

230. Orbital Correspondence Analysis in Maximum Symmetry

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Summary. A method is described in which the 'allowed' course of a reaction is determined by means of an analysis – within the symmetry point group common to reactants and products – of their molecular orbitals and of the distortions that occur along the reaction path connecting them. The procedure, and its relation to and advantages over conventional correlation methods, is illustrated with a few very well known reactions: Cyclization of hexatriene, the 'photochemical *Diels-Alder* reaction' and the stepwise and concerted [2+2]-cycloadditions.

1. Introduction. – The simple and powerful rules of *Woodward & Hoffmann* [1] are derived from the transformation properties of the molecular orbitals of reactants and products with respect to a few selected symmetry elements. Several years ago, the author devised a procedure for deducing them from an analysis carried out in terms of the transformations of molecular orbitals and displacement coordinates within the full symmetry point group to which the system belongs. Based on the same assumptions as those of the classical correlation procedures of *Woodward & Hoffmann* [1] and of *Longuet-Higgins & Abrahamson* [2], it led to identical results in the simple systems that usually serve as textbook examples. Its principal advantages appeared to be didactic: a) The student was obliged to acquire some familiarity with elementary group theory; b) The analogy with spectroscopic selection rules had aesthetic appeal.

Further experience showed, however, that several of its features had more than purely educational value, and – now that its validity has been established within the framework of *time-dependent perturbation theory* and *group theory of non-rigid molecules* – it appears to be ripe for publication.

The theoretical aspects of *Orbital Correspondence Analysis in Maximum Symmetry (OCAMS)* are developed in a parallel communication [3], the principal findings of which can be summarized for present purposes as follows:

1) The conclusions of *OCAMS*, as to whether a given reaction is 'allowed' or 'forbidden' by symmetry, are identical with those of the classical procedures [1] [2], provided that the latter are carried out so that *all ways of breaking the symmetry of the system are explored*, and that – for each such pathway – *no symmetry elements retained along that pathway are ignored*;

2) The method incorporates a technique for formally restoring the original symmetry of the reactant, whenever it is higher than that of the product. It thus allows reactions to be analysed which present difficulties to the construction of conventional correlation diagrams [1] [2];

3) The geometrical requirements of stepwise reactions can be ascertained as easily as those of reactions ordinarily characterized as 'concerted';

4) When, as is commonly done in the *Woodward-Hoffmann (W.-H.)* procedure, a restricted set of symmetry elements is chosen for the characterization of orbital symmetry [1a], any reaction forbidden by *W.-H.* will also be forbidden by *OCAMS*. The converse is not necessarily true, so a '*W.-H.*-allowed' reaction may turn out to be forbidden by the more stringent requirements of *OCAMS*.

The ensuing discussion is limited to two simple, thoroughly documented, reacting systems: The thermal and photochemical reactions of cyclohexatriene and the cyclo-dimerization of ethylene. These will suffice to illustrate the following aspects of the method:

1) Straightforward application of *OCAMS* to reactions in which its conclusions are identical with those of *W.-H.* (Sect. 2, Subsect. 4.1).

2) Analysis of the stereochemical course of a reaction leading to a completely unsymmetrical product (Sect. 3).

3) Determination, based on orbital symmetry considerations, of the stereochemistry of a stepwise reaction (Subsect. 4.2).

4) Analysis of a 'concerted, *W.-H.* allowed' reaction which – after breaking the reaction coordinate down into its component symmetry coordinates – *OCAMS* characterizes as 'forbidden' (Subsect. 4.3). The source of the discrepancy is shown to be the insufficiently high symmetry chosen in the *W.-H.* treatment (Subsect. 4.4).

The application of the method to other reactions – thermal, photochemical and non-adiabatic – will be deferred to subsequent publications.

2. Cyclization of hexatriene. – Our model reactant, *cis*-hexatriene, and the product of its cyclization, cyclohexadiene, are both oriented in C_{2v} geometry, as in Fig. 1. The molecular orbitals of reactant and product are ordered energetically in the usual manner, and labelled according to their symmetry species in the C_{2v} symmetry point group, using the appropriate character table¹⁾. An orbital symmetric to all of the symmetry elements is designated a_1 , one symmetric only to (the identity operation and) rotation about the z -axis is a_2 ; one symmetric only to reflection in the xz - or yz -plane is b_1 or b_2 respectively. Orbitals of the same symmetry species are joined by *correspondence lines*, which are drawn so as to obey the *non-crossing rule* in the original symmetry group. The orbital pairs so connected – in our example: $\psi_1 \rightarrow \chi_1(b_2)$; $\psi_2 \rightarrow \chi_2(a_2)$; $\psi_3 \rightarrow \chi_3^*(b_2)$; $\psi_4^* \rightarrow \chi_4^*(a_2)$ – retain identical transformation properties under any deformation of the system. In the language of perturbation theory, these are *zero-order* correspondences.

Although any reduction of symmetry below C_{2v} , two of which will be considered shortly, would leave these paired orbitals in the same symmetry species of the ensuing group of lower symmetry, a subgroup of C_{2v} , it will also map other symmetry species of C_{2v} onto the same species of the subgroup. In such a case, the correspondence lines

¹⁾ Character tables can be found in [4] and [5], or in any of many other books on group theory, molecular structure and spectroscopy. In this paper and others of this series, capital letters (A_1, B_2 etc.) are reserved for the designation of state symmetries and irreducible representations. The symmetry properties of orbitals and coordinates, are designated in lower case (a_1, b_2 etc.).

