predicted curves is that they depend almost entirely on the rate of helix propagation for the longer oligomers, when the temperature jumps are limited to the melting zone, and are relatively insensitive to the rate of helix nucleation. We expect that it will be possible to use this approach to measure the rate constant for propagation and eventually to work out the kinetics of a defined loop migration reaction (see Figure 2).

The Möbius–Hückel Concept in Organic Chemistry. Application to Organic Molecules and Reactions

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In 1966[1] we presented an approach to determine the forbiddenness or allowedness of organic reactions which is a suitable alternative to the thoroughly documented methods of Woodward and Hoffmann.[2] The present Account summarizes the original approach and applications presented in various subsequent publications and describes some further examples of interest. These include application of the concept not only to prediction of allowedness of reactions but also to description of some ground-state organic systems.

The Concept

One concept which has been of special value in organic chemistry is the Hückel rule[3] which says that, for ground-state molecules with a cyclic array of orbitals, $4N + 2$ electrons lead to aromaticity and special stability deriving from the presence of a closed shell. Systems which have $4N$ electrons are said to be antiaromatic.[4] This rule holds not only for cyclic polyenes but also for cyclic transition states.

However, the $4N + 2$ rule can be shown to apply only to cyclic systems composed of orbital arrays in which there are zero or an even number of sign inversions resulting from plus–minus overlaps.[1] Ordinary cyclic polyenes and other cyclic π systems such as cyclopropenyl, cyclobutadiene, cyclopentadienyl, benzene, cycloheptadienyl, etc., fit this requirement. These are conveniently termed Hückel systems since

they fit the Hückel rule and have molecular orbital solutions of the normal Hückel type.

However, many systems in organic chemistry consist of monocyclic arrays of orbitals in which there is one or, alternatively, an odd number (*vide infra*) of overlaps between adjacent orbitals of different sign. These molecules do not have a closed shell with $4N + 2$ electrons but rather need $4N$ electrons for stability. With $4N + 2$ electrons they are antiaromatic.[1] We have termed such molecular species Möbius because the molecular orbital situation is quite like that of Heilbronner's[5] Möbius cyclic polyenes.[1]

Hence the first problem is to learn to recognize which orbital arrays are of the Hückel type and which are Möbius. Figure 1 depicts two unlikely but instructive arrays of arbitrarily chosen orbitals; **1a** is a Hückel system while **1b** is a Möbius one. Note that these arrays may consist of p orbitals, hydrogen 1s orbitals, carbon 2s orbitals, etc., and will roughly approximate situations where all are of the same type.

In Figure 1 it should be clear that the orbitals shown are "basis set orbitals," namely, the assortment of orbitals present *prior to* a molecular orbital calculation; such a set can be chosen with the orientations and assignment of sign selected for convenience. However the molecular orbital calculation results prove independent of the orientations selected. Any concern about adjacent plus–minus overlap as unfavorable is premature. Hence the categorization of a system as Hückel *vs.* Möbius does not require an explicit MO calculation but is made from inspection of the basis orbitals available to the system.

(1) (a) H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564 (1966); (b) *ibid.*, **88**, 1566 (1966); (c) *Science*, **153**, 837 (1966).

(2) (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); (b) *ibid.*, **87**, 2511 (1965); (c) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); (d) *ibid.*, **87**, 4389 (1965); (e) R. B. Woodward and R. Hoffmann, *Accounts Chem. Res.*, **1**, 17 (1968); (f) *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) E. Hückel, *Z. Phys.*, **70**, 204 (1931); **76**, 628 (1932); **83**, 632 (1933).

(4) R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(5) (a) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964). (b) This is equivalent to defining X as $X = (\alpha - E)/\beta = [E - \alpha]/-\beta$. (c) Note also that where parallel p orbitals with opposed signs are present, this counts as only one node although there are two sets of lobes; this is because a single node is the occurrence of two adjacent oppositely signed orbitals (not lobes). Also, there is no node between lobes of a single p orbital.
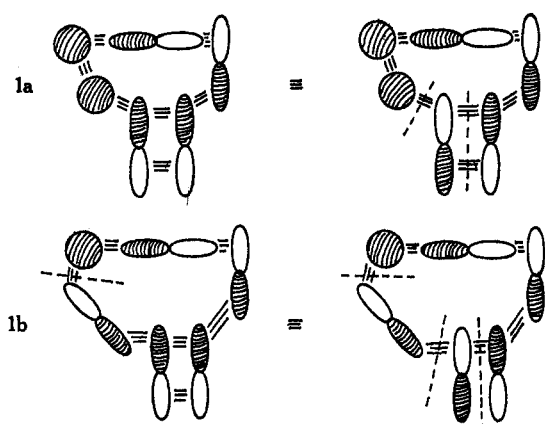
Figure 1. Examples of Hückel and Möbius orbital arrays: (a, top) two alternative choices of basis sets for an arbitary Hückel array; zero and two sign inversions, respectively. - - - - - represents the site of one inversion. (b, bottom) Two alternative choices of basis sets for an arbitary Möbius array; one and three sign inversions, respectively. - - - - - represents the site of one inversion.

Figure 2. Hückel and Möbius circle mnemonics for obtaining MO energies.

As defined in Figure 1, whether a system is Hückel or Möbius depends on the evenness or oddness of the number of sign inversions in going around the cycle. The Hückel systems have zero or an even number of sign inversions while the Möbius arrays have one or some other odd number. It is readily seen that turning any p orbital upside down (*i.e.*, changing its sign) does not change the evenness or oddness of inversions since two new inversions are introduced if the orbital turned upside down was not adjacent to a node. If it was adjacent to a node, no new node results (see Figure 1).[5c]

Chart I[6] summarizes the conclusions about molecular energy as a function of number of electrons and the categorization of the system as Hückel or Möbius. Before considering specific systems having these electronics and discussing practical uses of these categorizations, let us consider the source of the conclusions cited above and summarized in Chart I.

