

Intermolecular cycloadditions

The more difficult case of an electrocyclic reaction involving cyclization by two or more reactant molecules cannot be treated in terms of simple molecular orbital diagrams, as mentioned earlier. It is therefore necessary in every case to use energy level correlation diagrams, and it is preferable to amplify and justify the explanation of the resulting selection rules by using state-correlation diagrams as well. To illustrate the procedure involved in treating intramolecular processes, let us first consider the simplest possible case, the (2 + 2) cycloaddition of two ethylenes to give cyclobutane (24). It is first of all necessary to

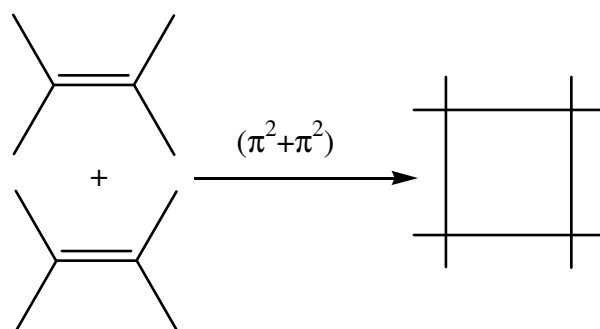


Fig 1

assume a reasonable geometry of approach of the two ethylenes. Although other stereochemical approaches are feasible, it is most reasonable to assume that the two ethylenes approach each other perpendicularly with respect to the parallel nodal planes of their two

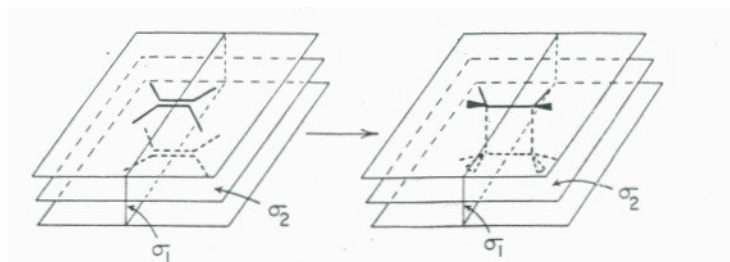


Fig 2

π -systems (as shown in Fig 2). In this way the π -lobes will overlap most directly to form the new σ -bonds of the cyclic product. It is evident that two essential elements of symmetry are retained by the system as the cyclobutane is formed. These are the plane of symmetry σ_1 that bisects the two ethylenes, and the plane σ_2 that lies midway between the parallel nodal planes of the approaching π -systems. Each of these planes is a symmetry element of the product cyclobutane, and each bisects bonds being made or broken during the reaction.

Without necessarily considering the relative energies of the MOs involved, it is clear that as the four π -level of the two ethylenes interact to give cyclobutane, there will arise four corresponding σ -levels. It is reasonable to depict these levels as shown in Fig. 3. The question is: How do the π -MOs corresponding to these levels interact and what are their symmetries with respect to the two planes σ_1 , and σ_2 ? In looking at the reaction in the direction of cyclization, it is necessary to treat the two ethylenes as one system, since once overlap begins to occur they will in effect be one system. Only in this way can the appropriate symmetry elements be considered. It is simplest to project the above diagrams of reactants and products onto the plane that contains