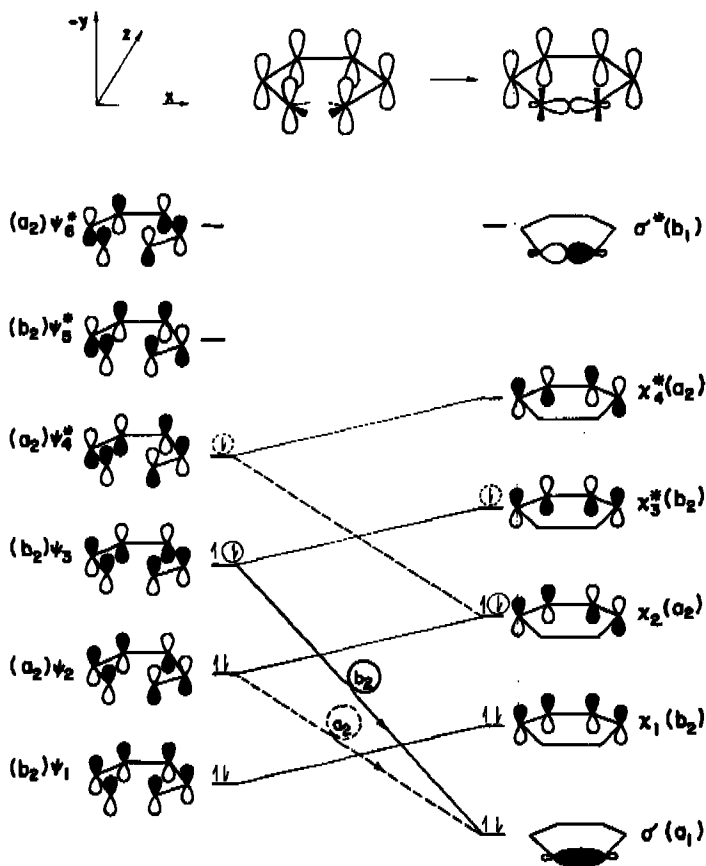


Fig. 1. Correspondence diagram for cyclization of hexatriene

will still cross one another, with apparent disregard of the non-crossing rule. In this respect they differ from true *correlation lines*, which obey the non-crossing rule along the entire reaction path. It was in order to maintain the necessary distinction between a *correlation* and a *correspondence* that the latter term was coined²⁾.

In order for thermal cyclization to be 'allowed', the three doubly occupied orbitals of the reactant must go over smoothly into those of the product. Two such pairs are already in correspondence, but ψ_3 of the reactant corresponds to an unoccupied antibonding orbital, χ_3^* , of the product, whereas the all-important σ orbital of the product has no counterpart in the reactant. The reaction is therefore clearly 'forbidden' under any totally symmetric displacement, *i. e.* unless the symmetry of the system is reduced below C_{2v} .

The nature of the deformation called for is easily determined from the requirement that it be capable of bringing $\psi_3(b_2)$ and $\sigma(a_1)$ into correspondence. In analogy to the method routinely employed in deriving spectroscopic selection rules [4], we require

²⁾ The author is grateful to Prof. E. Heilbronner for impressing upon him the necessity for making this distinction.

that the symmetry species of a displacement coordinate capable of *inducing* the correspondence be the direct product of those of the two orbitals to be interrelated, in our case: $b_2 \times a_1 = b_2^3$). In the *Woodward-Hoffmann* notation, we would formulate this requirement as: $SA \times SS = SA$, where SA, for example, represents an orbital, or coordinate, symmetric to the mirror plane (yz) and antisymmetric to the twofold rotational axis (z).

Fig. 2 depicts, by means of suitable sets of arrows, several representative symmetry coordinates. The number of independent symmetry coordinates in any given molecular system that transform as each of the symmetry species could, in principle, be obtained by standard methods [5a]; those in Fig. 2 are merely an illustrative selection. Examination of the various sets of arrows shows that one of the b_2 motions, all of which retain symmetry with respect to reflection in the yz-plane, is a disrotation. It follows that a disrotation is capable of bringing all three pairs of occupied orbitals into one-to-one correspondence and, as a result, of 'allowing' the ground

Displacement	Representation in C_{2v}	W-H. Notation ($m-C_2$)
	A_1	SS
	B_2	SA
	A_2	AS
	B_1	AA
	B_2	SA
	A_2	AS

Fig. 2. Symmetry coordinates of hexatriene in C_{2v}

³⁾ Rigorously, $\Gamma_1 \times \Gamma_d \times \Gamma_1$ must contain the totally symmetric representation. For commutative symmetry point groups, to which the present method restricts itself, the simpler forms, $\Gamma_1 \times \Gamma_j = \Gamma_d$ or $\Gamma_1 \times \Gamma_d = \Gamma_1$ are adequate for the identification of a *first order correspondence* between orbitals i and j that is induced by the displacement d . The advantages of this restriction to commutative groups are discussed elsewhere [3].

state cyclization. To be sure, the *induced correspondence* $\psi_3 \rightarrow \sigma$, will not appear in the final correlation diagram, since it will have been frustrated by the non-crossing rule after the symmetry of the system has been reduced to C_8 by the disrotation. The eventual orbital *correlations* are $\psi_3 \rightarrow \chi_1$ and $\psi_1 \rightarrow \sigma$, but the reaction remains thermally allowed nonetheless, as predicted from the correspondence diagram⁴).

Turning to the photochemical reaction, our formal requirement is that the lowest excited states of reactant and product be brought into correlation. In the lowest excited state, one electron will have been promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), so two kinds of correspondence must be brought about: (a) Direct or cross-correspondences between the singly occupied HOMO's and LUMO's. In Fig. 1 the desired pair of interrelations $\psi_3 \rightarrow \chi_3^*(b_2)$ and $\psi_4^* \rightarrow \chi_2(a_2)$ is evident; (b) Correspondence of the remaining, doubly occupied, orbitals between reactant and product. Of the two in our example, one, $\psi_1(b_2) \rightarrow \chi_1(b_2)$, has already been noted, but the other, $\psi_2(a_2) \rightarrow \sigma(a_1)$, has to be induced by a displacement of the a_2 symmetry species, *i. e.* a conrotation. The excited state cyclization is thus confirmed to be conrotatory.

In the present simple example, and other polyene cyclizations, OCAMS supports the Woodward-Hoffmann rules fully [1b]. In their analysis, these authors retain two symmetry elements, C_2 for the conrotatory cyclization and $\sigma_{yz} (= m)$ for the alternative disrotatory mode. These two elements, their product, σ_{xz} , and the ubiquitous identity operation, E, which results from applying any operation twice, comprise the full symmetry point group, on which our Fig. 1 was based. For complete consistency with OCAMS, we might also ask for consideration of a possible b_1 pathway, but since any distortion that transforms as b_1 retains reflection symmetry in the molecular plane, it is evidently useless for forming a sigma-bond between the two end carbon atoms, and can safely be discarded on intuitive chemical grounds.