Mnemonic Devices for MO Energies

In 1964 Heilbronner gave expression 1b as analytically affording the MO energies of a cyclic, singly twisted polyene in which there is only one side to the π surface (*i.e.*, a Möbius cyclic polyene).[5a] We note that this is quite similar to the expression given by Hückel for ordinary cyclic polyenes (note eq 1a);

$$X = -2 \cos (2\pi k/n) \qquad (1a)$$

$$X = -2 \cos [(2k + 1)\pi/n] \qquad (1b)$$

the energy units are positive, as is $|\beta|$,[5b] k is the MO number ranging from 0 to $n - 1$, and n is the number of p orbitals in the cyclic array. Also, eq 1b is slightly modified from Heilbronner's orginal formulation which took into account the decreased overlap due to twisting.
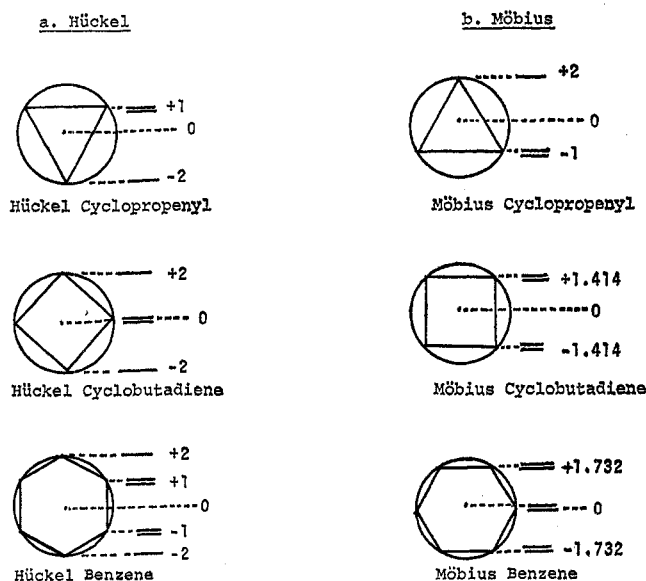
Chart I
Energetics of Hückel and Möbius Systems[6]

No. of electrons	Type of System	
	Hückel	Möbius
$4N + 2$	Allowed (aromatic)	Forbidden (antiaromatic)
$4N$	Forbidden (antiaromatic)	Allowed (aromatic)

This is not necessary as long as we take the energy units to be diminished with twisting, as will also be true for twisting of Hückel systems.

A number of years ago Frost described[7a] a simple but useful mnemonic device which paraphrases Hückel's formula for MO energies as given in eq 1a; this is shown in Figure 2a. With the appropriate polygon inscribed with a vertex down in a circle of radius $2|\beta|$, the vertical displacement of each intersection of the circle with the polygon gives one MO energy value; the center of the circle is taken at an arbitrary zero corresponding to the energy of an electron in an isolated p orbital.

Some years ago the present author noted that a similar mnemonic device is possible for Möbius systems.[1] This paraphrases the Heilbronner formula in the same way that the Frost device gives Hückel energies. In our device,[1] however, a side of the polygon is inscribed at the bottom of the circle to obtain the energies of the desired Möbius system. This is illustrated in Figure 2b. This device is useful in quickly obtaining the delocalized energies of Möbius orbital arrays. Additionally, it may be used to give the energetic disposition of molecular orbitals as a function of the geometric arrangement of the basis set orbitals (*e.g.*, atomic orbitals) of the system. With such knowledge, one can often predict MO crossings along a reaction coordinate, the nature of correlation diagrams, and the facility of molecular transformations. These applications are discussed below.

(6) H. E. Zimmerman and H. Iwamura, *J. Amer. Chem. Soc.*, **92**, 2015 (1970).

(7) (a) A. Frost and B. Musulin, *J. Chem. Phys.*, **21**, 572 (1953). (b) Thus $\epsilon = \beta'/\beta$. E is used in the same context throughout the discussion.

Figure 3. MO's of twist trimethylenemethane as derived from Möbius circle mnemonic.

Ground-State Examples of Möbius Systems

To begin with, let us look at ground-state molecular systems which are Möbius. One molecular system which is instructive is "twist trimethylenemethane," illustrated in Figure 3. It is seen that the planar array of three p orbitals necessarily has one or three sign inversions in proceeding around the array and is thus Möbius; the basis set chosen with one sign inversion is arbitrarily selected for this figure. The molecular orbitals are then given analytically by the circle mnemonic; however, in using the device, we must realize that the radius of the circle is twice the magnitude of the resonance integral β' between adjacent orbitals and that this radius (i.e., $2\beta'$) is smaller than the usual 2β, say a quantity $2\epsilon\beta$.[7b] Twist trimethylenemethane is thus noted to be a system which will have a closed shell with four electrons (i.e. $4N$), as would be expected for a Möbius molecule.

Related to this is the Walsh model[8] for cyclopropane as depicted in Figure 4. Here we note two arrays of orbitals which can be treated separately as an approximation. One of the two sets consists of a cyclic array of three sp^2 orbitals directed toward the center of the three ring. This cycle is seen to be Hückel, and the resulting three MO's are given by the Frost circle device. The other set is composed of three p orbitals arranged very much as the set in twist trimethylenemethane and is Möbius. Here the Möbius mnemonic[1] is used to give the resulting three MO's shown on the right in Figure 4. The Möbius circle is placed higher on the energy scale than the Hückel circle since sp^2 hybrid orbitals are lower in energy relative to p orbitals. Additionally, the radii of the two will differ somewhat since each of these is twice the corresponding resonance integrals, that is, between p orbitals and between sp^2 orbitals, and these will not be exactly the same. Nevertheless, the model qualitatively indicates the need for six electrons to make up the delocalized σ framework of the Walsh model.

