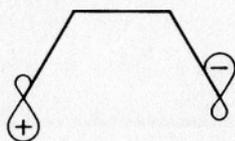
In section 4.4 we showed that, as far as being symmetry-allowed, cyclobutene could open by means of a conrotatory motion to yield 1,3-butadiene. In that example, a reaction path was guessed and then tested for orbital-symmetry conservation. That reaction can also be viewed in a different way. In section 4.5 we showed that breaking bonds utilizes mixing of configurations having antibonding- and bonding-orbital partners. Cyclobutene has, in C_{2v} symmetry, doubly occupied $a_1(\sigma)$ and $b_1(\pi)$ active orbitals and corresponding empty $b_2(\sigma^*)$ and $a_2(\pi^*)$ orbitals. If we proposed to add in configurations (through $\langle \psi_0 | \partial h_e / \partial Q | \psi_k \rangle$) that include one or both of the excitations $a_1 \rightarrow b_2$

symmetry of the direct product of its singly occupied orbitals. On the other hand, $a_1 \rightarrow a_2$ ($\sigma \rightarrow \pi^*$) and $b_1 \rightarrow b_2$ ($\pi \rightarrow \sigma^*$) excitations could be caused by a distortion of a_2 symmetry. The CH_2 twisting motions of cyclobutene, which are needed to break the σ bond between the carbon atoms 1 and 4, have b_1 (disrotatory) and a_2 (conrotatory) symmetry (Cotton, 1963); b_2 motion would be an in-plane deformation of the carbon ring, not a twisting motion. Hence, the conrotatory motion produces proper bonding-to-antibonding orbital mixing and this causes bond breakage. This reaction, in which a new π bond is formed from the termini of a conjugated π system, is called an *electrocyclic reaction*.

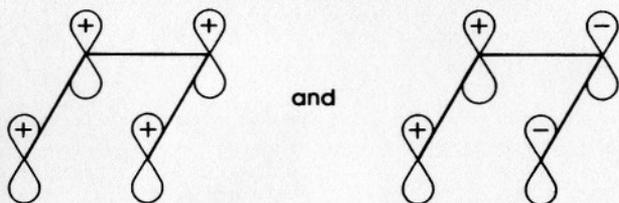
Notice that in this example knowledge of the symmetry of the molecular orbitals of the product molecule was not used. Instead, mixing of bonding and antibonding orbitals of the reactants was the approach employed. Consequently, the technique can only predict the kind of motion that can *break* certain bonds and is independent of the bonds that form. This idea of mixing the bonding molecular orbital of one fragment with the antibonding molecular orbital of the other fragment (e.g., $\sigma \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$) is very important. This mixing allows charge density to flow from the old bonds into regions of space (orbitals) that allow these bonds to break while new bonds form. Recall from introductory quantum chemistry (Cook, 1978; Shavitt, 1979; Appendix A) that singly excited configurations are used to describe orbital polarization or orbital relaxation. That is, an excitation of the form $\sigma^2\pi^2 \rightarrow \sigma\pi^2\pi^*$ gives rise to polarization of the σ orbital in a way that mixes in some π^* character. If this polarized orbital ($\sigma + \chi\pi^*$) looks like a bonding orbital of the product, the reaction is favored. Earlier in this book the *change* in charge density $\Sigma_{k \neq 0} \delta\rho_{k0}$ caused by mixing singly excited configurations was considered, and it was seen that nuclei move to regions of space in which $\Sigma_{k \neq 0} \delta\rho_{k0}$ is positive. Hence, in order to propose that nuclei move from one part of a molecule to another (e.g., when conrotatory and disrotatory openings of cyclobutene were examined), it is necessary to look for single excitations that give positive values of $\Sigma_{k \neq 0} \delta\rho_{k0}$ for those regions of the molecule. If these same single excitations also give rise to $\Sigma_{k \neq 0} \delta\rho_{k0}$ patterns that allow the "new" bonds to form as the "old" bonds are being broken, the *concerted* reaction should be symmetry-allowed. Hence, for cyclobutene, when we mix the $\sigma^2\pi^2$ configuration with the $\sigma\pi^2\pi^*$ and $\sigma^2\pi\sigma^*$, we are trying to allow electron density to flow from σ to π^* and from π to σ^* , respectively. Clearly, these excitations (orbital polarizations) allow the σ and π bonds of the reactants to rupture. Moreover, flow of charge into the π^* orbital produces electron density in an orbital of the form