3. The photochemical Diels-Alder reaction. - Although the excited state conrotatory cyclization of hexatriene to cyclohexadiene is clearly allowed, it is a well known experimental fact that the principal product is not cyclohexadiene, but bicyclo[3.1.0]hexene, the formation of which by the 'photochemical Diels-Alder reaction' has been postulated to be allowed by either a $[\pi 4_s + \pi 2_s]$ or a $[\pi 4_a + \pi 2_s]$ concerted internal cycloaddition [1c].

The reaction is indeed formally a $[\pi 4 + \pi 2]$ cycloaddition, but it hardly seems justified to ignore the fact that the reactant is a conjugated triene. If photochemical formation of the bicyclic product in fact occurs from the [s-cis, s-cis] isomer (*vide infra*) it does so in preference to the patently allowed conrotatory cyclization to cyclohexadiene. There is a strong presumption that it occurs in a single step, also under the influence of a motion of a_2 character, and that its driving force derives from the simultaneous formation of two sigma bonds, rather than one sigma and one π -bond.

A relatively simple a_2 motion is the conrotatory distortion of the sigma framework until it buckles into the conformation illustrated in Fig. 3. This motion, in either

⁴) The OCAMS requirement, that occupied orbitals in reactant and product be in *correspondence*, is thus slightly less restrictive than that of Woodward & Hoffmann [1] which requires that *orbital correlation* be maintained. It is somewhat more restrictive than that of Longuet-Higgins & Abrahamson [2], which is based on configuration correlation, but ultimately insists only on *state correlation*.

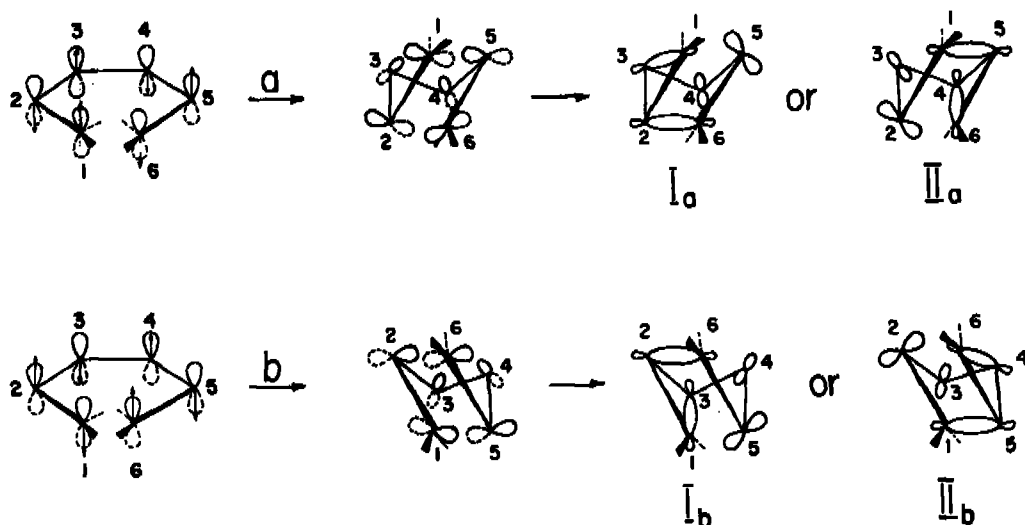


Fig. 3. Reaction coordinate for photochemical Diels-Alder reaction. Legend: In the drawings representing the orientation just before bonding, the lobes of the p -orbitals that are originally above the xz -plane ($-y$) are outlined with a full line and those that were originally below the plane ($+y$) are outlined with a dashed line

phase a or b , allows the 3-membered ring to be formed by bonding between C_1 and C_3 or between C_4 and C_6 . In one case, the five membered ring is formed by bonding between C_2 and C_6 , in the other – between C_5 and C_1 . Let us assume that bonding occurs during phase a of the motion and consider the first alternative product, I_a : C_1 and C_3 evidently bond using p -lobes on the same (upper) face of the π -system; C_2 uses its lobe on the other (lower) face to bond with the upper face of C_6 . In this conformation the lower face of C_6 is properly oriented for alternatively bonding with C_4 . We see that C_1 and C_2 bond at opposite faces (antara) whereas C_3 and C_6 bond at the same face (*supra*); the reaction is thus indeed a $[\pi 4_s + \pi 2_s]$ cycloaddition.

The stereochemical requirements of the conrotatory mode enable us to construct the correspondence diagram for this reaction in an unambiguous way, a task that at first sight appears to be rather difficult, since the product has no symmetry elements left at all, except for the identity operation, E .

We first note, in Fig. 3, that the reactants and products can be formed in either of two bonding sequences, I and II, each of which is represented by two enantiomers (a and b). We restore C_{2v} symmetry to the products by combining corresponding molecular orbitals of the four products (I_a , I_b , II_a , II_b) into linear combinations that are either symmetric or antisymmetric with respect to the symmetry elements of the group.

Let us begin by restoring symmetry with respect to σ_{xz} , *i.e.* reflection in the original molecular plane of hexatriene. Consider the combination representing the π -bond between C_4 and C_5 in I_a and I_b . In principle, it could be either ($\pi_{Ia} + \pi_{Ib}$) or ($\pi_{Ia} - \pi_{Ib}$). OCAMS requires, however, that the proper combination retain its symmetry properties when the system is constrained to a conformation intermediate between that of the two components [3]. If C_4 and C_5 are forced into the xz -plane, π_{Ia}

and π_{1b} coalesce and their negative combination necessarily vanishes, so $(\pi_a + \pi_b)$ must be the correct combination to take. Identical considerations require the positive combinations of the sigma orbitals in I_a and I_b to be taken. Evidently, we can replace this pair of enantiomers with a single model molecule in the planar conformation intermediate between them, represented at the top of Fig. 4 by I; the pair II_a and II_b is similarly represented by II.