Still another example is afforded by barrelene.[9] This may be treated using the Möbius circle device (note Figure 5). Here we utilize the fact that a cyclic array may be made up of MO's rather than AO's, and we then consider quantum mechanical interaction of the three bonding π orbitals of the three ethylenic moieties. Separately we look at the admixing of the three anti-
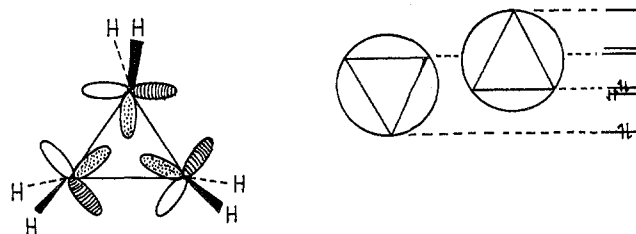

Figure 4. Use of Hückel and Möbius circle mnemonics to obtain MO's for the Walsh model for cyclopropane: ⊠, sp^2 hybrid orbitals, + lobes; ▨, p orbitals, + lobes; ▢, p orbitals, − lobes.
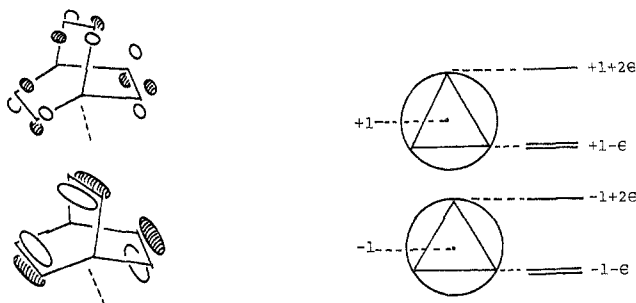

Figure 5. Möbius interaction of the three antibonding ethylenic MO's and similar interaction of three bonding ethylenic MO's to give the energies of the six barrelene molecular orbitals. - - - -, nodes between bridge MO's.

bonding π^* ethylenic MO's (i.e., one on each two-carbon bridge). The circle describing the energetic result of mixing the three π MO's is centered at $-|\beta|$, the energy of the isolated π orbitals; and the circle corresponding to interaction of the π^* orbitals is centered at $+|\beta|$, the energy of the separate antibonding ethylenic components. The transannular interaction, corresponding to a resonance integral β' which is smaller in magnitude than the normal $|\beta|$ integral between parallel and adjacent p orbitals, is taken as the fraction ϵ relative to β.[7b] The circle radius then will be 2ϵ. The MO energies predicted then by this treatment are given in Figure 5 and are analytically those obtained by direct solution of the MO problem by use of a secular determinant.

In deciding to treat the barrelene problem in this fashion, it is only necessary to note that the antibonding ethylenic MO's are indeed Möbius, as are the bonding MO's; note the dotted lines in Figure 5 which reveal the single nodes between the sets of MO's localized on the two-carbon bridges. An equally good approach would have utilized the Möbius admixture of the three p orbitals on the front face of the barrelene system to give a twist trimethylenemethane moiety. The MO energies of this are readily obtained as above. Then the interaction of two such sets of MO's with ± 1 splitting due to vicinal interaction gives the final barrelene MO's. This approach will not, however, be detailed here.

On filling in the barrelene MO's with six electrons we note a total π energy of $-6|\beta|$. Thus the ϵ contributions cancel. This is the same π energy as for three isolated ethylenes. Yet the barrelene MO's are not

(8) A. D. W. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).
(9) (a) H. E. Zimmerman and R. Paufler, *J. Amer. Chem. Soc.*, **82**, 1514 (1960); (b) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).
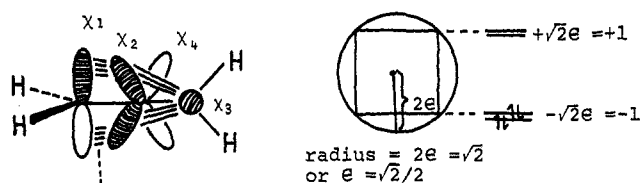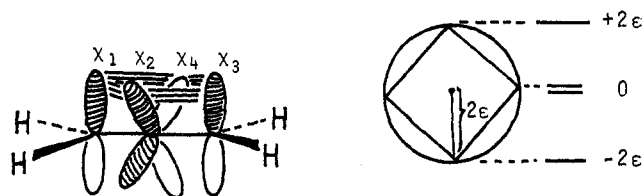
Figure 6. The Möbius model for allene.

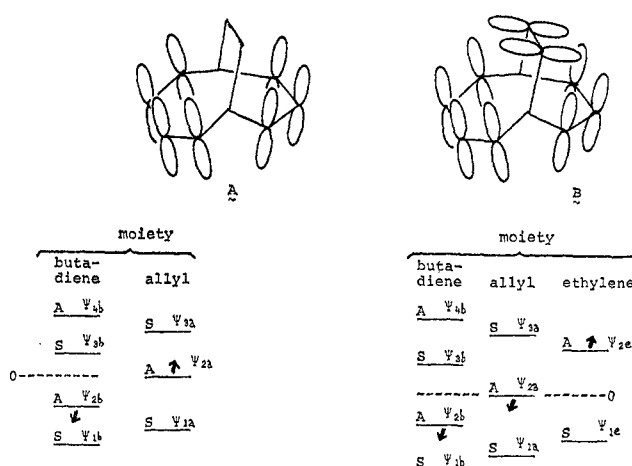Figure 7. Allene twisted by 90° depicted as a Hückel system.

Figure 8. One example of bicyclohomoconjugation: mixing of bridge MO's. S and A refer to symmetry or antisymmetry with respect to a plane bisecting all three bridges. The MO subscripts refer to butadienyl, allyl, and ethylenic MO's.

those of isolated ethylenes (*i.e.*, at $\pm 1|\beta|$). Thus, as noted by us earlier,[9] barrelene is a unique molecule in having electron delocalization without the commonly attendant electron delocalization energy; it is not aromatic.

A particularly fascinating example is that of allene. Although ordinarily this molecule is envisioned as being composed of two π systems perpendicular to one another, a different view is instructive. In building this new model, we take the central carbon p orbitals with an angle of 45° with respect to the terminal p orbitals. This is acceptable since any linear combination of two perpendicular p orbitals is quantum mechanically equivalent as part of a basis set to any other such pair.