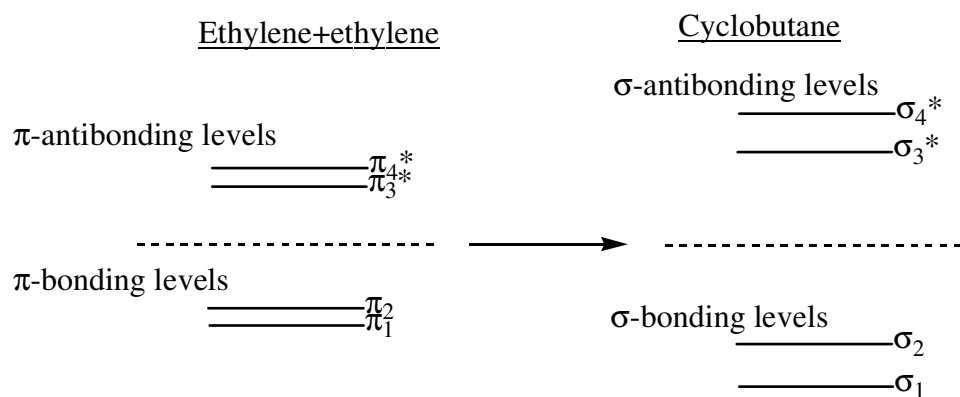


Fig 3

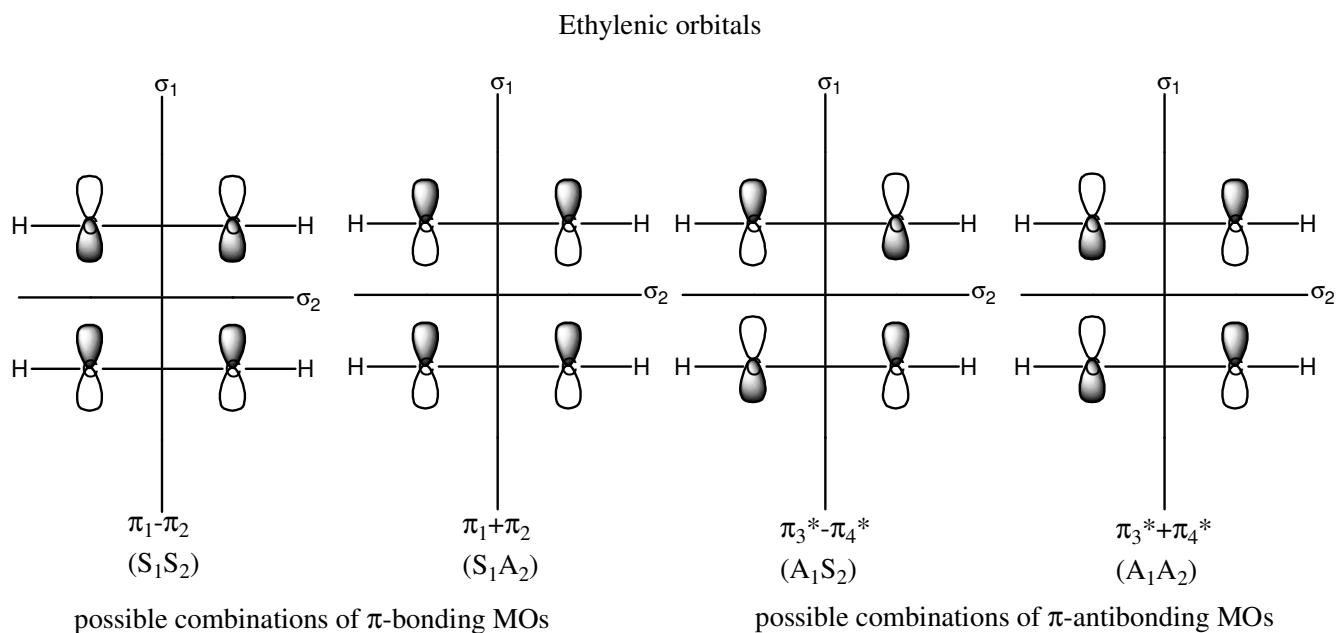


Fig. 4

all four carbons and depict all possible combinations of the two sets of ethylenic π -orbitals. The planes σ_1 and σ_2 then become the orthogonal lines shown in Fig. 4. It is seen that only four combinations are possible. These are the symmetric and antisymmetric combinations of each pair of either bonding or antibonding π -orbitals. Other combinations are not allowed, since they would lead to formation of product MOs that are unacceptable wave functions for the cyclobutane system.

If these interactions are allowed to continue to form the final σ -type orbitals of cyclobutane, they can be represented as shown in Fig. 5. As before only the σ -envelopes in the regions of the newly formed