whereas, after the conrotatory rotation, the σ^* orbital appears to be



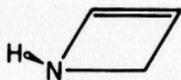
Notice that these orbitals have the same nodal patterns (phase relations) as the two occupied molecular orbitals of the product 1,3-butadiene:



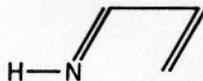
Thus, the same excitations that lead to rupture of the reactant bond also form the product bond. We shall make use of the idea of charge flow from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) again. In still other examples, it will be seen that orbitals other than the HOMO and LUMO can play important roles. What is important is that low-energy single excitations are present that permit new bonds to form as old bonds break—this is the essence of the concerted reactions we are studying.

4.7. Electrocyclic Reactions by Occupied-Orbital Following

Another feature of chemical reactions can be seen by again considering the opening of a four-membered ring but with a heteroatom present. The (hypothetical) opening of



to give



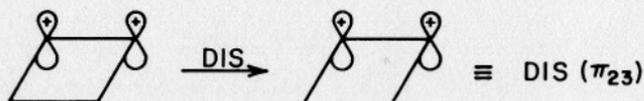
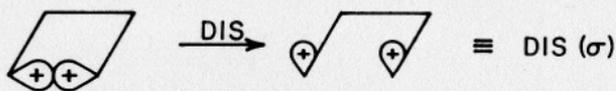
has the same orbital-symmetry constraints as the reaction examined in pre-

of the barrier to disrotatory opening of cyclobutene—the true origin of symmetry barriers is the noncorrelation of *nodal patterns* among the reactant and product orbitals (Pearson, 1976). Such nodal-pattern noncorrelation is examined in this section.

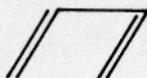
By applying a disrotatory motion to the two *occupied* orbitals of



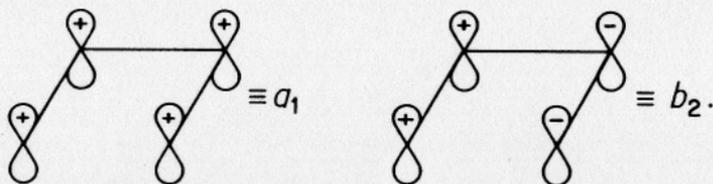
one obtains



[in which $\text{DIS}(\sigma)$ denotes the effect of the disrotatory opening on the σ orbital].
In the product

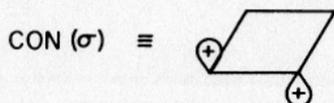


the occupied π orbitals look like



Notice that although $\text{DIS}(\sigma)$ has the same nodal pattern (phase relationship) between the atomic orbitals as occurs in orbital a_1 , the $\text{DIS}(\pi_{23})$ orbital does not match in its phase relationship with b_2 . Thus, such ring opening is forbidden. It is important to keep in mind that we are examining the effect of the DIS opening on the *occupied* reactant orbitals to see whether the *occupied* product orbitals result—exactly what is done when constructing an orbital-correlation

On the other hand, a conrotatory (CON) motion applied to the occupied active orbitals of cyclobutene gives



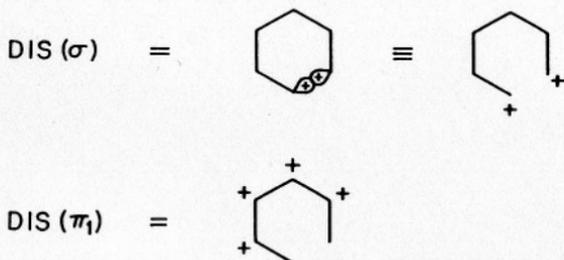
and $\text{CON}(\pi_{23})$ is identical to $\text{DIS}(\pi_{23})$. The phases of $\text{CON}(\pi_{23})$ and $\text{CON}(\sigma)$ agree with those of the product a_1 and b_2 orbitals, respectively, so for this motion the *occupied* orbitals correlate. For disrotatory motion they do not.