The basis set of orbitals so chosen is depicted in Figure 6. It is evident that χ_1 overlaps with χ_2, χ_2 with χ_3, and χ_3 with χ_4; all of these overlaps are of the plus–plus (and minus lobe–minus lobe) type and between vicinal orbitals having a 45° dihedral angle. However, additionally, χ_4 and χ_1 overlap with a 45° angle but with plus–minus interaction. Hence the system is composed of a cyclic array of basis orbitals with a single sign inversion and is truly Möbius. The MO's are delocalized over the entire molecule in this model and have energies given by the circle trick as in Figure 6. We note that the overlap of two p orbitals with a dihedral angle of 45° is $\cos 45° = 2^{1/2}/2$ of normal and the radius of the circle then is twice this, or $2^{1/2}$. The MO energies come out to ± 1, which is what we would obtain for two separated ethylenes in the traditional model.

In similar fashion allene which has been twisted at one end by 90° can be pictured to be a Hückel system using similar reasoning. This is outlined in Figure 7. It is seen that the MO energies are the same as derived from an allyl orthogonal to a p orbital on the central carbon atom: *i.e.*, MO's at $-2^{1/2}$, 0, 0, and $+2^{1/2}$. The orthogonal allyl and p-orbital set corresponds to the more orthodox picture of twisted allene.

One can deal with other cumulenes and twisted cumulenes if one is willing to make the approximation that parallel and 45° overlaps are roughly equivalent. The nonterminal p-orbital sets are selected all canted

45° to the end p orbital. This leads to the odd-carbon cumulenes being Möbius and the even-carbon cumulenes being Hückel. The twisted species have the reverse electronics.[10]

Another application of the Hückel–Möbius concept involves bicyclohomoconjugation. Of interest are compounds of types A and B (note Figure 8). For the present discussion we focus attention on the effect of juxtaposition of the two or three π bridges present. We are concerned with the effect of such juxtaposition on the energy of the nonbonding MO of the odd-carbon bridge. To the extent that MO interaction raises this MO's energy, a system is engendered which is most likely to be stable as a cation. If the nonbonding MO is lowered by transannular interaction, then a carbanion should be more stable. This point has been noted by Goldstein.[11] Goldstein has concentrated attention on the tendency of MO's from the different bridges to "repel" one another in pairs. There is, however, an additional effect which may become overriding, namely an interaction between *three* MO's of the same symmetry.

For consideration of such mixing we follow Goldstein's suggestion of inspecting interaction of the nonbonding MO with the closest lying MO of the same symmetry if there is only one additional bridge, as in molecule A. However, where there are three bridges we include the nearest lying MO of the same symmetry from the third bridge. For simplicity, the transannular resonance integrals are again taken as ϵ relative to the normal β.

Molecules A and B are particularly instructive. The interaction in molecule A leads to the nonbonding MO ψ_{2a} becoming slightly antibonding, as shown in Figure

(10) An intriguing example presents itself in the twisting of a terminal allene methylene group by 180°. Consideration of the one-electron MO's as a function of angle of twist reveals an example of violation of the noncrossing rule wherein MO's of the same geometric symmetry do cross. These MO's differ in permutation symmetry in the Hückel approximation, and a crossing is permitted.

(11) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

8. Similar reasoning applied to molecule B and using only the odd-carbon bridge and the larger of the two even bridges would lead to a similar result.

However, we recognize that in the three-bridge molecules any three MO's of the same symmetry where one MO is derived from each bridge will constitute a Möbius array analogous to the barrelene situation. This leads to a tendency for two of the MO's considered to go down in energy and one to go up; remember, for example, the splitting of MO's in Möbius cyclopropenyl. Where this Möbius effect is opposite to the tendency for the two closest lying MO's to repel, the Möbius effect often dominates and therefore is important to note. In fact, in molecule B the nonbonding MO ψ_{2a} is found from independent calculation to go down in energy. This result would not have been predicted if one considered that the two closest MO's (here ψ_{2a} of the allyl and ψ_{2b} of the butadiene bridges) were to "repel" most; in such a case the zero level of the allyl moiety would become antibonding. Finally, we note that this "Möbius splitting effect" occurs despite the difference in energies of the three basis molecular orbitals which are interacting and thus is a useful result to remember when considering interaction of three orbitals in general.

Paraphrased, three orbitals (AO's or MO's) will interact to give two lowerings and one increase in energy if the product of the three overlaps is negative (*i.e.*, a negative overlap corresponds to + to − overlap). Where the product of the three overlap integrals is positive, two MO's go up and one goes down.

Application of Möbius–Hückel Differentiation to Reaction Allowedness and to Correlation Diagrams. This concept may be applied to predicting the forbidden or allowed nature of organic reactions in several ways. One considers the array of orbitals in the reaction transition state of an electrocyclic reaction and inquires whether this has the number of electrons appropriate (*i.e.*, 4N or 4N + 2) to the Möbius or Hückel system in order to thus minimize its energy. A second approach uses the circle mnemonics to predict where along the reaction coordinate one expects pairs of MO's (*i.e.*, degeneracies) in order to ascertain which MO's cross. This then allows construction of the correlation diagram. If bonding and antibonding MO's cross, then the reaction is a ground-state forbidden one since two electrons originally in a bonding MO of reactant find themselves in an antibonding MO of product to the extent that one considers an adiabatic change.

