

to the *in vivo* situation of antenna chlorophyll, and to suggest that antenna chlorophyll consists of units of chlorophyll dimers in which the macrocycles show overlap between the individual chlorophyll molecules. The presence of extraneous nucleophiles, concentration, and/or the nature of the environment determine the relative populations of the conformers.

The extent of macrocycle overlap and the ease of population change of conformers in antenna chlorophyll in the plant should have tremendous influence on the performance of bulk chlorophyll in its light-gathering role in photosynthesis. The great similarity between the deconvoluted red bands of antenna chlorophyll in the plant and that of a concentrated Chl *a* solution in aliphatic hydrocarbon solvents, which contain chlorophyll *a* oligomers with molecular weight of 20,000, provides a basis for the identification of *in vivo* antenna chlorophyll in green plants with $(\text{Chl}_2)_n$ dimers. The problems involved in obtaining structural informa-

tion on antenna chlorophyll *in situ* and chlorophyll oligomer *in vitro* are formidable. The indications that the spectral properties of the oligomer, and inferentially of antenna chlorophyll, are largely determined by the Chl-Chl interaction in the dimer unit make the structural conclusions derived from the joint application of ^1H nmr and visible absorption spectroscopy particularly relevant to the *in vivo* situation.

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Communications to the Editor

Orbital Isomerism as a Controlling Factor in Chemical Reactivity¹

Sir:

Pericyclic reactions² have mostly been interpreted either in terms of correlations of states³ or orbitals^{2,4} between reactants and products, based on the assumption that some element of symmetry is retained throughout the reaction, or in terms of the idea first put forward by Evans⁵ that the transition states of pericyclic reactions are isoconjugate with cyclic π systems and so can likewise be specifically stabilized or destabilized relative to open chain analogs, *i.e.*, aromatic or antiaromatic.⁶ Here we wish to put forward a more general approach that represents in effect a synthesis of the earlier ones.

Consider a pericyclic reaction involving an even-numbered ring. We assume that the alternant property is retained throughout, there being no interactions between AO's of atoms in the pericyclic ring other than between nearest neighbors, *i.e.*, those implied either in the valence structure of the reactant or in that of the product. The course of such a pericyclic reaction involving an even-numbered ring is topologically equivalent to, or isoconjugate with, the interconversion of two classical (Kekulé) structures for an analogous cyclic polyene.⁶ The two classical polyenes (R and S) and the intermediate hybrid (RS) can be derived by

(1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

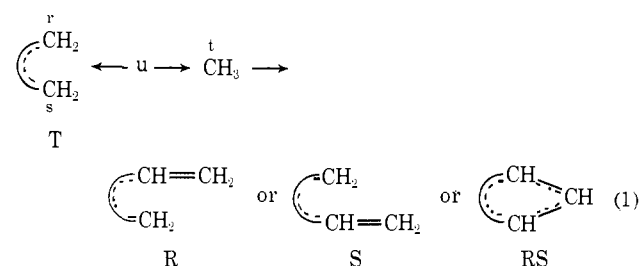
(3) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(4) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(5) M. G. Evans, *Trans. Faraday Soc.*, **35**, 824 (1939).

(6) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

union⁷ of methyl with an odd AH alternant hydrocarbon⁷ (T) derived from R, S, or RS by loss of one carbon atom; *i.e.*



The HOMO and LUMO arise⁷ in each case from an interaction between the NBMO of T and the 2p AO of methyl, the HOMO-LUMO splitting, ΔE , being given by

$$\Delta E = 2|(a_{or}\beta_{rt} + a_{os}\beta_{st}) \quad (1)$$

where a_{oi} is the NBMO coefficient at atom i in T, β_{ij} is the ij resonance integral, and the lettering of atoms is as indicated in eq 1.

