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 (Ph·) 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.

(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 Processes[1]

Sir:

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

claim[2] 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' principle[3] but it is not clear how biradical processes can be included in this. In the preceding communication[4] 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 distortion[6] 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 then 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 lumomers[4] 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 rule[4] that interconversion of homomers[4] is allowed while that of lumomers[4] 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).

1 2 3 4 5 6 7

8 9 10 11 12 13 14 15

16 17 18 19 20 21 22

23 24 25 26 27 28 29 30
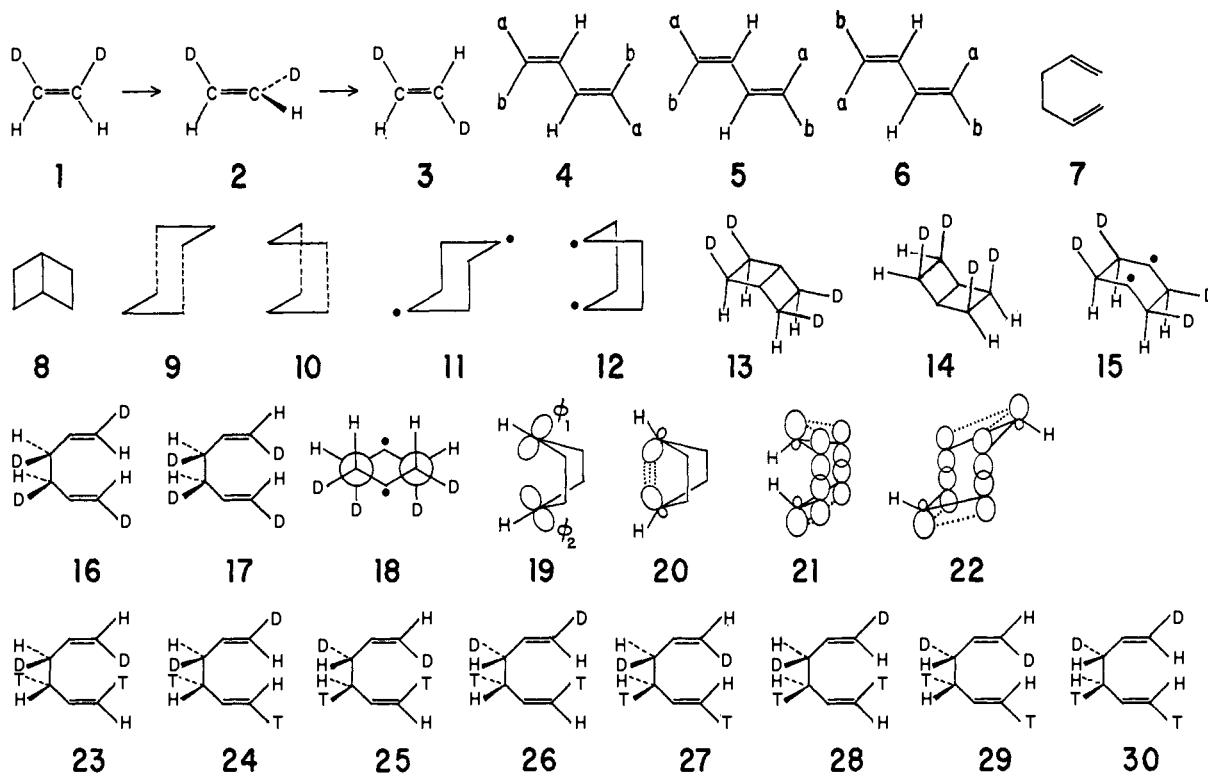
homomers[4] and their interconversion should be "allowed." Consequently the conversion of **4** to **6** by simultaneous rotation about both double bonds should—and does[8]—take place more readily than a single rotation to give **5**.

The geometric distortions needed to stabilize a biradical can be deduced from the forms of the key orbitals ψ_1 and ψ_2. The energy of each is determined by a balance between bonding and antibonding contributions. One Jahn–Teller isomer arises by a distortion that strengthens the bonding interactions in ψ_1 and weakens the antibonding ones, having the opposite effect on ψ_2. The converse distortion stabilizes ψ_2. The required distortions can be deduced from the forms of the orbitals; cf. the analysis of benzene isomers in the preceding communication.[4]

The thermal rearrangements of 1,5-hexadiene (**7**) and of bicyclo[2.2.0]hexane (**8**) provide an excellent example.