This kind of orbital-following works equally well on the hypothetical reaction involving aza-substituted cyclobutene. The phase relationships of the *occupied* reactant orbitals are followed as the molecular deformation of interest takes place. Only the *occupied* molecular orbitals need to be considered because of the bond-symmetry rule discussed in section 4.4. By ignoring the unoccupied molecular orbitals, work is reduced, but the opportunity is lost to guess how large a symmetry barrier is expected, because to know how steeply uphill the configuration-correlation diagram should be drawn, the relative energies of the excited orbitals must also be known.

We now examine another electrocyclic reaction

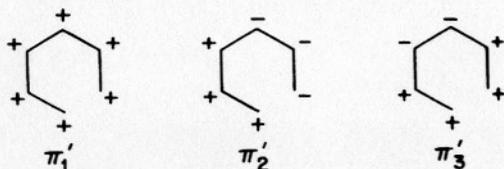


and ask whether CON or DIS motion is allowed. Disrotatory motion is considered first. To simplify the diagrams in this and several of the following examples, the symbols + and - are used to indicate whether positive π -orbital components project up or down from the plane of the page. Thus, for disrotatory motion,

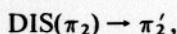
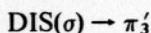
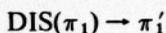


and

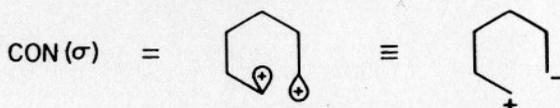
The occupied π orbitals of the product are described by



The orbitals can be correlated according to their phase relationships as



so disrotatory ring opening is allowed. In contrast, for conrotatory motion,



which could correlate with π'_2 but then $\text{DIS}(\pi_2)$ would have no product orbital with which to connect. Hence, conrotatory motion is forbidden. Note that the motion (CON or DIS) that is allowed varies, depending upon the length of the conjugated π network connecting the two termini (Woodward and Hoffman, 1970).

These electrocyclic reactions can also be treated by the HOMO-LUMO mixing concept. For example, in the disrotatory opening of



the reaction coordinate preserves the σ_v phase running through the molecule. As a result, the HOMO-LUMO single excitations ψ_k must have the same symmetry under σ_v as ψ_0 for $\langle \psi_0 | \partial h_c / \partial Q | \psi_k \rangle$ to be nonvanishing. This means that the HOMO and LUMO themselves must have the same symmetry under σ_v . The relevant HOMO's are

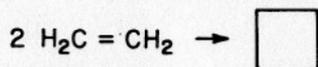




Clearly σ and π^* have the same symmetry as π and σ^* , and the HOMO-LUMO excitations give rise to patterns that allow the new bonds to form. Thus, this reaction is also allowed according to the LUMO-HOMO mixing criterion.

4.8. Cycloaddition Reactions by Orbital Following

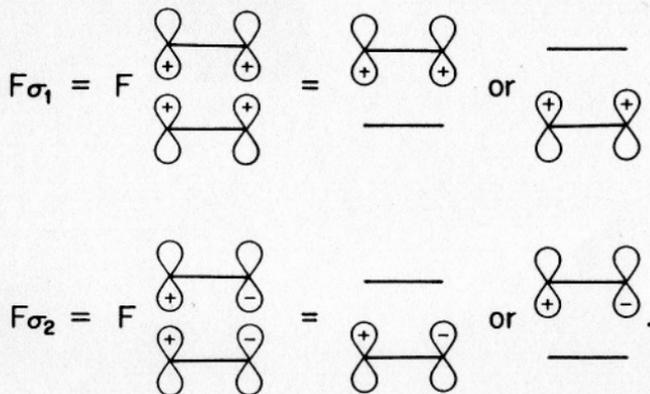
The cycloaddition reaction



considered in section 4.4 is now reexamined by using the orbital-following procedure. The fragmentation F of the two σ bonds in



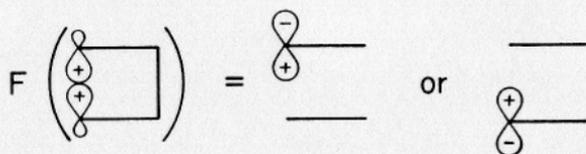
gives



Here, for example, $F\sigma_1$ is used to represent the result of fragmentation on the σ_1 orbital.