Cycloadditions and Electrocyclic Ring Closures. One of the simplest applications is the 2 + 2 cycloaddition of two ethylenes to give cyclobutanes. There is, in principle, more than one stereochemical course for the reaction. The simplest is a direct, face to face, cycloaddition as shown in Figure 9. This has been termed a $_\pi 2_s + _\pi 2_s$ reaction course, meaning that the two π bonds are utilized suprafacially.[2] The correlation diagram in Figure 9 is that traditionally written for the formation of cyclobutane from two ethylene molecules by a direct approach. It is seen that there is a point
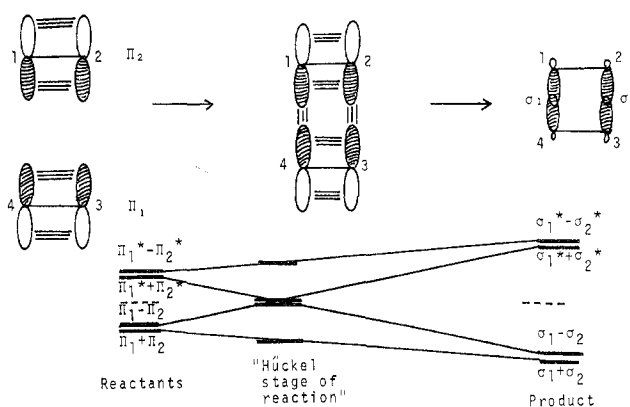

Figure 9. Correlation diagram for $_\pi 2_s + _\pi 2_s$ cycloaddition of two ethylene molecules to give cyclobutane and showing the Hückel transition state.

along the reaction coordinate where the distribution of MO's is that which is characteristic of cyclobutadiene, that is, there is a degenerate nonbonding pair plus a bonding and an antibonding molecular orbital. The reason for occurrence of this distribution of MO's is that there will be a point where the overlap between AO's 1 and 4 and that between 2 and 3 is equal to that between 1 and 2 as well as 3 and 4. At this stage in the reaction the secular determinant is that of cyclobutadiene if we do not worry about hybridization effects; if we do worry about such effects, the situation is changed quantitatively but not qualitatively.

The MO distribution at this point, where intermolecular overlap is equal to intramolecular overlap, can be obtained directly from use of one of the two circle mnemonic devices, that of Frost or that of Zimmerman. Which one should be used is determined in each instance by whether the cyclic array of basis orbitals in the reaction transition state is Hückel or Möbius.

By inspecting the degeneracies afforded by the mnemonic device, one can quickly ascertain which pairs of MO's cross. If bonding and antibonding MO's cross during a reaction, then the reaction is of the ground-state forbidden variety, since the occupation of bonding MO's of reactant by electrons results in the occupation of antibonding MO's of product in an adiabatic transformation (*i.e.*, one without change in electron occupation). Similarly a vacant bonding product MO derives from an antibonding reactant MO. To the extent that a reaction proceeds adiabatically with retention of the original electronic configuration, it will lead to a doubly excited state of product and be excessively energy demanding.

One could merely add up the energy of a Hückel transition state and compare it with a Möbius one in order to decide which is the favored one. This leads to the same conclusions. Here one would refer to Chart I, and the requirement is quickly seen that 4N + 2 electrons are needed for minimization of energy of a Hückel transition state and to avoid occupied bonding MO's becoming antibonding in product. Similarly, 4N electrons are required not only for energy minimization at the Möbius transition state but again to avoid occupied antibonding product MO's.
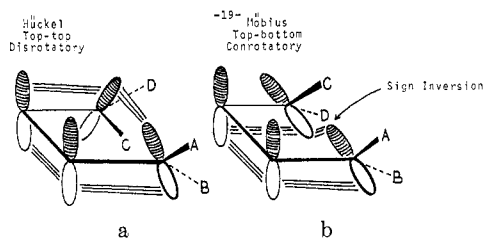
Figure 10. Disrotatory Hückel-like closure of butadiene (left); conrotatory Möbius-like closure of butadiene (right).
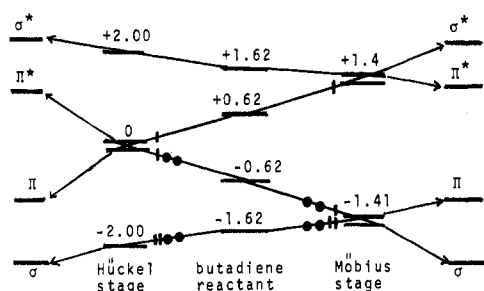

Figure 11. Correlation diagrams for two types of butadiene closure.

Figure 12. Correlation diagrams for two types of hexatriene closure.

A more interesting example than that of ethylene is the electrocyclic closures of linear polyenes. As an example the two orbital arrays possible for closure of butadiene to cyclobutene (and the microscopic reverse) are shown in Figure 10. These are similar in consisting of a somewhat square array of four orbitals each. The overlap between any pair of basis orbitals is the same in magnitude. However, in one type of closure there is terminal top–top overlap (i.e., disrotatory), and the system is seen to be a Hückel one (note Figure 10a). In the other type of closure, there is terminal top–bottom (i.e., conrotatory) overlap, and the transition state is Möbius, since in no way can one avoid having an odd number of sign inversions. In the basis set selected in Figure 10b, the inversion is between the terminal orbitals, but it might be found elsewhere if a different basis set were selected. If one turned the orbital at atom 1 upside down, the inversion would then be between atoms 1 and 2.

With the knowledge afforded by the circle mnemonics (note Figure 1 for the four-ring case), it is possible to write the two sets of transition-state MO's shown in Figure 11. At the left is that for the Hückel geometry and at the right the distribution of MO's for Möbius geometry. The reactant (i.e., butadiene) MO's are given in the center and correlation lines are drawn in. Ground-state electron populations are given as solid dots and the electronically excited-state distribution is shown with vertical lines. It is seen that, for a ground-state reaction, only the Möbius correlation diagram leads to a closed-shell transition state and to a ground-state electron distribution for the product. Conversely, for the singly excited-state reaction, only the Hückel geometry (i.e., top–top closure) gives an excited-state product which is not doubly excited. Additionally, for the photochemical process, one finds that the reaction proceeds to a point where the ground and excited states are degenerate, and a rapid electronic
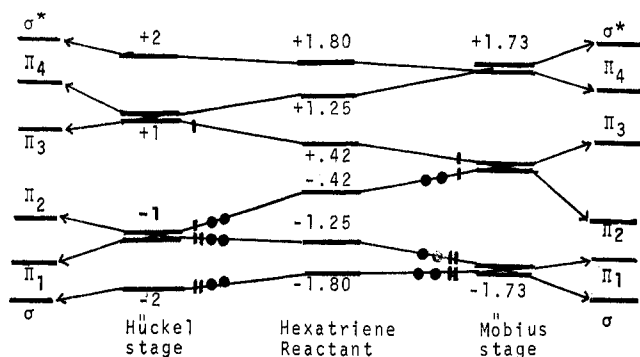
transition to the ground-state potential energy curve leading to cyclobutene product is likely. Thus at the Hückel stage in the reaction both the promoted, antibonding electron and the single bonding electron are in a degenerate pair at 0, and this configuration has the same energy as if the two electrons were in the same MO at 0.