The Cope rearrangement of **7** can take place via intermediates of "chair" (**9**) or "boat" (**10**) type.[9] The effect of substituents on the rate of rearrangement indicates[10] that the "chair" intermediate is akin to the "biradical" **11**. Presumably the same is true of the "boat" intermediate (i.e., **12**). On heating the labeled bicyclohexane, **13** rearranges[11] to **14** presumably via an intermediate **15** of biradical type. If this were the same as **12**, one would expect it to undergo fission to **16**. Some deuterated **7** was indeed formed in the reaction but it had the structure **17**, derived from **15** by isomerization to the "chair" structure **18**. This is presumably the chair intermediate in the normal Cope rearrange-

ment of **17**. Two questions at once arise. First, what is the difference between **12** and **15**? Secondly, why does **15** dissociate to **17** via **18** rather then directly to **16**?

Consider the classical biradical (**19**) with two singly occupied AO's ϕ_1 and ϕ_2. These can interact either directly across space (**20**) or hyperconjugatively via the intervening C–C $p\sigma:p\sigma$ bonds (**21**). As Hoffmann, et al.,[12] have pointed out, direct coupling leads to a negative matrix element β between ϕ_1 and ϕ_2 while indirect coupling leads to a positive one. If the direct coupling predominates, the lower of the resulting perturbed MO's will be $(\phi_1 + \phi_2)$ while if the indirect coupling predominates, $(\phi_1 - \phi_2)$ will be the lower. Now the direct coupling will be increased, and the indirect one reduced, by the deformation indicated in **20** while that indicated in **21** will have the opposite effect. At some intermediate geometry the direct and indirect couplings may cancel; β will then be zero so ϕ_1 and ϕ_2 remain degenerate. This structure will then correspond to a biradical, **20** and **21** being the isomers derived from it by Jahn–Teller distortion. Clearly **20** and **21** are lumomers, the biradical being the transition state for their "forbidden" interconversion. MINDO/3 calculations[13] have confirmed that these relationships hold. Thus the "boat" intermediate in the Cope rearrangement has the geometry **21** while **20** collapses to **8** without activation. The interconversion of **20** and **21** does indeed involve a HOMO–LUMO crossing and the hydrogen atoms at the radical centers are displaced from planarity in the expected manner. The conversion of **13** to **17** via **15** and **12** would therefore be a "forbidden" reaction.

The "chair" Cope intermediate **11** can likewise be shown to have the geometry **22**, corresponding to in-

(8) L. M. Stephenson, R. V. Gemmer, and J. I. Brauman, *J. Amer. Chem. Soc.*, **94**, 8620 (1972).

(9) W. v. E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962).

(10) M. J. S. Dewar and L. E. Wade; (a) *J. Amer. Chem. Soc.*, **95**, 290 (1973); (b) unpublished work.

(11) M. J. Goldstein and M. S. Benzon, *J. Amer. Chem. Soc.*, **94**, 5119, 7147 (1972).

(12) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Amer. Chem. Soc.*, **90**, 1499 (1968).

(13) Unpublished work by L. E. Wade.

direct coupling between the radical centers, the phases of the AO's ϕ_1 and ϕ_2 in the occupied combination being as indicated. It is easily seen that inversion of 12 to 11 should give rise to 19 without an orbital crossing and this has been confirmed by McIver and Komornicki[14] in a very detailed MINDO/2 study of the C_6H_{10} potential surface. Thus conversion of 13 to 18 via 15 and 19 is an "allowed" process.

At first sight this result might seem to contradict the treatment of such reactions in terms of orbital isomerism on the grounds that the "forbidden" conversion of 20 to 21 can be carried out in an "allowed" manner via 22 and 7. This, however, is not the case. The problem arises only because the lack of labels makes it impossible to distinguish between species that are formally distinct.

Consider the doubly labeled hexadiene 23. This can be converted into a lumomer by inversion at any CHD or CHT center (cf. 1 → 3). Inversion at two centers then generates a homomer of 23 (cf. 4 → 6). One can in this way derive seven homomers (24–30) of 23. The remaining eight possible stereoisomers of 23 can be derived from 23–30 by a single inversion. Thus the 16 isomers fall into two groups of eight, such that any isomers in the same group are homomers whereas isomers from different groups are lumomers. The 16 isomers of each other relevant species (8, 20, 21, 22) can likewise be divided into two groups of eight such that members of the same group are homomers while members of different groups are lumomers. The entire set of 80 structures (5 × 16) can thus be divided into two subsets of 40 each, such that members of the same subset are homomers while members of different subsets are lumomers. It is easily seen that all the members of a given subset can be interconverted by allowed processes 21 ⇌ 7 ⇌ 22 ⇌ 20 ⇌ 8. It turns out that the homomeric species 20 and 21 differ by inversion at one CHD or CHT center, this balancing the orbital crossing implied by the change from direct to indirect 1,4-interaction. Members of different subsets are lumomers and cannot be interconverted by any combination of "allowed" processes. These conclusions are supported by the MINDO calculations[13,14] which show that all the "forbidden" interconversions involve orbital crossings.[4]