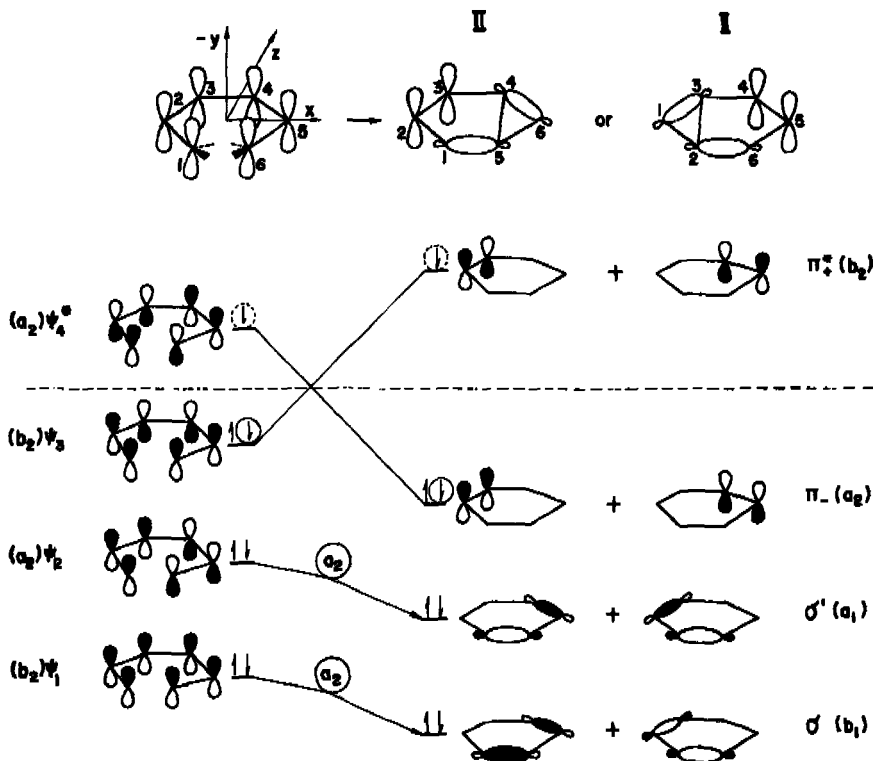


Fig. 4. Correspondence diagram for photochemical Diels-Alder reaction

The proper choice of combinations between the corresponding orbitals of I and II is less trivial, because the bonding pattern is different in the two possible products, and is governed by the options open to the system just before the bonds are formed.

The pivotal role is played by C_1 (or equivalently by C_6). Consideration of the mutual disposition of the atoms just before bonding (Fig. 3) makes it clear that – a moment before reacting – C_1 must 'decide' whether to form a three membered ring by bonding to C_3 or a five membered ring by bonding to C_5 . Geometric considerations require that a different p-lobe of C_1 be turned towards each of its possible bonding partners, whereas symmetry demands that both interactions be bonding at the same time, or the 'choice' is not a genuine one. Thus if, at the moment of choice, the *negative* lobe of the C_1 is incipiently bonding with C_3 , its *positive* lobe must be bonding to that of C_5 . The antisymmetric (b_1) combination is therefore the correct one to take for σ , whereas σ' must be chosen to be symmetric (a_1). Similar considerations of simultaneous antibonding of C_1 with C_3 and C_5 dictate the symmetry species of the

antibonding sigma orbitals, but they are not of direct interest, and have been omitted from the correspondence diagram in Fig. 4.

The assignment of the π -orbitals to symmetry species can be misleading. It would be a mistake to choose the positive (b_2) combination of the π -orbitals at C_2 - C_3 and C_4 - C_5 on the grounds that, in analogy to χ_1 of cyclohexadiene (Fig. 1), it is bonding between C_3 and C_4 . Unlike cyclohexadiene, in which there is a genuine bonding interaction between C_3 and C_4 stabilizing $\chi_1(b_2)$ relative to $\chi_2(a_2)$, the present product has just one double bond, which can be formed *either* between C_2 and C_3 *or* between C_4 and C_5 . There is no π -bonding between C_3 and C_4 , so there is no energetic advantage to the symmetric over the antisymmetric combinations or *vice versa*. The choice between them is made on the basis that, a moment before bonding, formation of the double bond between either pair of atoms must be equally probable. It is clear from Fig. 3 that in order to be equally bonding with each of the opposite faces of C_1 , C_3 and C_5 must have lobes of opposite phase on the same face of the reacting system, so the alternative double bonds formed with each of them must also have lobes of opposite phase on the same face. The proper orbital to describe both eventualities is thus the negative combination $\pi_-(a_2)$; for the same reason, the antibonding orbital has to be $\pi_+^*(b_2)$.

The only zero-order correspondences in Fig. 4 are those connecting the HOMO of the reactant to the LUMO of the product and *vice versa*. In addition, if the reaction is to be photochemically allowed, the two doubly-occupied orbitals must be brought into correspondence by the conrotatory motion depicted in Fig. 3. Evidently, since this motion transforms as a_2 , it can induce the correspondences: $\psi_1(b_2) \rightarrow \sigma(b_1)$ and $\psi_2(a_2) \rightarrow \sigma'(a_1)$, as required⁵⁾.

The internal photochemical *Diels-Alder* reaction of hexatriene has thus been confirmed to be a [$\pi 4_s + \pi 2_s$] cycloaddition, which is characterized as 'allowed' if the reaction proceeds along the conrotatory pathway shown in Fig. 3. The experimental evidence cited by Seeley [6] *against* concerted cycloaddition is not inconsistent with reaction along this particular pathway. Recent studies [7] [8] confirm the [$\pi 4_s + \pi 2_s$] nature of the reaction, but show that the product is preferentially formed from those trienes in which substituents stabilize the [*s-trans*, *s-cis*]-rather than the [*s-cis*, *s-cis*] conformation depicted in Fig. 3. It might be noted, however, that application of the present method to triene isomerization predicts the excited states of the various isomers to be readily interconvertible, confirming the doubts raised by *Havinga et al.* [8] as to whether it is justified to relate the product distribution unambiguously to the ground state conformation. Moreover, in the [*s-trans*, *s-cis*] isomer C_1 and C_6 are not equivalent, and the terms 'disrotation' and 'conrotation' do not apply, except - loosely - when applied locally to specific bonding regions [7]. Consequently, sym-