In summary, the ground-state butadiene closure and its microscopic reverse prefer the Möbius transition state since $4N$ electrons are involved in the cyclic array of orbitals and this combination ($4N$ + Möbius) corresponds to the closed shell, lower energy potential energy surface.

For hexatriene closure the reverse preference is seen. Here top–top overlap (Hückel) geometry is preferred since six electrons ($4N$ + 2) are delocalized. The correlation diagram again may be drawn to emphasize the preference, and the circle mnemonics are used to predict the MO distributions at the reaction transition states. This is shown in Figure 12.

In both the butadiene and hexatriene reactions, it is necessary to be able to write the MO distributions for the reactant polyenes and for the closed valence tautomers. This requires only the knowledge that the polyenes have symmetrically arranged sets of MO's as shown in Figures 11 and 12 and the products will have the π MO's of the remaining polyene moieties plus bonding σ and antibonding σ MO's. Hence the exact MO energies shown in Figures 11 and 12 are not needed.

The correlation diagrams in Figures 11 and 12 could have been drawn using symmetry. However, the Hückel–Möbius method does not require this.

Thus in examples where there is no symmetry one can predict reaction allowedness. One example of interest is the suprafacial and antarafacial migrations of hydrogen atoms and alkyl groups. Figure 13 depicts, as an example, the 1,7-hydrogen migrations of the suprafacial and antarafacial type. It is recognized that the delocalized system contains eight (i.e., $4N$) electrons and will prefer the Möbius geometry involving one sign inversion (i.e., as in Figure 13A). This involves delivery of the hydrogen from the bottom of the π system to the top.

Another case of interest is the rearrangement of bicyclo[3.1.0] cations and zwitterions[12] to give isomeric cations and bicyclo[3.1.0]hex-3-en-2-ones, respectively.
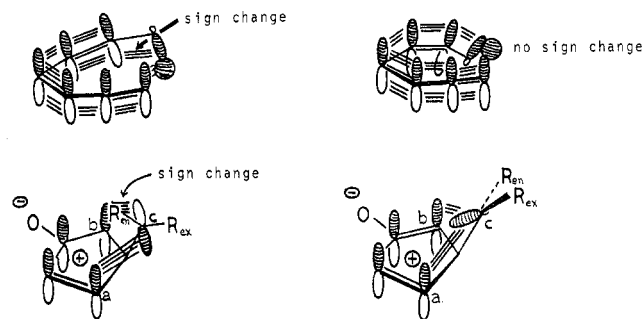
Figure 13. Two alternative 1,7-hydrogen migrations (A, B) and intermediate species in type A rearrangement of cyclohexadienones, slither and pivot mechanisms (C, D). A (top left), 1,7-antarafacial hydrogen transfer, a Möbius system thus favoring the $4N$ electron ground-state process. B (top right), 1,7-suprafacial hydrogen transfer, a Hückel system favoring the $4N$ electron redistribution in the excited state. C (bottom left), inversion mechanism (observed): the partially rearranged Zwitterion of the type A rearrangement. One sign inversion, i.e., Möbius system, favored for the $4N$ electron redistribution process in the ground state. D (bottom right), pivot mechanism (not observed): R_{en} originally endo becomes exo. Zero sign inversions, i.e., Hückel system; a $4N$ electron population affords an antiaromatic ground-state process. ▨, positive orbital sign; ☐, negative orbital sign.

The observed reaction stereochemistry involves the exo group (R_{ex}) remaining exo and the endo group staying endo. This is tantamount to inversion of configuration at the migrating carbon atom c which originally is bonded to atom a in Figure 13C and which then migrates to atom b. With inversion of configuration, both lobes of the p orbital at carbon c are used, and there is one sign inversion, giving a Möbius system. With $4N$ electrons in the cyclic array (i.e., one π bond plus two electrons from the three-ring bond broken), one can understand this preference. The alternative pivot mechanism would have involved one lobe of an orbital on carbon c simultaneously bonding with atoms a and b and would have given an unfavorable Hückel system.

An illustration of the complexity of a reaction whose allowedness can be analyzed at a glance without resort to explicit drawing of correlation diagrams is the reaction of alkynes with 1,4-cyclohexadienes, as shown in Figure 14. Inspection of the photochemical reaction of acetylenes with 1,4-cyclohexadienes reveals that there is a cyclic array of orbitals without sign inversion (i.e., Hückel array). This is seen in Figure 14 where the orthogonal π orbitals are arbitrarily chosen so that the component p orbitals aim at the p orbitals of the cyclohexadiene. Then we see that there is π overlap between the orbitals labeled 1 and 2, these composing one π bond of the acetylene, then orbitals 2 and 3 overlap σ fashion in generating a product σ orbital. In turn, 3 and 4 overlap in a π fashion, making up one π bond of the cyclohexadiene. Orbital 4 overlaps with 5 which is part of the other acetylene π bond, and 5 therefore overlaps with 6. Similarly there is the con-
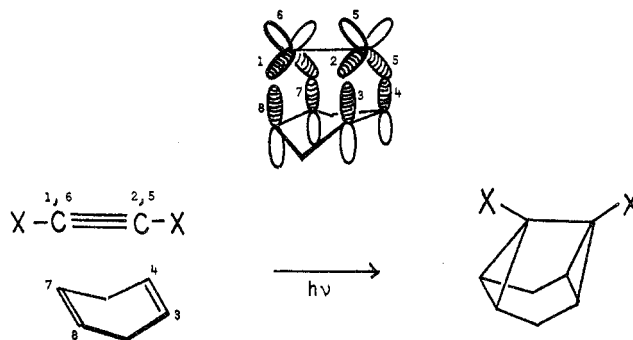

Figure 14. Photochemical addition of acetylenedicarboxylic acid to 1,4-cyclohexadiene and the Hückel orbital array involved.

tinued sequence 6,7,8,1. Nowhere is a sign inversion enforced. If one were to reverse the choice of orientation of one of the AO's of the system, there would then be two inversions, and the system would still be Hückel. With a Hückel system and eight delocalized electrons, the reaction becomes photochemically allowed (note Chart I).