Cyclobutane MOs

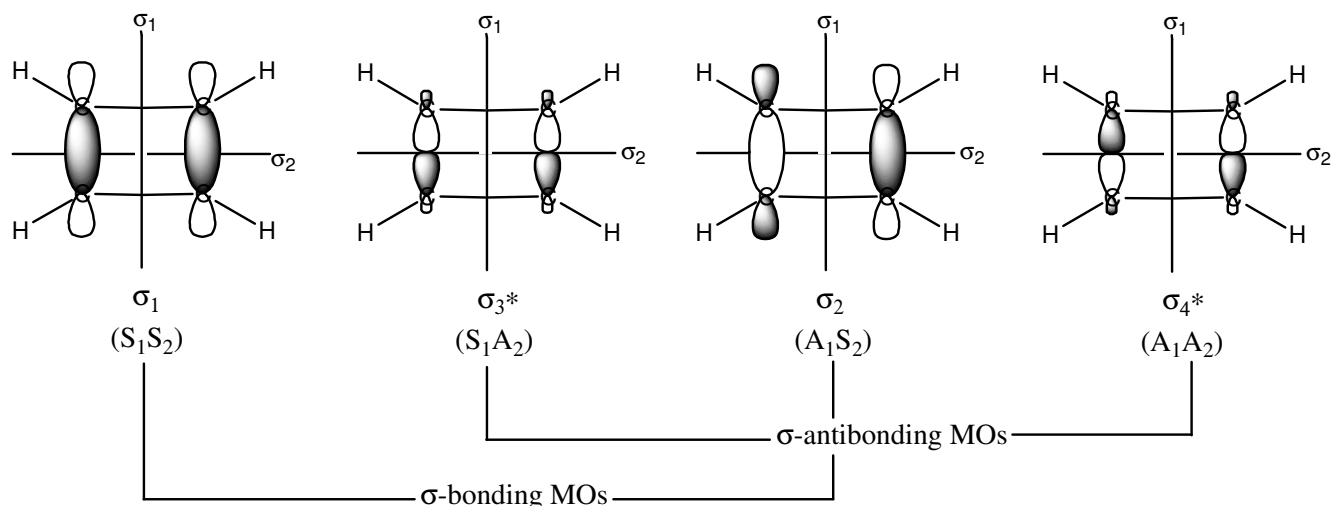


Fig 5

bonds are shown, although the σ -orbitals of cyclobutane will be completely delocalized. The symmetries of the orbital combinations of the two ethylenes can now be assigned with respect to σ_1 and σ_{\square} . The first combination ($\pi_1 - \pi_2$) is symmetric with respect to both σ_1 and σ_{\square} and is designated as (S^1S^2) or more simply (SS). The second combination ($\pi_1 + \pi_2$) is (S^1A^2) or (SA), and so on. The cyclobutane σ -orbitals have corresponding symmetries, as indicated in parentheses in the diagram.

It can be seen from the two orbital diagrams Figs. 4 and 5 that the original π -bonding orbitals of the ethylenic systems combine to give the (SS) and (SA) orbitals of the interacting system, but the final σ -bonding orbitals of cyclobutane are (SS) and (AS). This is shown more clearly in schematic form (Fig 6), where the two π -levels are initially shown as degenerate, as are the two π^* -levels. The σ -levels are ranked according to their increasing numbers of nodes. The main point is that the bonding orbitals of the reactant system do not correlate directly with the bonding orbitals of the product, thus level-crossings must occur between bonding and antibonding levels during reaction. Although the π_{ss} combination decreases in energy along the reaction coordinate, the π_{sa} combination increases markedly as the reaction proceeds as it tries to correlate with an antibonding level in the product. The reaction is therefore thermally forbidden, since to conserve orbital symmetry the ground-state reactants are trying to form a doubly excited product and the reaction has a large symmetry-imposed barrier. However, if one of the ethylenic π -electrons is excited to a π^* -level, the reaction will then be allowed since the reactant system now correlates directly with a singly excited state of the product, as shown in Fig. 7. (This point will be shown more clearly later by means of a state-correlation diagram (Fig 14).)

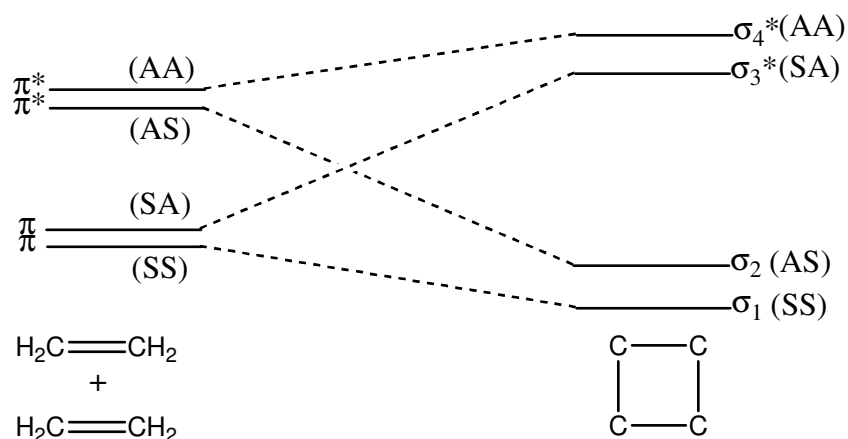


Fig 6

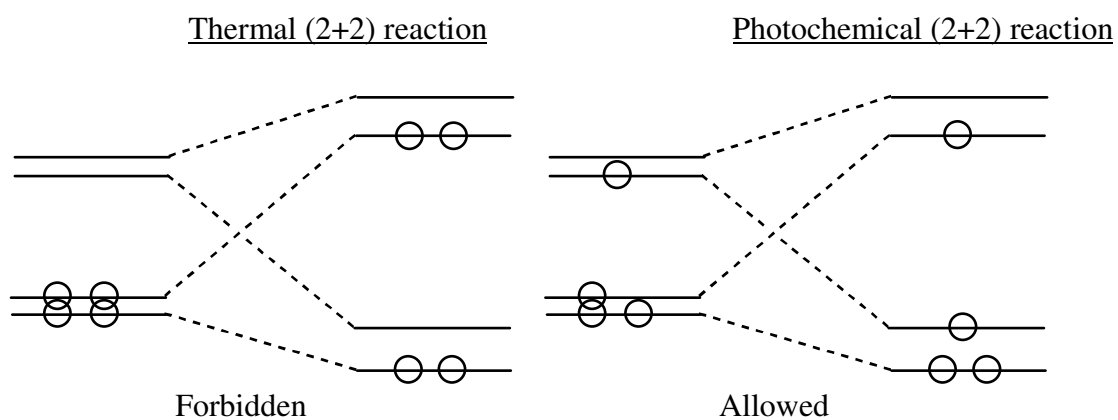


Fig 7

We next consider the reaction of ethylene and butadiene to form cyclohexene. This prototypical Diels–Alder reaction is called a ($\pi_4 + \pi_2$), or simply a (4 + 2) cycloaddition. The transition state for this addition is reasonably considered to have the diene and dienophile in parallel planes with the reacting termini as close together as possible. Thus reactants and products are arranged as shown in Fig. 8 Now there is only one element of symmetry that is common to the reactant "molecule" (the interacting diene and dienophile) and the product. This is the plane of symmetry σ_1 that bisects both the interacting ethylene and butadiene, and also bisects the newly formed cyclohexene double bond.