⁵⁾ Superficially, a *disrotation* (b_2) could also 'allow' the reaction by inducing the correspondences $\psi_1(b_2) \rightarrow \sigma'(a_1)$ and $\psi_2(a_2) \rightarrow \sigma(b_1)$. However, the orbitals that appear in Fig. 4 were characterized on the explicit basis of the *conrotatory* motion described in Fig. 3. An analogous attempt to generate the same product by means of a disrotatory motion would, if successful, yield a different set of molecular orbitals for the product and require a different correspondence diagram. It might be pointed out that various disrotations lead more naturally to bicyclo-[2.2.0]hex-2-ene or to a tricyclohexane (305 of [1]). Whether either of these reactions is thermally or photochemically allowed must also be determined by separate analyses, and cannot be deduced from Fig. 4.

metry-imposed barriers to this and other reactions that may exist for the [s-cis, s-cis] isomer vanish after the unsymmetrical conformation has been achieved. In any event, our analysis merely confirms the $[\pi^4_g + \pi^2_a]$ reaction of the [s-cis, s-cis] isomer to be allowed *via* conrotation; it does not presume to choose between this and other allowed pathways.

4. Cyclodimerization of ethylene. – A great deal of attention has been paid in recent years to $[\pi^2 + \pi^2]$ cycloaddition, and numerous questions have arisen concerning its allowedness, concertedness, polar nature and stereochemistry in various circumstances [1d] [9–11]. Following *Woodward & Hoffmann* [1e], we will limit our formal analysis to the prototype reaction: [ethylene + ethylene], and defer to a subsequent publication the attempt to reinterpret the abundant stereochemical evidence in terms of its conclusions [12].

4.1. Direct application of OCAMS. The simplest initial disposition of reactants to consider is the parallel approach, illustrated in Fig. 5, in which the reactants have the symmetry elements of D_{2h} .

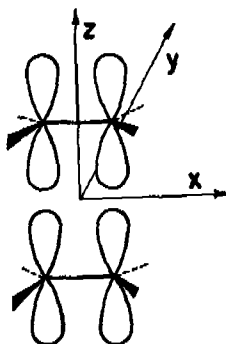


Fig. 5. $[\pi^2 + \pi^2]$ -cycloaddition: parallel approach

Planar cyclobutane has the still higher D_{4h} symmetry, but, if the two new sigma bonds (C_1-C_3 and C_2-C_4) are lengthened slightly relative to the two already present (C_1-C_2 and C_3-C_4), our slightly elongated product molecule reverts to D_{2h} .

The correspondence diagram, Fig. 6, is readily constructed: The energy sequence on either side is self-evident and the *transformation* properties are easily confirmed⁶⁾.

The two lowest a_g orbitals correspond directly. π_+ , the HOMO in the reactants corresponds with σ^* , the LUMO of the product (both b_{1u}) as also do π^* and σ' (both b_{3u}). Evidently the first excited states correlate directly: $(a_g^2 b_{1u}^1 b_{3u}^{*1}) \rightarrow (a_g^2 b_{3u}^1 b_{1u}^{*1})$, so the photochemical reaction is 'allowed'. The thermal reaction cannot take place under a totally symmetric motion, *i.e.* direct approach in the parallel orientation, and is thus 'forbidden'. We have thus far merely reproduced the well known conclusions of all the conventional treatments. *OCAMS*, however, goes on to specify the nature of the displacement of the two ethylene molecules that would allow their thermal cycloaddition. The orbitals between which correspondence must be induced are

⁶⁾ It is sufficient to note that A implies symmetry with respect to all three rotational axes whereas B_1 , B_2 and B_3 are symmetric to rotation about only one axis, z , y and x respectively. Symmetry or antisymmetry to inversion is denoted by g and u respectively.

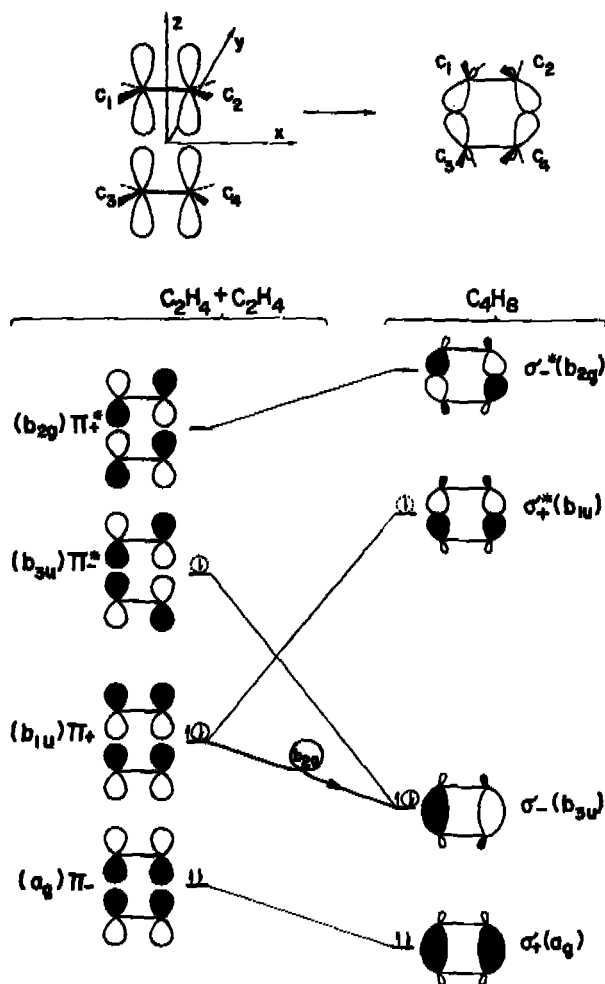


Fig. 6. Correspondence diagram for $[\pi 2 + \pi 2]$ -Cycloaddition in D_{2h} symmetry

of symmetry species b_{1u} and b_{3u} , so the inducing symmetry coordinate must transform as their direct product: $b_{1u} \times b_{3u} = b_{2g}$.

It is instructive to consider several pathways, the confirmation or exclusion of each of which by conventional procedures would have required a separate correlation diagram: Direct approach along the z -axis (a_g) has already been excluded. A twist of the ethylene molecules about the z -axis towards the perpendicular orientation is a_u . Bringing together two of the adjacent carbon atoms C_1 and C_3 , while moving the other two (C_2 and C_4) apart, so as to form a planar *cisoid* four-carbon chain, is b_{3u} . It is not difficult to ascertain that any approach along a symmetry coordinate of the required b_{2g} character will tend to retain coplanarity of the four carbon atoms and will bring C_1 closer to C_4 while separating C_2 and C_3 , or *vice versa*.