$F\sigma_1$ has the same phase properties as the bonding π orbital of one ethylene fragment. However, $F\sigma_2$ looks like an antibonding π^* orbital of the other ethylene fragment, so this fragmentation is forbidden, in agreement with the results of section 4.4.

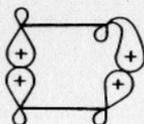
Notice that the symmetry-combined σ orbitals, σ_1 and σ_2 , were used because orbitals were needed that, on bond rupture, would have amplitude on *both* atoms of the resultant ethylene molecule. If we had considered



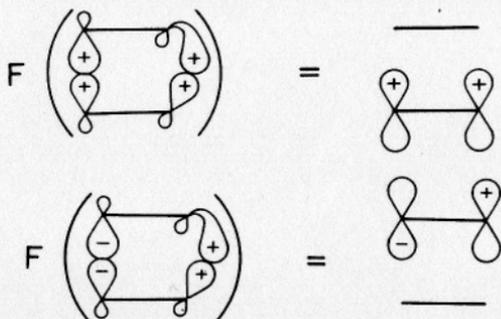
we would achieve no *phase* information, because two or more pieces of a wavefunction or orbital are needed to make a statement about phase.

The above cycloaddition reaction is labeled $[2_s + 2_s]$. The 2's denote the conjugation lengths of both fragments; the subscripts *s* show that fragments react in a suprafacial manner. The term *suprafacial* refers to an attack on the same face of the π system; *antarafacial* (subscript *a*) means that the newly formed or broken bonds occur on opposite faces of the π system.

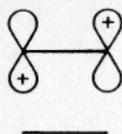
We now consider the $[2_s + 2_a]$ cycloaddition of two ethylenes. To indicate the fact that the one ethylene is bonded in a suprafacial manner and the other in an antarafacial manner, cyclobutane is drawn as follows:



in which the + and - signs again indicate the directions of the orbital lobes participating in the bonding. The fragmentation results in the following orbital mappings:

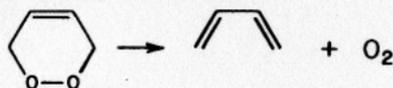


The fragmented orbitals with the lowest-energy nodal pattern that results have been chosen to correlate. For example,

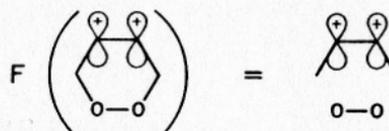
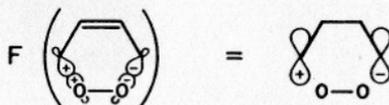
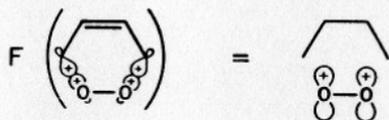


is not drawn in the first case. These fragmented orbitals have the proper phase relationships to correlate with the bonding π orbitals of both ethylenes; hence, the $[2, + 2_a]$ reaction is allowed.

The retrograde Diels-Alder reaction



is a more difficult example. The fragmentation process gives rise to the following orbital mappings:



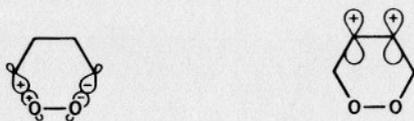
These three fragmented orbitals have the same phase patterns as in the three occupied active orbitals of



hence, the retrograde Diels-Alder reaction is allowed via a $[4, + 2_s]$ mechanism. Notice that the lengths of the conjugated π systems in the two ene

systems determine whether the cycloaddition reaction is allowed via the supra-supra mechanism (Woodward and Hoffman, 1970).