We now try to relate the six reactant levels, which are all π -type (four from butadiene, two from ethylene) to the resultant four σ -type and two π -type levels of the product cyclohexene. These are depicted in

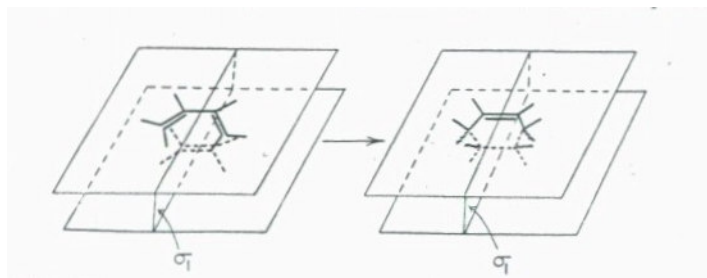


Fig 8

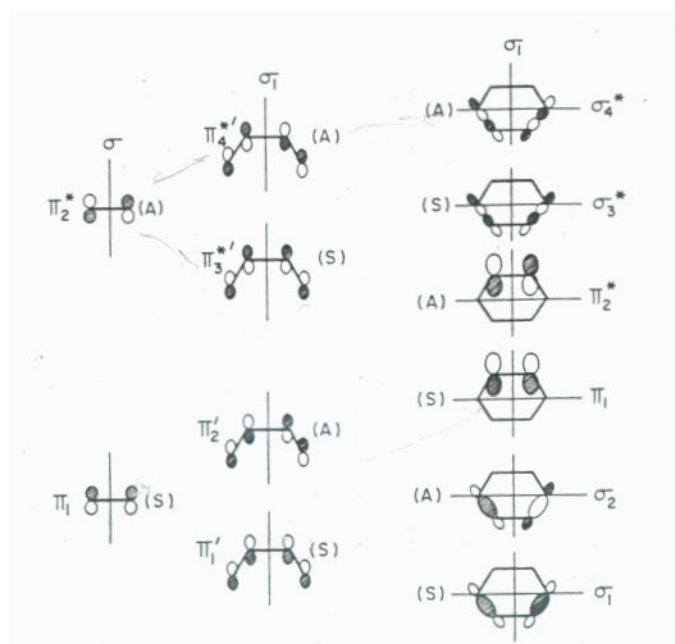


Fig 9

Fig. 9 There is no problem in representing the two sets of reactant MOs., which are shown side-by-side for convenience, and their symmetries with respect to the plane σ . Similarly there is no problem in describing the p and π^* orbitals of the product, which are taken to be like the HMO orbitals of ethylene. To deal with the σ -type orbitals in the product, clearly there must be two σ -orbitals and two σ^* -orbitals. These will be delocalized over both newly formed σ -bonding regions and can only be reasonably represented in those regions as shown. It is also reasonable to rank the more symmetrical s (or σ^*) orbital as being lower in energy than the less symmetrical one, since it has fewer nodes. The symmetries of the cyclohexene orbitals with respect to s are also shown.

An energy level correlation diagram (Fig. 10) can now be constructed. Although the particular ordering and spacings shown for the various energy levels is reasonable, this is not essential to the discussion. Again, it is only the separation into either bonding or antibonding levels that is important.

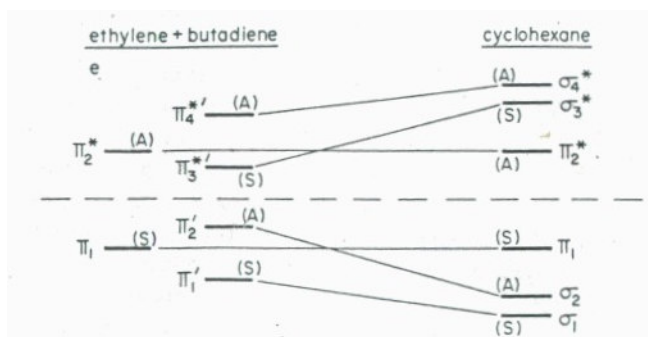


Fig 10.