From the D_{2h} character table, we see that the symmetry elements to which any b_{2g} displacement must be symmetric are $[E, C_2(y), i, \sigma_h(xz)]$. These are just the ele-

ments of C_{2h} , the particular subgroup of D_{2h} to which the symmetry of the system has been reduced by the displacement. Obviously, the new geometry is not suitable for concerted formation of both new bonds of cyclobutane, but rather describes a *transoid* four-carbon chain intermediate, such as a singlet biradical, which will have to rotate its free ends into mutual proximity before the cyclobutane ring is closed in a second step.

4.2. Stereochemistry of stepwise cycloaddition. The conclusion just arrived at raises an apparent difficulty: The motion required to induce the essential orbital correspondence between the b_{1u} orbital of the reactants and the b_{3u} orbital of cyclobutane, was found to be a symmetry coordinate of species b_{2g} , which - by its nature - cannot lead to direct formation of cyclobutane, but produces a *transoid* chain intermediate instead! Should not the analysis have been performed in the true geometry of the presumed product?

This could have been done by a procedure, analogous to that employed in Sect. 3, which restores D_{2h} symmetry to the product by generalizing it to be a superposition of the two possible intermediates, [1234] and [1243], and forming suitable linear combinations of their corresponding molecular orbitals. Instead, we will make use of the fact that distortion along a b_{2g} symmetry coordinate generates C_{2h} geometry. Having used OCAMS to chose the pathway, we can now adopt the Woodward-Hoffmann point of view and construct the correspondence diagram - which is now the same as the correlation diagram appropriate for that pathway.

Comparing the C_{2h} character table with that of D_{2h} , which includes it as a subgroup, we see that orbitals which transform as b_{1u} or b_{3u} in D_{2h} , and thus do not correspond in the rectangular conformation, go over into the same species, b_u after the symmetry has been reduced to C_{2h} . We can thus set up the reactants and products in the latter geometry, and construct the correspondence diagram in C_{2h} symmetry.

We see from Fig. 7 that all the molecular orbitals lie in the xz -plane and, being necessarily symmetric to σ_h , must be either a_g or b_u . The energy sequence of the reactant orbitals differs from that in the parallel orientation (Fig. 6) only in that the two unoccupied antibonding orbitals are inverted. The orbitals of the product are best considered in two steps: Let us begin by assuming unrealistically that the central σ -bond is completely independent from the p^z orbitals at the ends of the chain. Of the 'zero-order' orbitals, shown at the extreme right of Fig. 7, σ is certainly the most stable and σ^* the least. In the *trans* conformation depicted, the 'through-space' interaction between the end p^z orbitals is expected to be quite small but it should still split the degeneracy between their two linear combinations, making $\pi_-^z(a_g)$ slightly more stable than $\pi_+^z(b_u)$. We then take account of 'through-bond interaction' [13] by recognizing that the two a_g orbitals interact as do the two of species b_u ; the lower of each pair is decreased in energy at the expense of the upper. The important consequence of 'through-bond interaction' is that - in our *trans* configuration - $\pi_+^z(b_u)$ is the HOMO and $\pi_-^z(a_g)$ is the LUMO. As a result, the reactant-product correlation is direct, and the thermal generation of a *transoid* singlet biradical is confirmed to be 'allowed'.

Fig. 7 also lends insight into the nature of the second step of the reaction, ring closure. If the biradical is twisted about its central C_2-C_3 σ -bond towards the *cis* configuration, the p^z lobes at C_1 and C_4 increasingly overlap, so that the 'through-space

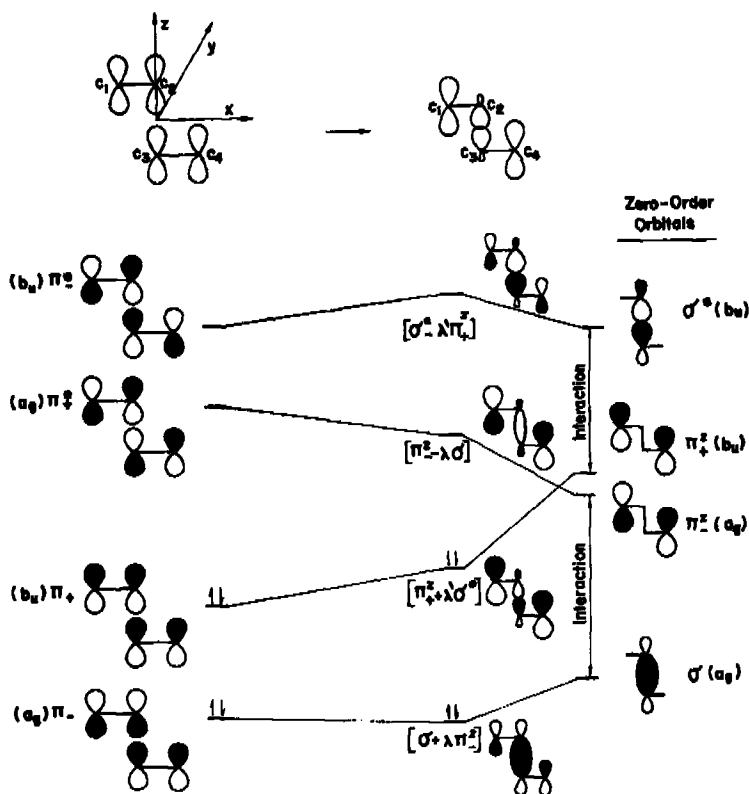


Fig. 7. Correspondence (or correlation) diagram for stepwise $[\pi_2 + \pi_2]$ -Cycloaddition in C_{2h} symmetry

interaction' increasingly stabilizes π_x^- and destabilizes π_x^+ . In some intermediate geometry, the energies of these two orbitals will be equal, and thereafter the stable biradical will not have the orbital occupancy ($\sigma^2\pi_x^+{}^2$) but rather ($\sigma^2\pi_x^-{}^2$) - which correlates directly with cyclobutane.