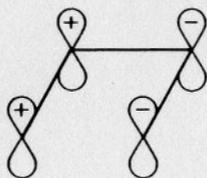
The above reaction can also be examined by the HOMO-LUMO method. The relevant HOMO's of the σ and π moieties are



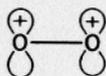
and the LUMO's are



As the fragmentation of the two carbon-oxygen bonds begins, the σ_{CO} and π^* can be combined to form a new π bond in the diene



and σ_{CO}^* and π can combine to give the π bond on O_2

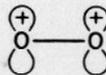


Thus, the $[4, + 2,]$ reaction is allowed.

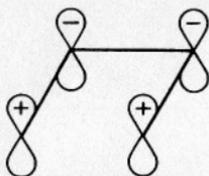
The fragment HOMO's and LUMO's could also be chosen to refer to the O_2 and



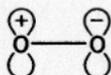
product molecules. In this case, the O_2 HOMO



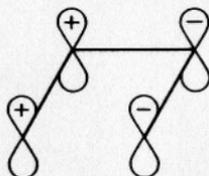
has good overlap with the diene LUMO



and the O₂ LUMO



overlaps favorably with the diene HOMO



again leading to the prediction that the Diels-Alder reaction is symmetry-allowed.

In section 4.4 the four-center concerted-addition reaction typified by the dimerization of ethylene to give cyclobutane was shown to be thermally forbidden. However, in some circumstances, products can still be formed. For example,



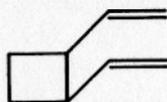
can dimerize to give 1,5-cyclooctadiene



What makes this reaction occur so easily (i.e., with low activation energy), when the analogous ethylene dimerization has a very large activation barrier, is the availability of a *two-step* reaction path. By first combining two reactant molecules to give the radical intermediate



and, in a subsequent step, coupling the two allyl radicals, one obtains



which can then rearrange via an *allowed* Cope rearrangement (Pearson, 1976) to give the final product 1,5-cyclooctadiene. The stability of the well-known allyl radical intermediates make this reaction path thermally favored. This path does not contribute to the ethylene dimerization because the 1,4-biradical



is very unstable. In contrast, perfluoroethylene F_2CCF_2 can thermally dimerize via the radical pathway because of the strong radical-stabilizing influence of the electron-withdrawing fluorine atoms. These examples illustrate the point made in the introduction to Part 2. The symmetry analysis can be applied to any *single* reaction step, but if that step is predicted to be forbidden, one must keep in mind that other pathways might be available and even favorable.

4.9. Sigmatropic Migrations via HOMO-LUMO Overlaps

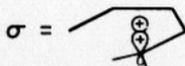
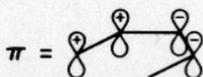
The reaction



utilizes the [1,5] suprafacial shift of a hydrogen atom. If the product were



it would be a [1,5] antarafacial migration. This class of reaction can be examined by considering HOMO-LUMO charge-flow interactions (i.e., a singly excited configuration interaction caused by $\langle \psi_0 | \partial h_c / \partial Q | \psi_k \rangle$): The HOMO's of the two relevant fragments are

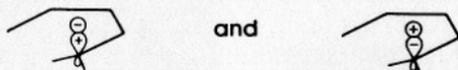




As the hydrogen atom is moved from the right carbon terminus to the left terminus, both the σ and π^* orbitals and the π and σ^* orbitals develop substantial σ - and π -bonding overlap. If σ^* were drawn

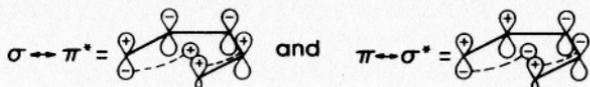


the singly excited configuration $\sigma^2\pi\sigma^*$ would still give rise to bonding interactions, because this configuration would simply enter into the perturbation description of ψ_k (or $\delta\rho_{k0}$) with an opposite sign (relative to the sign it has with σ^* drawn as originally drawn.) Another way to say this is that

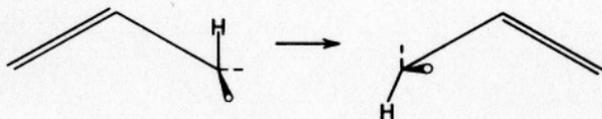


are equivalent descriptions of the same orbital. An *overall* sign change never has any influence on the physical content of an orbital (or a wavefunction)—it is only the internal *relative* phases that are important.