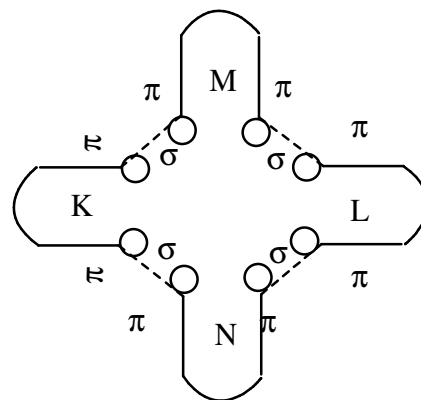
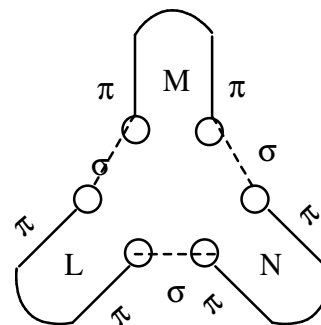
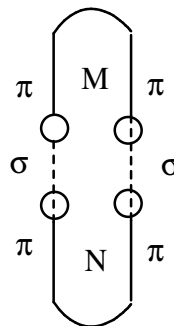
Again, levels of like symmetry that are closest in energy are connected. Since there are equal numbers of bonding levels of a particular symmetry in both reactants and product, there are no correlations between bonding and antibonding levels. Thus there is no symmetry imposed barrier and the (4 + 2) reaction is thermally allowed. The most accessible excited state of the reactants would involve promotion of an electron from π_2 ' to π_3^* of butadiene. This would then give a direct correlation with a much higher and different type ($\sigma - \sigma^*$) of excited state of the product, thus the (4 + 2) cycloaddition is

photochemically forbidden. (Again it is not clear why other possible excited state processes should not be allowed. However, it will be shown later by means of state-correlation diagrams that there is a symmetry imposed barrier to all reasonable photochemical processes and that the reaction is forbidden in this mode.)

To summarize, and compare the above types of intermolecular cycloaddition, it is seen that the ($\pi 2 + \pi 2$) process should be thermally very difficult because orbital symmetry conservation requires a correlation between a bonding level in the reactants and an antibonding level in the product. Thus the energy of the system increases along the reaction coordinate and the reaction is said to be symmetry forbidden. Excitation of an electron in one of the reactants causes the energy, change along the reaction coordinate to be decreased, and the reaction becomes more favorable photochemically and is said to be symmetry allowed. On the other hand, the ($\pi 4 + \pi 2$) cycloaddition involves no such correlations of bonding levels in the reactant and antibonding correlations of bonding levels in the reactant and antibonding levels in the product, hence the energy does not increase along the reaction coordinate. Thus the thermal ($\pi 4 + \pi 2$) reaction is said to be symmetry allowed. However, excitation of an electron in the reactants causes the energy change along the reaction coordinate to be increased, and the photochemical ($\pi 4 + \pi 2$) reaction is said to be forbidden.

Similar considerations can be applied to other types of intermolecular cycloaddition reactions, which may involve two or more reactant molecules. Using this type of approach, Woodward and Hoffmann have extended the selection rules to cover the general types of intermolecular cycloaddition. These rules are given in Table VII. 3. The basis of these rules is exactly as described for the two simple cases above: If orbital symmetry conservation requires one or more correlations between bonding levels in the initial state and antibonding levels in the final state, the reaction will be energetically unfavorable in a thermal sense, but favorable photochemically. If no such correlation

Allowed processes		
Type	Thermal ^a	Photochemical ^b
	Numbers of p-electrons involved in each open-chain system	
$2\pi \rightarrow 2\sigma$	M N	M N
	4 2	2 2
	6 4	4 4
	8 2	6 2
$3\pi \rightarrow 3\sigma$	L M N	L M N
	2 2 2	4 2 2
	4 4 2	
	6 2 2	
$4\pi \rightarrow 4\sigma$	K L M N	K L M N
	4 2 2 2	2 2 2 2



^a Note that in all the thermally allowed processes the sum of the π -electrons involved in the cycloaddition is $(4n + 2)$.

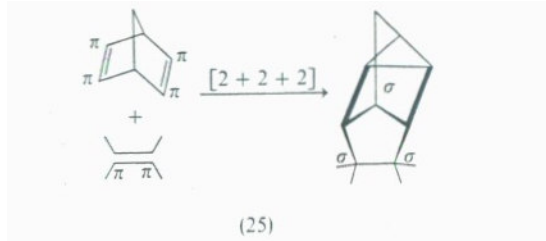
^b In all the photochemically allowed processes the sum of the π -electrons involved in the cycloaddition is $(4n)$

exist, the reaction will be favorable thermally, but difficult photochemically.

These selection rules are in excellent accord with experiment for the many known cases of thermal and photochemical cycloadditions and cycloreversions. A few general illustrations of the success of these rules are as follows.