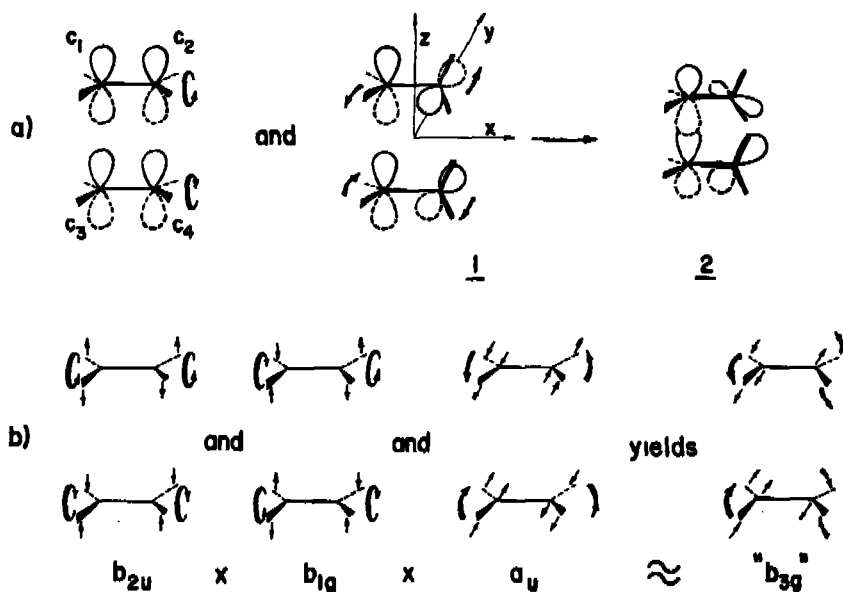
Once it is realized that the intermediate biradical has two distinct closed-shell singlet states, one of which is *trans*-stable and the other *cis*-stable, it becomes clear that there must be a potential barrier between them. If a *cisoid* radical were formed as the first intermediate, we would have to accept *Baldwin & Kapecky's* argument, according to which the stepwise and concerted mechanisms are essentially indistinguishable [14]. However, since symmetry requires the intermediate to be formed in the *trans*-stable state, it follows that the reaction is genuinely stepwise, the interconversion of two states of the biradical - each stable in a different conformation - providing the necessary barrier to ring-closure. *Dewar & Kirschner* have reached similar conclusions about the 'homomerism' of the reactants with a *trans*-stable biradical and of the product with a *cis*-stable one, and have calculated the energy barrier between them by MINDO-3 [15]⁷⁾. The *ab initio* calculations of *Segal* establish the existence of two stable biradicals, *trans* and *gauche* (rather than *cis*) and explore the reaction surface connecting them [16].

7) The author is grateful to Prof. *Dewar* for making these results available to him prior to publication.

4.3. $[\pi 2_s + \pi 2_a]$ Cycloaddition. Woodward & Hoffmann characterize as 'allowed' the $[\pi 2_s + \pi 2_a]$ cycloaddition, in which one of the two reacting ethylene molecules reacts antarafacially [1d]. Let us defer to the following subsection consideration of the particular mode of approach prescribed by these authors, and - starting from the familiar parallel orientation of Fig. 5 - investigate the geometric requirements of the reaction. In a $[2_s + 2_a]$ cycloaddition, the suprafacial reactant uses both p^z lobes facing its partner whereas the latter must turn one of its methylene groups so as to bond with a p^z lobe that was originally facing the 'wrong' way. When, as in our prototype reaction, the two reactants are symmetrical and identical, either reactant can play the antarafacial role. Our analysis must allow for this duality, and also for a further ambiguity: Assuming that $C_1 = C_2$, rather than $C_3 = C_4$, is the antarafacial reactant, is it C_1 or C_2 that turns towards $C_3 = C_4$ the face that was originally away from it?

Fig. 8 shows how the mutual orientation of the reactants that is consistent with one of the four equivalent $[2_s + 2_a]$ schemes ($C_1 = C_2$ reacts antarafacially, with C_2 turning its upper face towards C_4) can be achieved by a sequence of displacements that are symmetry coordinates of D_{2h} :

1) We impose a relative disrotation of the two ethylene molecules, rotating each about its own longitudinal axis. This displacement, which is merely a reorientation



$[2_s + 2_a]$ Cycloaddition (in D_{2h})

Fig. 8. Reaction coordinate for concerted $[\pi 2_s + \pi 2_a]$ -cycloaddition and its decomposition into D_{2h} symmetry coordinates. p^z -Orbital lobes originally directed along $+z$ are outlined with a full line; those originally along $-z$ are outlined with a dashed line.

of the reactants and costs very little energy provided that they are not too close, is a symmetry coordinate of species b_{2u} .

2) Next, a disrotatory twist of each molecule about its molecular axis (b_{1g}), reverses the relative rotation of two methylene groups - in the phase pictured, those at C_1 and C_3 - while reinforcing that of the other two.

The superposition of two such symmetry coordinates generates a *composite motion*, that behaves as if it were a coordinate of the symmetry species: $b_{2u} \times b_{1g} = b_{3u}$, in the sense that it is capable of inducing, *in second-order*, those correspondences that would be induced *in first-order* by a b_{3u} symmetry coordinate [3]⁸⁾. If carried just far enough, it would bring the methylene groups of C_2 and C_4 into coplanarity while restoring those at C_1 and C_3 to their original positions. The system will thus have been taken into C_{2v} symmetry, in which the symmetry elements retained are those with respect to which a b_{3u} displacement is symmetric: $\{E, C_2(x), \sigma_{xz}, \sigma_{xy}\}$.

3) In order to allow the formation of a σ -bond between C_2 and C_4 , the two displacements just discussed must be followed - or preceded - by a relative rotation of the two molecules about their common z -axis. In the phase pictured in Fig. 8, the initially upper faces of C_2 and C_4 are now turned towards each other, as specified. This third displacement transforms in the original D_{2h} symmetry as a_u , so the entire ternary sequence behaves like: $b_{3u} \times a_u = b_{3g}$. This is, of course, quite different from b_{2g} , so it is incapable of inducing the correspondence between $\pi^*_i(b_{1u})$ and $\sigma_-(b_{3u})$. It follows that $[\pi 2_s + \pi 2_a]$ cycloaddition of two ethylene molecules is 'forbidden', a finding in keeping with the semi-empirical calculations of *Okada, Yamaguchi & Fueno* [17] who show a biradical mechanism to be preferred, even along the pathway most favorable for concerted $[2_s + 2_a]$ cyclodimerization of ethylene. The same conclusion has been reached by *Dewar & Kirschner* [15].