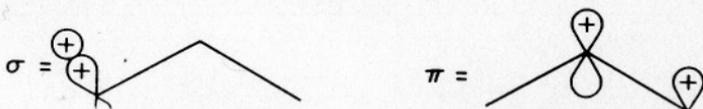
Based on this analysis, the [1,5] suprafacial shift is allowed according to the criterion of HOMO-LUMO overlap criterion. The antarafacial shift is forbidden because the orbital of the hydrogen atom attaches to the bottom of the p_π orbital of the left carbon terminus. As a result, the σ and π^* orbitals and the π and σ^* orbitals no longer have *totally* favorable overlap for the product molecules (they have some favorable and some unfavorable overlap):



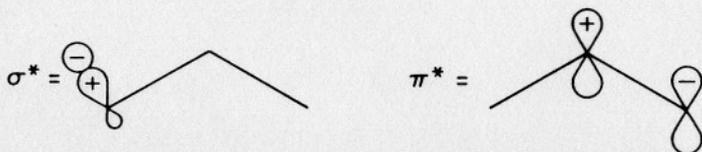
In contrast, the [1,3] antarafacial migration



is allowed because the relevant HOMO's



and LUMO's

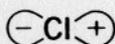


develop good overlap ($\sigma \leftrightarrow \pi^*$ and $\pi \leftrightarrow \sigma^*$) as the hydrogen moves to the bottom of the left terminus. The [1,3] suprafacial shift is forbidden because the feature that determines which reaction (antara or supra) is allowed is the phase pattern of the π orbital of the reactant (Woodward and Hoffmann, 1970).

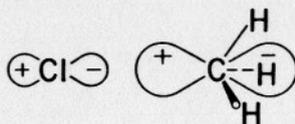
Fukui (1971) has extended the idea of good fragment HOMO-LUMO overlap to predict *where* in a molecule the reaction is most likely to occur. For example, in the reaction



the HOMO of the attacking Cl^- is



and the LUMO of ClCH_3 is



The other HOMO-LUMO pair is very high in energy because it involves the excited state of Cl^- ; hence, it contributes little to the charge flow. Attack of the Cl^- should occur either on the back end of the ClCH_3 , where the LUMO has large amplitude, to give $\text{Cl}^- + \text{H}_3\text{CCl}$, or on the Cl end of ClCH_3 to give $\text{ClCl} + ^-\text{CH}_3$. The former reaction is thermodynamically favored because of the differences in bond strengths ($\text{C}^-\text{Cl} > \text{Cl}^-\text{Cl}$) and electron affinity ($\text{Cl} \gg \text{CH}_3$). The fundamental point in using the Fukui method is to identify the HOMO and LUMO pairs of the fragments and then to let them interact in a way (i.e., along some molecular distortion) that allows them to overlap *maximally*.

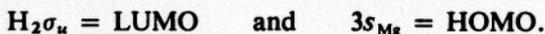
4.10. A Topology-Based Method

In this section, a final technique for predicting whether a reaction is allowed is described. This method, as developed by Zimmerman (1966) and by Dewar

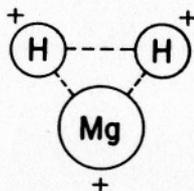
approach, the energy is governed by the aromatic or antiaromatic nature of the transition state. By concentrating on aromaticity, this tool is limited to reactions that pass through a *cyclic* transition state—a class of reactions called *pericyclic* (Woodward and Hoffman, 1970). The primary advantage of this technique is that it requires knowledge of only the *topology* of the transition state and of the number of active electrons—it is not necessary to examine individual molecular orbitals, HOMO's, or LUMO's.