The $(2 + 2)$ cycloaddition of two ethylenic systems is a widely observed photochemical reaction, whereas the reaction does not readily take place thermally. The reverse reaction, such as the pyrolysis of cyclobutane, is known, but there is evidence that it is a stepwise process involving a radical intermediate. On the other hand, thermal Diels-Alder or $(4 + 2)$ cycloaddition reactions are extremely widespread and there is overwhelming evidence that these are concerted processes. Photochemical Diels-Alder reactions are much less common and there is less evidence available on whether these are

stepwise or concerted. The (4 + 4) cycloaddition is a well-known reaction, but has only been observed photochemically. Thermal [6 + 4] cycloadditions were unknown until formulation of the principle of conservation of orbital symmetry and the selection rules stimulated a search for such processes; they are now well-known reactions. Cycloadditions involving more than two molecules are less well known since entropy factors do not favor such processes, but the thermal reaction of three acetylene molecules to give benzene is an example of a (2 + 2 + 2) cycloaddition. Similar processes are known where two of the three π -systems are incorporated into the same molecule, in a nonconjugated arrangement, such as in (25). Many specific examples of cycloaddition and



cycloreversion reactions are given in Woodward and Hoffmann's original monograph on the subject of conservation of orbital symmetry. It is sufficient to say that the success of their selection rules both in explaining known results and in predicting new ones has been truly remarkable.

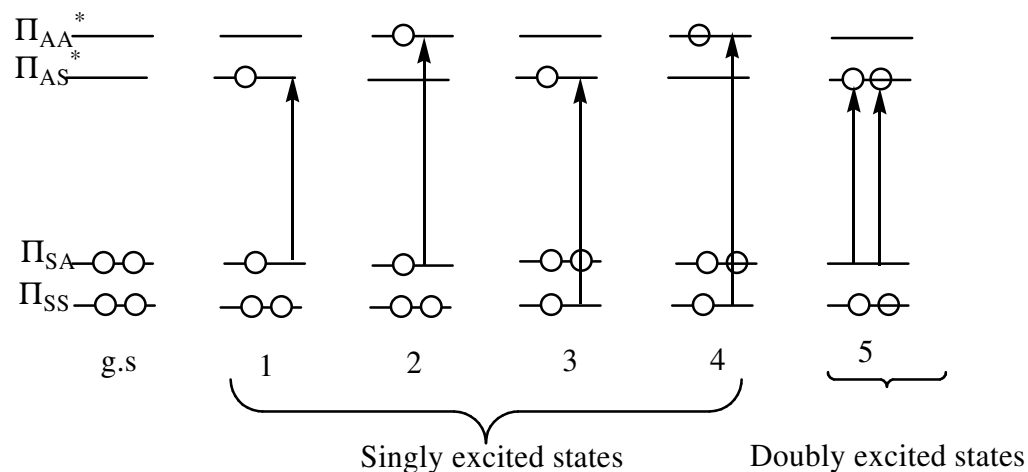
It has been pointed out that for intramolecular cycloadditions it is necessary to consider state-correlation diagrams to provide a fully satisfactory explanation of the differences in stereochemical preference exhibited by thermal as against photochemical modes of a given reaction. This is also true for intermolecular cycloadditions, since we have already seen that it is not always evident from energy level correlation diagrams why an allowed thermal process should necessarily be photochemically forbidden, or vice versa. Construction of state diagrams for the (2 + 2) and (4 + 2) cycloadditions just considered will illustrate more clearly why this difference occurs between the thermal and photochemical reactions.

State-correlation diagrams for intermolecular cycloadditions and cycloreversions

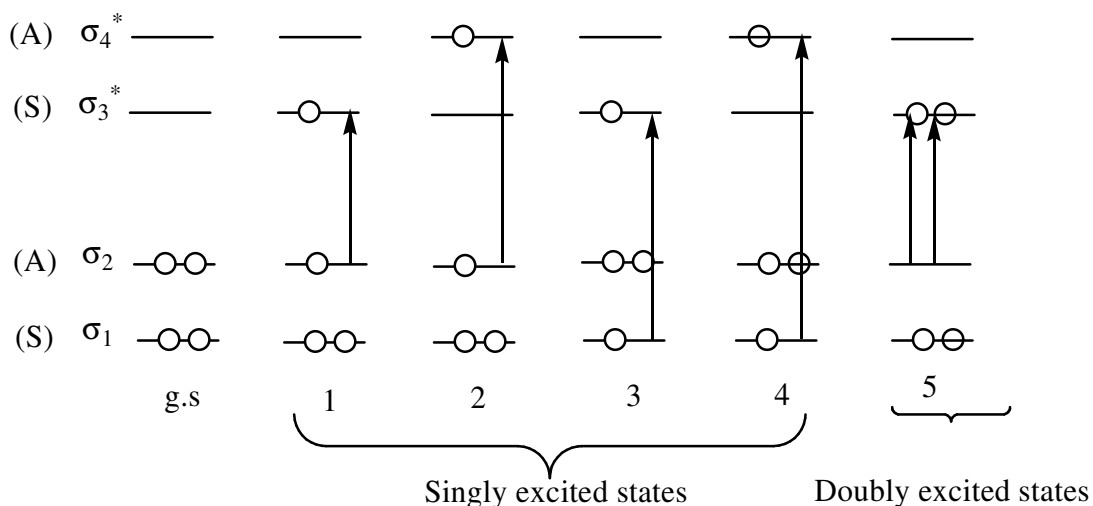
We proceed in the same way as before by considering the various possible excited states of the reactants and products, and their total state symmetries as well as the symmetry characteristics of the individual electronic components. For the (2 + 2) cycloaddition of two ethylenes, the ground-state configuration of the reactant system and those of its various electronically excited states are shown in Fig. VII 26. The corresponding ground-state and excited state configurations of the product are given in Fig. VII 27.