4.4. *Contravention of the W.-H. Rules.* In their primary analysis of $[2 + 2]$ cycloaddition, *Woodward & Hoffmann* used two mirror planes, m_1 and m_2 , bisecting the reactant π -orbitals and product σ -orbitals respectively [1e]. These two elements, their product, $C_2(y)$, and the square of each of them, E , together comprise one of the C_{2v} subgroups of D_{2h} . It differs from that on which Fig. 1 and 2 are based, in that rotational symmetry is retained about the y -axis rather than the z -axis. Their procedure is thus equivalent to applying the present method in C_{2v} , rather than D_{2h} , symmetry and, as has been noted in *Sect. 1*, any reaction pathway that is forbidden by *W.-H.* will also be forbidden by *OCAMS*. It is thus hardly surprising that both methods of analysis find concerted $[2_s + 2_s]$ cycloaddition to be forbidden. Furthermore, an application of *OCAMS* in that particular C_{2v} geometry would have been sufficient to determine that a motion generating a *transoid* intermediate (AA in the *W.-H.* notation) is able to induce correspondence between bonding orbitals of unlike symmetry ($AS \rightarrow SA$).

For the concerted $[2_s + 2_a]$ cycloaddition, a different geometry, that of Fig. 9, was chosen. This also has C_{2v} symmetry, but now - as in Fig. 1 rather than y is the unique rotational axis of symmetry. Note first that the two ethylene molecules are no longer equivalent: The upper is preordained to act as the antarafacial com-

⁸⁾ The analogy with selection rules for combination bands in vibrational spectroscopy is immediate [5b].

ponent, whereas the lower cannot choose but react suprafacially. Moreover, this geometry does not adequately fulfill one of the basic requirements of the *W.-H.* procedure, namely: 'The symmetry elements chosen for analysis must bisect bonds made or broken in the process' [1a]. Each mirror plane bisects one π -bond and the rotational axis bisects both, but none of the symmetry elements bisects the new σ -bonds formed. The perpendicular orientation shown in Fig. 9 is simply of too low symmetry for reliable conclusions to be drawn from it.

Finally, it should be pointed out that full D_{2h} symmetry is not really required for the analysis. Suppose the third motion in Fig. 8, marked a_u , were allowed to occur *before* the analysis is carried out. The system will have been twisted out of coplanarity into the conformation shown in Fig. 10, in which symmetry with respect to inversion and to reflection in all three mirror planes has been lost. The remaining symmetry elements [E , $C_2(z)$, $C_2(y)$, $C_2(x)$] constitute yet another subgroup of D_{2h} , D_2 .

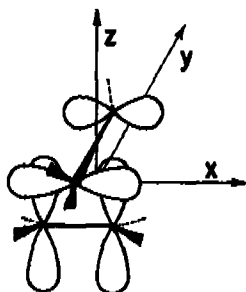


Fig. 9. $[\pi 2_u + \pi 2_d]$ -Cycloaddition: *Perpendicular Approach* [1d]. The reaction is completed by a twist of the two methylene groups of the upper and/or lower molecule about its longitudinal axis

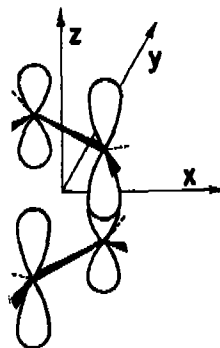


Fig. 10. $[\pi 2 + \pi 2]$ -Cycloaddition: *Off-parallel (D_2) approach*

After symmetry has been reduced in this way, the two reacting ethylene molecules remain equivalent. The composite twist required to generate the required geometry for $[2_s + 2_a]$ cycloaddition, which in D_{2h} was equivalent in second-order to $b_{2u} \times b_{1g} = b_{3u}$, behaves, in D_2 - in which there is no distinction between g and u - like b_3 . However, the orbital correspondence to be effected has become $b_1 \rightarrow b_3$, and so requires motion along a symmetry coordinate of species b_2 , and not b_3 , to induce it. The distinction between these two symmetry species rests in the fact that any b_2 coordinate must be symmetric with respect to rotation about the y -axis and anti-symmetric with respect to rotation about the x -axis, whereas for a b_3 coordinate the two properties are reversed. In the perpendicular orientation of Fig. 9, neither $C_2(x)$ nor $C_2(y)$ is a symmetry element, so it does not allow this essential distinction, which categorizes $[2_s + 2_a]$ cycloaddition as 'forbidden', to be made.

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231. An Anomalous Oxidation of β -Pinene

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Summary. The oxidation of β -pinene with aqueous alkaline potassium periodate and catalytic amounts of potassium permanganate gave, in addition to the expected oxidation product nopinone, a β -ketol. The structure of the latter was shown to be 1-(2-hydroxyisopropyl)bicyclo[3.1.0]hexan-2-one. The formation of this anomalous side-product represents a new type of rearrangement of the pinane skeleton.

In connection with a programme of research where sizeable quantities of nopinone were needed, it was decided to oxidatively cleave the double bond of β -pinene with an aqueous solution of sodium periodate in the presence of potassium permanganate as catalyst. This method was originally exploited for the semiquantitative analysis of terminal methylenes and isopropylidene groups [1]. The gross mechanistic features of the oxidation are that permanganate anion converts the double bond to the vicinal diol which is subsequently cleaved by the more powerful oxidant periodate to two carbonyl fragments. As the permanganate is only present in catalytic amounts it is constantly regenerated from the spent manganate ion by excess periodate. As side reactions are claimed to be unimportant this analytical procedure has been adapted to the oxidation on a preparative scale of many cyclic olefins, in particular bicyclic monoterpenes. Both α - and β -pinene and sabinene have been reported to undergo straightforward oxidative cleavage in high yield to the corresponding ketone products. However, camphene, in addition to the expected camphenilone produced in 50% yield, gave numerous acidic by-products [2].