In the case of a "forbidden"⁸ pericyclic reaction, the AH RS isoconjugate with the transition state is antiaromatic. In that case^{7,9} a_{or} and a_{os} in eq 1 have opposite signs. Since the conversion of R to S via RS corresponds to a decrease in β_{rt} from its initial value (β_{rt}^0) to zero and a simultaneous increase in β_{st} from zero to its final value (β_{st}^0), at some point in the reaction $a_{or}\beta_{rt}$ must become equal to $-a_{os}\beta_{st}$ so that ΔE van-

(7) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

(8) If the terms "allowed" and "forbidden" are used in this connection, it is well to put them in quotation marks because "forbidden" pericyclic reactions are not in fact truly forbidden. They merely occur less easily than analogous "allowed" processes. See ref 6.

(9) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc., Ser. A*, **214**, 432 (1952).

ishes. The conversion of **R** to **T** therefore involves a crossing of the HOMO and LUMO and the same must be true of the isoconjugate pericyclic reaction. In the case of an "allowed" pericyclic reaction the situation is entirely different since the coefficients a_{or} and a_{os} in eq 1 now have similar signs. The HOMO-LUMO splitting consequently differs from zero throughout the reaction.

There has been much discussion in the literature concerning the conditions under which the noncrossing rule may fail so that orbitals may cross. The case discussed here does not seem to have been previously considered. Indeed it has often been assumed that orbital crossings cannot occur except in systems where elements of symmetry are retained, orbitals of different symmetry then being free to cross. This indeed was the basis of the treatment of pericyclic reactions proposed by Longuet-Higgins and Abrahamson³ and by Woodward and Hoffmann,⁴ HOMO-LUMO crossings occurring in "forbidden" pericyclic reactions when the two MO's differ in symmetry. If, however, the crossings were due solely to symmetry, they should vanish not only when the reactants and/or products lack symmetry but also in reactions involving symmetrical reactants and products if the intermediates are unsymmetrical. In both cases removal of symmetry would lead to a HOMO-LUMO mixing so that no orbital crossing could occur. Our arguments imply that the HOMO-LUMO crossings in "forbidden" even pericyclic reactions are much more fundamental in nature, depending on orbital topology rather than orbital symmetry. Detailed MINDO/3¹⁰ calculations have indeed shown that such reactions invariably involve HOMO-LUMO crossings regardless of symmetry.¹²

Our PMO arguments can be extended to odd pericyclic reactions where bond reorganization takes place in an odd-numbered ring, provided that no other odd-numbered ring is involved. MINDO/3 calculations for a number of "forbidden" reactions of this type have again shown that they invariably involve unsymmetrical intermediates and also invariably involve HOMO-LUMO crossings. The distinction between "allowed" and "forbidden" reactions again seems to be one of topology rather than symmetry, there being a qualitative distinction between pairs of isomers that can be interconverted by a pericyclic reaction without a HOMO-LUMO crossing and pairs that cannot be so interconverted without a HOMO-LUMO crossing.

These considerations have led us to postulate that a similar topological distinction may apply to all pairs of isomers even if their interconversion involves other kinds of chemical processes. According to this hypothesis any collection of isomers can be divided into sets, such that members of the same set can be interconverted without a HOMO-LUMO crossing whereas members of different sets cannot be so interconverted. The only restriction is that the interconversions must not involve pericyclic processes where the mesomeric system in the transition state involves two fused odd-numbered rings.¹³ Isomers of the same set may be

(10) MINDO/3 is an improved version of the MINDO/2¹¹ semi-empirical SCF MO method; R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.

(11) See M. J. S. Dewar, *Fortschr. Chem. Forsch.*, 23, 1 (1971).

(12) These calculations also indicate that symmetry is never retained during reactions of this kind unless enforced by geometrical constraints, as in the conversion of bicyclo[2.1.0]pentene to 1,3-cyclopentadiene.

termed *homomers* (short for HOMO-HOMomers) and isomers of different sets *lumomers* (short for HOMO-LUMomers). Since the distinction is presumed to be topological, it should apply regardless of the path followed in the interconversion. Thus while a pair of homomers may be interconverted by a path involving a HOMO-LUMO crossing, this can be the case only if the path involves a second subsequent HOMO-LUMO crossing, retrieving the original topological pattern.