The symmetries corresponding to the individual levels have already been determined for the energy level correlation diagram in Fig. VII. 21.

Reactant states (two ethylenes)



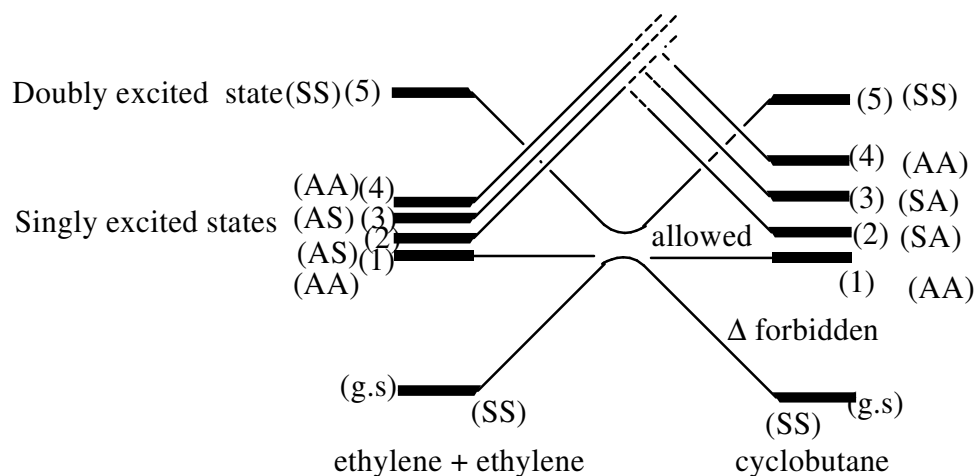
Product states (cyclobutane)



A table of reactant and product-state symmetries (with respect to elements σ_1 and σ_2 , respectively) can now be drawn up (Table VII. 4), based on the various electronic configurations.

In order to conserve orbital symmetry, both states and levels of like symmetry correlate, as shown in the state diagram in Fig. VII.28. It can be seen that thermally, the ground-state reaction $(p)_2(p)_2 \rightarrow (\sigma_1)_2(\sigma_2)_2$ has a high symmetry-imposed barrier, since $(SS)_2(SA)_2$ in the reactants correlates with $(SS)_2(SA)_2$ in the products, which is the highly excited state configuration $(\sigma_1)_2(\sigma_3^*)_2$. Therefore, the $(2+2)$ reaction is thermally forbidden. Photochemically one of the degenerate reactant excited states $(SS)_2(SA)_1(AS)_1$ correlates directly with the lowest of the cyclobutane excited states $(SS)_2(AS)_1(SA)_1$ with no barrier due to, orbital symmetry conservation. Therefore, the reaction is allowed photochemically. The other excited states [(2)-(4)] only correlate with more highly excited states (not shown in the diagram).

Reactant states		Product states	
g.s	$(SS)^2(SA)^2 \rightarrow (SS)$	g.s	$(SS)^2(AS)^2 \rightarrow (SS)$
(1)	$(SS)^2(SA)^1(AS)^1 \rightarrow (AA)$	(1)	$(SS)^2(AS)^1(SA)^1 \rightarrow (AA)$
(2)	$(SS)^2(SA)^1(AA)^1 \rightarrow (AS)$	(2)	$(SS)^2(AS)^1(AA)^1 \rightarrow (SA)$
(3)	$(SS)^1(SA)^2(AS)^1 \rightarrow (AS)$	(3)	$(SS)^1(AS)^2(SA)^1 \rightarrow (SA)$
(4)	$(SS)^1(SA)^2(AA)^1 \rightarrow (AA)$	(4)	$(SS)^1(SA)^2(AA)^1 \rightarrow (AA)$
(5)	$(SS)^2(AS)^2 \rightarrow (SS)$	(5)	$(SS)^2(AS)^2 \rightarrow (SS)$