To implement this method, one begins by assigning phases to the atomic orbitals involved in the cyclic transition state in order to give positive overlaps—as far as possible—as one walks along the bonds being broken and the bonds being formed throughout the transition state. It may not be possible to have positive overlap throughout, for one or more *interorbital* sign inversions may be forced by the nature of the *atomic* orbitals being used. If an odd number of such sign inversions occurs, the transition state is said to be *Möbius*; no inversions or an even number of inversions give rise to a *Hückel* transition state. A Hückel transition state is said to be stable if it contains $4n + 2$ electrons and unstable if it contains $4n$; Möbius transition states are stable if they contain $4n$ electrons.

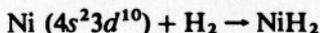
Let us use this method to determine whether the reaction $\text{Mg} (3s^2) + \text{H}_2 \rightarrow \text{MgH}_2 ({}^1A_1)$ is allowed. For C_{2v} symmetry, $3s_{\text{Mg}}$ is a_1 and $\text{H}_2\sigma_g$ is a_1 , but the MgH σ bonds are a_1 and b_2 ; thus, the bond-symmetry rule indicates that the reaction is forbidden. The HOMO-LUMO overlap criterion yields the same result, namely,



In the Dewar-Zimmerman topology-based method the atomic orbitals are assigned phases as follows to permit no sign changes:



This is a Hückel system containing $4n = 4$ active electrons; hence, its transition state is unstable and the reaction is forbidden. In contrast,

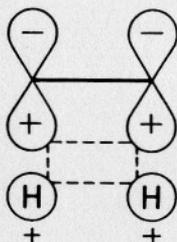


is allowed if Ni uses its *d* orbitals, since the system is now Möbius,

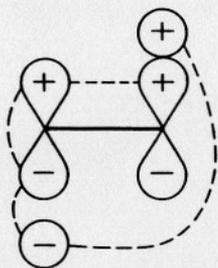


and contains $4n = 4$ active electrons (only the two electrons from H_2 and the two electrons from the one active d orbital count.)

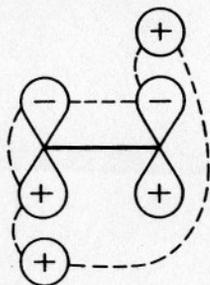
The suprafacial addition of H_2 to H_2CCH_2 is a 4-electron Hückel system.



It is forbidden, just as would be found via a LUMO-HOMO or full-symmetry-correlation treatment. The antarafacial addition reaction is allowed, since it has a four-electron Möbius transition state. The antarafacial attack diagram can be constructed by walking along the new-bond-old-bond cycle as follows (starting with the top hydrogen and moving to the neighboring carbon)



which shows one phase change, or alternatively, by walking from the top hydrogen to the bottom hydrogen

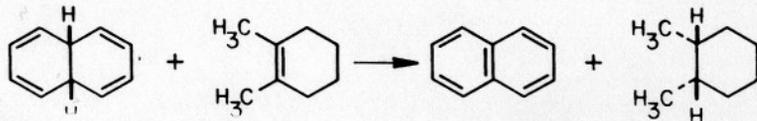


where again one *interorbital* phase change results. Hence, this reaction is Möbius and contains four electrons. Note that this method applies only to those systems having (proposed) transition states that are cyclic. Other methods that we have talked about (in particular, full orbital diagrams, configuration-correlation diagrams, and HOMO-LUMO interactions) can be used to solve any problem as long as some symmetry exists or as long as one can identify the proper HOMO and LUMO of the fragment.

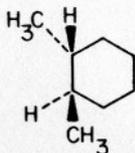
It would be good practice for the reader to go back through sections 4.4–4.9 and apply all of the Dewar-Zimmerman, HOMO-LUMO, symmetry-correlation, and orbital-following techniques. This would help one to see relationships among the methods. In particular, it is important to observe that most of the techniques that we have covered are closely interrelated. Each attempts to determine whether the *occupied* orbitals of the reactant (where electronic *configuration* information appears) evolve smoothly into *occupied* orbitals of the products. In the methods of the orbital-correlation diagram and the bond-symmetry rule, this is achieved by matching symmetries of occupied orbitals. In the orbital-following technique, one concentrates on phase relations of these orbitals. The HOMO-LUMO method monitors the evolution of the occupied orbitals by looking for low-energy virtual orbitals that can be mixed with the occupied orbitals of the reactant to generate product-occupied orbitals. Although the Dewar-Zimmerman method emphasizes the aromatic or nonaromatic nature of the *cyclic* transition state, even these properties are directly related to the occupied-orbital nodal patterns.