If a reaction involves a HOMO-LUMO crossing it will require more activation than an analogous one where no such crossing occurs. This was the basis of the treatment of pericyclic reactions proposed by Longuet-Higgins and Abrahamson³ and by Woodward and Hoffmann,⁴ the crossing of orbitals being regarded as a consequence of symmetry. Our hypothesis leads to a generalization that can be regarded as an extension of the Woodward-Hoffmann rules and Evans principle. It can be concisely stated in the terminology introduced above.

The interconversion of homomers is "allowed" while that of lumomers is "forbidden."

Since the distinction between homomers and lumomers is assumed to be topological, any method should give equivalent results. Thus in the case of pericyclic reactions we can use Evans' principle,^{5,6} while in cases where reactant and product share elements of symmetry, we can use orbital correlation diagrams. The latter will give the right answer, even if for the wrong reason, because interconversion of lumomers by *any* path must involve a HOMO-LUMO crossing. We can therefore arbitrarily choose a route where symmetry is retained. In the last resort we can follow the reaction by a direct MO calculation. Here again any treatment should lead to the same result.

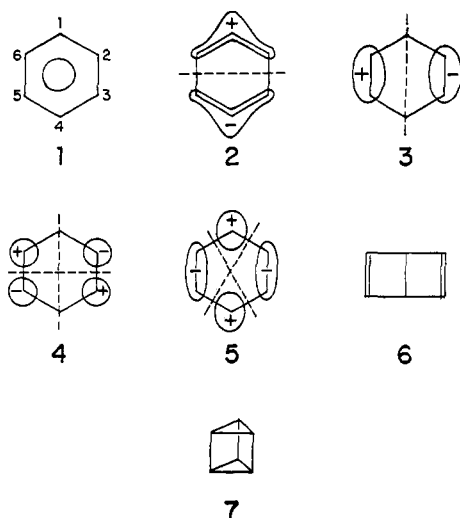
Yet another approach is to construct a lumomer of a given molecule by transferring two electrons from the HOMO to the LUMO and deducing the change in geometry that results. In the case of alternant hydrocarbons, the HOMO and LUMO have diametrically opposite bonding properties. Similar large differences should occur in other cases so transfer of two electrons from the HOMO to the LUMO should lead to a major change in geometry. This provides a further reason for the "forbidden" nature of reaction involving interconversions of lumomers.

Benzene (**1**) is a good example. Here both HOMO and LUMO are degenerate, the corresponding MO's (in real form) having the well-known shapes indicated in 2-5. In **1**, all the ortho π -bond orders are equal, all the meta bond orders are zero, and all the para bond orders are negative. Suppose now that we transfer two electrons from MO 2 to MO 4. Since 2 is antibonding

(13) Such a delocalized system can be derived from a single even-numbered ring by introducing a bridge; *cf.* azulene. Our MINDO/3 calculations indicate that HOMO-LUMO crossings do still occur in such cases provided that the bridging bond plays no direct role in the reaction. Thus the conversion of bicyclobutane to a lumomeric butadiene involves a HOMO-LUMO crossing whereas conversion to a lumomeric cyclobutene does not.^{14,15} However, cases of the latter kind necessarily involve such peculiar stereochemistries that they are likely to require prohibitive activation (*cf.* ref 15). Reactions of this kind, while "allowed" in the sense that no HOMO-LUMO crossing is involved, will then still be "forbidden" by stereochemical considerations.

(14) This curious possibility was pointed out by R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Springer-Verlag, Berlin, 1970.

(15) Unpublished work by Dr. A. Komornicki. The corresponding calculated activation energy is >60 kcal/mol.



between 23 and 56 whereas **4** is bonding, the 23- and 56-bond orders should increase. Likewise the 12-, 34-, 45-, and 61-bond orders should decrease, and, finally, since **2** is very strongly antibonding between 14 while **4** is correspondingly bonding, the 14-bond order should change from negative to large and positive. If we rewrite **1**, including these changes, we find that the resulting structure (**6**) is that of Dewar benzene. Thus **1** and **6** are lumomers. A similar argument shows that transfer of two electrons from MO **3** to MO **4** converts **1** to prismane (**7**).