A final example which is of considerable interest is the ketene addition to olefins to give cyclobutanones. This is known to be stereospecific[13] and thus contrasts with the forbidden $_\pi2_s + _\pi2_s$ alkene dimerization which does not occur thermally in simple systems and is two-step when it does occur.[14] One treatment of the ketene reaction is given by Woodward and Hoffmann,[2d] and this involves a $_\pi2_s + _\pi2_a$ four-center cycloaddition. This interpretation is equally readily presented in Hückel–Möbius terms, and such a transition state would have one sign inversion and be Möbius as well as allowed due to four electrons being delocalized. Nevertheless, an alternative view is that the reaction, while concerted, involves two important components. The first is an electrophilic attack of the carbonyl carbon on C-1 of the olefin; this leaves a cationic center at carbon 2 of the olefin and an enolate moiety in the ketene portion of the transition state (note Figure 15). The second component of the mechanism is then bonding between enolate and cationic moieties.

This interpretation demands attack of the olefin on p_y at the carbonyl carbon (i.e., the C=O π system) in the first stage of the reaction and subsequent attack of the other olefin carbon on p_z of the terminal ketene carbon (i.e., the enolate π system). This is shown in Figure 15. The oxygen p_y orbital is initially oriented horizontally but must end up z axis oriented for enolate overlap; it is depicted half rotated and labeled O_{p-yz} ($p_y \rightarrow p_{yz} \rightarrow p_z$).

Inspection of Figure 15 reveals that there are six delocalized electrons including those initially in the oxygen p_y orbital and there are zero overlaps in a six-orbital cyclic array (i.e., a Hückel system). This is

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(13) W. T. Brady, E. F. Hoff, R. Roe, and F. H. Parry, ibid., 91, 5679 (1969); W. T. Brady and R. R. Roe, ibid., 86, 616 (1964).
(14) P. D. Bartlett, L. K. Montgomery, and B. Seidel, ibid., 91, 5679 (1969); P. D. Bartlett and G. E. H. Wallbillich, ibid., 86, 616 (1964).
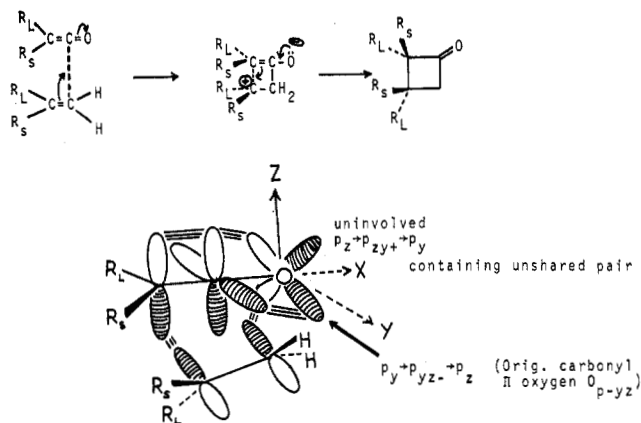
Figure 15. Ketene cycloaddition to alkenes.

then an allowed reaction. The geometry is such that avoidance of large groups R_L and R'_L leads to the thermodynamically less stable isomer as observed.[13]

Odd-Electron Systems. In reactions of odd-electron cyclic systems, the reaction behavior is seen to be the same as that closed-shell system resulting from addition of yet another electron. This prediction results from the assumption that reactions leading to products with one antibonding electron will be less unfavorable only in degree from those with two antibonding electrons.

Source of Stability of Möbius Systems. The organic chemist may inquire how it is possible that a Möbius system might be more stable than a Hückel one, when the Möbius array of necessity contains at least one plus–minus overlap in its basis set while the Hückel cycle does not. It is true that a plus–minus overlap represents a local antibonding and energy raising contribution. However, Möbius molecular orbitals have the property of having their LCAO–MO coefficients very small near the site of plus–minus overlap; this is particularly true of the lower energy Möbius MO's. Furthermore, Möbius MO's come in pairs beginning with the lowest energy set. For example, in each member of the lowest energy degenerate pair, the site of plus–minus overlap is controlled by the signs of the MO coefficients and where such an antibond occurs it is only weakly antibonding because of the small coefficients. This lowest energy degenerate pair will accommodate four electrons with each of four electrons experiencing one weakly antibonding node. In contrast, the lowest energy Hückel MO will have no nodes and will accommodate two electrons. Thereafter, higher energy MO's come in pairs. But here each MO has a number of antibonding nodes increasing by two per level. With two nodes in each of MO's 2 and 3, the coefficients cannot minimize the antibonding interaction as much as in the Möbius MO's 1 and 2 with only one node each. Thus, four electrons in the Hückel system experience no nodes in MO 1 and two nodes in (e.g.) MO 2. The total number of antibonding nodes is the same in the Hückel as the Möbius case, but the two-node MO's are more antibonding. However, if only two electrons were to be accommodated,

the Hückel system would be lower in energy since no MO's with nodes would have to be used. The same general trend follows through the Hückel and Möbius systems with increasing numbers of electrons.

Exceptions. None exist! Where electron redistribution in cyclic orbital arrays is the energetically controlling feature of a reaction, the Möbius–Hückel analysis is faithful in predicting minimum energy. It also should be noted that the Hückel–Möbius approach is not based solely on Hückel level reasoning. The same reasoning would work if the arguments were based on self-consistent field MO's.