Previous discussions of reactions of this kind have followed apparently similar lines. In them, however, the intermediates have been represented by biradical structures and the stereospecificities attributed to conservation of orbital symmetry. It would be surprising if symmetry could be conserved under these conditions (cf. ref 3 and 4). The present discussion is based on the relatively gross changes in geometry that accompany the Jahn–Teller distortions of such biradicals, the stable species being either normal molecules or biradicaloids[5b] such as 20–22. The orbital crossings during "forbidden" reactions are retained regardless of symmetry because of this.

(14) J. McIver and A. Komornicki, personal communication.

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Nature of the Transition States in "Forbidden" Electrocyclic Reactions[1]

Sir:

While the validity and value of the Woodward–Hoffmann rules is well established, the magnitude of the corresponding differences in activation energy between analogous "allowed" and "forbidden" reactions is still uncertain. Numerous attempts have therefore been made to arrive at estimates of this by quantum mechanical calculations.[2] In order to reduce the amount of computation required these have been confined to the simplest possible reactions, namely the electrocyclic opening of cyclopropyl ions and radical and of cyclobutene. Since such a reaction will proceed in the "allowed" direction if it can, it is necessary to apply geometrical constraints to follow the "forbidden" processes. All calculations so far have accordingly assumed that the terminal methylene groups rotate in unison, in the "forbidden" direction, the system retaining twofold symmetry throughout. We wish to report some results which invalidate this assumption (and hence all previous calculations) and which also lead to general conclusions concerning the course of processes of this kind.

In our initial studies,[3] using the MINDO/2' method, we also assumed twofold symmetry in order to reduce the amount of computation. Since we were restricted at that time to a relatively inefficient procedure for calculating geometries, and since "forbidden" potential surfaces are very complex,[3] we had no choice. Recently these restrictions have been removed by the development of a very much faster geometry program,[4] based on the Davidon–Fletcher–Powell algorithm.[5] Using this together with an improved version (MINDO/3[6,7]) of the MINDO[8] semiempirical SCF MO method, we have examined a number of "forbidden" electrocyclic reactions, viz: (a) disrotatory opening of cyclopropyl anion, (b) conrotatory opening of cyclopropyl cation, (c) (d) conrotatory or disrotatory opening of cyclopropyl radical, (e) disrotatory opening of cyclo-

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(2) (a) D. T. Clark and G. Smale, Tetrahedron, 25, 13 (1969); (b) Tetrahedron Lett., 3673 (1968); (c) D. T. Clark and D. R. Armstrong, Theor. Chim. Acta, 13, 365 (1969); (d) ibid., 14, 370 (1969); (e) M. J. S. Dewar and S. Kirschner, J. Amer. Chem. Soc., 93, 4290, 4291, 4292 (1971); (f) D. T. Clark and D. B. Adams, Nature (London), 233, 121 (1971); (g) E. Haselbach, Helv. Chim. Acta, 54, 2257 (1971); (h) G. Boche and G. Szeimies, Angew. Chem., Int. Ed. Engl., 10, 911 (1971); (i) G. Szeimies and G. Boche, ibid., 10, 912 (1971); (j) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, J. Amer. Chem. Soc., 93, 2117 (1971); (k) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, ibid., 93, 5005 (1971); (l) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, ibid., 94, 5639 (1972); (m) L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, ibid., 95, 6531 (1973).

(3) M. J. S. Dewar and S. Kirschner, J. Amer. Chem. Soc., 93, 4290, 4291, 4292 (1971).

(4) M. J. S. Dewar, H. W. Kollmar, D. H. Lo, H. Metiu, P. J. Student, and P. Weiner, to be submitted for publication.

(5) See R. Fletcher, "Optimization," Academic Press, New York, N. Y., 1969.

(6) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.

(7) The main errors in the earlier MINDO treatments[8] have been overcome in MINDO/3, in particular the overestimation of the stabilities of small rings and "nonclassical" structures. The errors in the heats of formation of small ring compounds are now no greater than those for compounds of other types.

(8) See N. Bodor, M. J. S. Dewar, and D. H. Lo, J. Amer. Chem. Soc., 94, 5303 (1972), and papers cited there.