Lumomers exemplify in a particularly striking fashion a general type of isomerism which may be termed *orbital isomerism* and which involves alternative occupation of distinguishable orbitals by electrons. This phenomenon is well recognized in carbenes (*cf.* the lowest singlet states of CH_2) and in species such as the phenyl cation C_6H_5^+ (where distinct isomers can be formed from the radical $(\text{Ph}\cdot)$ by loss of either a σ or a π electron). In the case of lumomers the rearrangement is much more drastic and leads to correspondingly greater changes in geometry, as indeed has been recognized^{16,17} in several discussions of reactions involving such processes.

Acknowledgment. We are grateful to Professor H. C. Longuet-Higgins for some very helpful comments and criticisms of the original version of this manuscript.

(16) R. Hoffmann and W. D. Stohrer in "Special Lectures Presented at the XXIIIrd International Congress of Pure and Applied Chemistry," Butterworths, London, 1971, p 157.

(17) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4291, 4292 (1971).

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Orbital Isomerism in Biradical Processes¹

Sir:

The possible importance of biradicals as reaction intermediates has recently been emphasized by the

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claim² that "forbidden" pericyclic reactions cannot take place in a concerted manner but must proceed *via* intermediate biradicals where "memory" of the reactants is lost. This view has been criticized on the basis of the interpretation of pericyclic reactions in terms of Evans' principle³ but it is not clear how biradical processes can be included in this. In the preceding communication⁴ pericyclic reactions were discussed in terms of orbital isomerism. Here we will show how biradicals and biradical-like species can be included in the same scheme.

In a simple MO description a singlet biradical is a species with two degenerate orbitals occupied by two electrons with opposite spins.⁵ Such a system should in general be unstable, undergoing a Jahn-Teller distortion⁶ to some more stable species. The distortion can be represented by a change (δq) in some generalized coordinate, q , from the value q_0 corresponding to degeneracy. The distortion replaces the orbitals ϕ_1 and ϕ_2 by linear combinations ψ_1 and ψ_2 . A distortion in one direction ($q_0 + \delta q$) will make ψ_1 lower in energy than ψ_2 while the opposite distortion ($q_0 - \delta q$) has the opposite effect. Passage from one *Jahn-Teller isomer* (A) to the other (B) therefore involves an inversion in the order of ψ_1 and ψ_2 , *i.e.*, a HOMO-LUMO crossing. A and B are thus lumomers⁴ of one another, and their interconversion is consequently "forbidden."

This argument shows that a "forbidden" pericyclic reaction cannot evade the Woodward-Hoffmann rules by following a nonconcerted path *via* an intermediate biradical. Such a biradical will be unstable with respect to two Jahn-Teller isomers A and B, one of which (A) is homomeric with the reactants and the other (B) with the products. The biradical is the transition state for the interconversion of A and B. Even if A and B are stable intermediates, their interconversion will still be "forbidden." The rule⁴ that interconversion of homomers⁴ is allowed while that of lumomers⁴ is forbidden therefore holds in all cases and can be used as a criterion without reference to the reaction path.

Consider for example rotation about double bonds. Interconversion of **1** and **3** involves a HOMO-LUMO crossing, the orbitals becoming degenerate in the orthogonal biradical intermediate **2**. Thus **1** and **3** are lumomers and their interconversion is "forbidden." The reaction has in fact a high activation energy (65 kcal/mol).⁷

Similar arguments apply to the conversion of **4** to **5** or of **5** to **6**. In each case a HOMO-LUMO crossing is involved. It follows, however, that conversion of **4** to **6** *via* **5** involves two HOMO-LUMO crossings, restoring the original orbital order. Thus **4** and **6** are

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(3) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(4) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *J. Amer. Chem. Soc.*, **96**, 5240 (1974).

(5) For a detailed discussion see (a) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972); (b) S. P. McGlynn, T. Azumi, and M. Kineshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

(6) We feel that the use of the term "Jahn-Teller" in this more general sense is less confusing than the introduction of additional terms such as "pseudo-Jahn-Teller."⁵ It is after all entirely analogous to the use by name of the Pauli principle in Hückel theory this representing an adoption of the true Pauli principle to simplified orbital treatment.

(7) R. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, **23**, 2439 (1955).