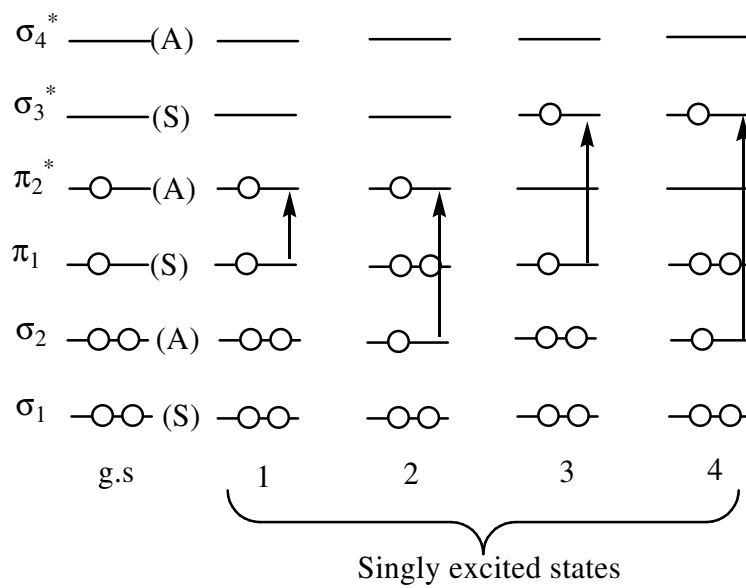


Turning to the (4 + 2) cycloaddition, the ground and various singly excited state configurations are shown in Fig. The corresponding reactant and product symmetries are given in Table VII.5.

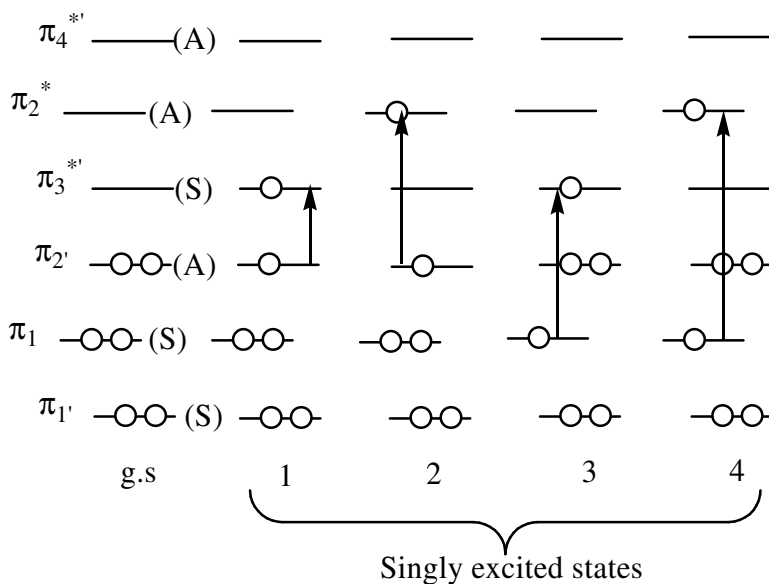
The state-correlation diagram can be constructed as before, conserving orbital symmetry with respect to both states and individual levels and keeping in mind the noncrossing rule. This is shown in Fig. VII 30. Unlike the case of the (2 + 2) reaction, there is now a direct correlation between reactant $[(S)2(S)2(A)2]$ and product $[(S)2(A)2(S)2]$ ground states, and the reaction is thermally allowed. Turning to the various excited state processes, the lowest excited state in the reactants $(S)2(S)2(A)1(S)1$ correlates directly with a much higher (doubly) excited state of the products $(S)2(A)1(S)2(S)1$. This process has a large barrier and will be difficult photochemically. It appears at first that either of the two (S) --- (S) interconversions, which have no symmetry-imposed barrier, would allow the reaction to take place photochemically. However, consideration of the energy level diagrams for (ethylene and butadiene) shows that neither of these processes is feasible, since each necessitates excitation from a bonding orbital in one reactant molecule to an antibonding orbital in the other. Thus (4 + 2) reaction is still photochemically forbidden.

Alternatively, in the reverse direction, these processes would involve starting from a $(\pi-\sigma^*)$ or $(\sigma-p^*)$ state of cyclobutane to give an ethylene product with one or three electrons and a butadiene with five or three.

Cyclohexene



Ethylene + butadiene



Reactant states		Product states	
g.s	$(S)^2 (S)^2 (A)^2 \rightarrow (S)$	g.s	$(S)^2 (A)^2 (S)^2 \rightarrow (S)$
(1)	$(S)^2 (S)^2 (A)^1 (S)^1 \rightarrow (A)$	(1)	$(S)^2 (A)^2 (S)^1 (A)^1 \rightarrow (A)$
(2)	$(S)^2 (S)^2 (A)^1 (A)^1 \rightarrow (S)$	(2)	$(S)^2 (A)^1 (S)^2 (A)^1 \rightarrow (S)$
(3)	$(S)^2 (S)^1 (A)^2 (S)^1 \rightarrow (S)$	(3)	$(S)^2 (A)^2 (S)^1 (S)^1 \rightarrow (S)$
(4)	$(S)^2 (S)^1 (A)^2 (A)^1 \rightarrow (A)$	(4)	$(S)^2 (A)^1 (S)^2 (S)^1 \rightarrow (A)$