Problems

1. Consider the reaction



The products could be those shown, or the cyclohexane could have the opposite stereochemistry, that is,

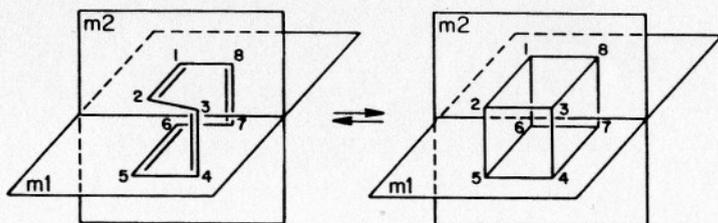


Which of these reactions is thermally allowed? Use HOMO-LUMO, the bond-symmetry rule, and Zimmerman-Dewar methods.

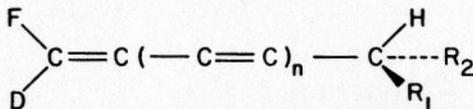
2. Which of the ketones shown below should be thermally unstable with respect to CO loss to give the diene and cyclotriene, respectively?



3. Use orbital-correlation diagrams, configuration-correlation diagrams (using the two mirror planes of symmetry), and orbital-following to predict whether the reaction given below is thermally allowed.



4. An all-cis polyene

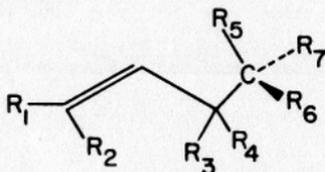


is known to undergo a thermal sigmatropic hydrogen shift to give a 50:50 mixture of two compounds that have identical chemical formulas but differ in their geometrical and absolute configurations. What are the two products if n is even? What are they if n is odd? You may assume that steric factors are unimportant in formulating your answer. Use the Zimmerman-Dewar method to answer this problem.

Even though the [1,3] suprafacial hydrogen shift



is forbidden, the corresponding methyl-group migration is allowed. Why? What products (including absolute and geometrical isomer considerations) are expected in the [1,3] suprafacial migration of the R_5 , R_6 , R_7 substituted methyl group in



You may neglect steric factors.

6. Ammonia NH_3 is known to have C_{3v} symmetry. The bonding in this molecule can be explained by using the $2s$ and $2p$ orbitals of nitrogen and the $1s$ orbital of hydrogen.
 - a. Use symmetry projectors to combine the $1s_{\text{H}}$ orbitals to form symmetry-adapted orbitals. What are the symmetries of the resulting orbitals?
 - b. Repeat step (a) for the $2s_{\text{N}}$ and three $2p_{\text{N}}$ orbitals.
 - c. Show in a qualitative orbital-energy-level diagram how the N and H atomic orbitals combine to produce bonding, nonbonding, and antibonding molecular orbitals of NH_3 . Label the orbitals. Assume that the $1s_{\text{H}}$ orbitals are lower in energy than the $2p_{\text{N}}$ orbital but higher than the $2s_{\text{N}}$ orbital.

For use in the following questions, *seven* molecular orbitals are labeled in order of increasing energy $\phi_1 \dots \phi_7$.

- d. Consider the singlet excited state that can be generated by exciting an electron from ϕ_3 into the lowest available molecular orbital. Is this excited state stable, first-order Jahn-Teller unstable, or second-order Jahn-Teller unstable? If it is Jahn-Teller unstable, what symmetry of vibration would be expected to distort the molecule (NH_3 has $2A_1$ and $2E$ vibrations)?
- e. Repeat step (d) for an excitation out of ϕ_3 into the highest-available-valence molecular orbital.