Relation to Other Approaches. The most closely related approach is that of Woodward and Hoffmann and that of Longuet-Higgins.[15] The original approaches presented[1a–c] differ considerably in that they require knowledge of reactant, product, and transition-state symmetries. For sigmatropic rearrangements the signs of the highest occupied MO of two separate moieties were needed. These interpretations led to sets of rules. The Hückel–Möbius approach really uses only one rule, namely: "$4N + 2$ electron systems prefer Hückel geometries and $4N$ electron systems prefer Möbius geometries."

However, the most recent version of Woodward and Hoffmann[2f] is very closely related to the Hückel–Möbius analysis, since the use of $_\pi 2_s$ and $_\pi 2_a$ designations is just another way of discerning sign inversions, each $_\pi 2_a$ contributing one sign inversion. The Hückel–Möbius treatment does offer the advantage of supplying the underlying reasons for geometric preferences.

It should be noted that both Fukui[16] and Oosterhof[17] were early contributors. Oosterhof recognized the importance of the sign properties of the highest occupied MO, and Fukui made very extensive use of this approach with perturbation methods. Also many years ago the present author both presented a local symmetry treatment in dealing with the Sommelet–Hauser rearrangement[18] and also noted the use of energy level reaction diagrams and the energetic difficulties arising when the highest occupied MO becomes antibonding as in carbanion rearrangements.[19] Dewar[20] has presented an approach based on his ubiquitously useful nonbonding MO perturbation method and has arrived at basically the same $4N$ vs. $4N + 2$ rules as the Hückel–Möbius method. Oosterhof[21] has found a second and also independent confirmation of the importance of basis set sign inversions by an interesting valence bond treatment. Further approaches which

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(18) H. E. Zimmerman in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 525 ff.

(19) H. E. Zimmerman and A. Zweig, *J. Amer. Chem. Soc.*, **83**, 1196 (1961).

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(21) J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305, 307 (1970).

are more dependent on detailed calculations will not be surveyed here.[22-24]

(22) Recently an interesting review of the Woodward–Hoffmann rules has appeared as well as a discussion of the "Dewar–Zimmerman

rules": N. T. Anh, "Les Regles de Woodward Hoffmann," Edi-science, Paris, 1970.

(23) Applications of the Möbius–Hückel concept to photochemistry are presently not discussed in detail due to space limitations. For leading references see ref 24.

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Catalysis of Strained σ Bond Rearrangements by Silver(I) Ion

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The capability of Ag+ to form coordination complexes with unsaturated and aromatic molecules is now widely recognized.[1] In contrast, unsuccessful attempts to prepare alkylsilver compounds date back to the middle of the last century[2] and, with few exceptions, these difficulties persist to the present time.[3]

Chief among the factors behind the often fleeting existence of such substances is their low thermal stability. Alkenylsilver compounds, which likewise share this tendency for facile decomposition, were isolated for the first time approximately 15 years ago.[4] The appreciably greater stability of alkynylsilver compounds has enabled them to be known for over a century.[5]

Very recently, the unique capability of certain transition metals to catalyze so-called "symmetry-forbidden" reactions under exceedingly mild conditions has been recognized. Examples of the phenomenon are the facile $[_\pi2_s + _\pi2_s]$ dimerization[6] of norbornadiene (**1**) under the influence of zerovalent iron,[7] nickel,[8] and cobalt catalysts.[9] Another is the Fe(CO)₅-catalyzed suprafacial 1,3-sigmatropic shift of hydrogen (a $[_\sigma2_s + _\pi2_s]$ change)[6] in **2**;[10] the epimeric alcohol **3** is unaffected.

Also, Pettit and his coworkers have demonstrated that the thermally forbidden $[_\sigma2_s + _\pi2_s]$ ring opening of certain cyclobutenes (disrotatory motion)[6] occurs readily in the presence of silver(I) ion.[11] The smooth rhodium-(I)-catalyzed valence isomerization of **4** to hexamethylbenzene further illustrates the impressive alteration in transformation restraints attainable under such conditions.[12]
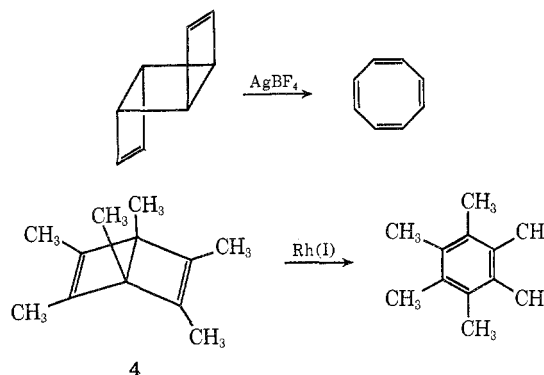
The remarkable capability of these metals to promote such transformations is thought to be a result of the

(1) (a) R. N. Keller, *Chem. Rev.*, **28**, 229 (1941); (b) M. A. Bennett, *ibid.*, **62**, 611 (1962).

(2) (a) G. B. Buckton, *Justus Liebigs Ann. Chem.*, **109**, 225 (1859); (b) J. A. Wanklyn and L. Carius, *ibid.*, **120**, 70 (1861).

(3) An excellent recent review of organosilver chemistry has appeared: C. D. M. Beverivizk, G. J. M. van der Kerk, A. J. Lensink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, **5**, 218 (1970).

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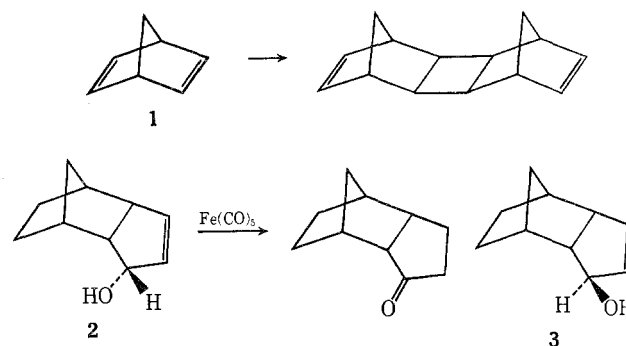
(6) For an explanation of this terminology and a listing of the applications thereof, consult R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

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