

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 Komornicki¹⁴ 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** \rightarrow **3**). Inversion at two centers then generates a homomer of **23** (*cf.* **4** \rightarrow **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** \rightleftharpoons **7** \rightleftharpoons **22** \rightleftharpoons **20** \rightleftharpoons **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.

Michael J. S. Dewar,* Steven Kirschner
Herbert W. Kollmar, Leslie E. Wade

Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received December 1, 1973

Nature of the Transition States in "Forbidden" Electrocyclic Reactions¹

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 MINDO⁸ 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-

(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) (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 treatments⁸ 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.

butene, (f) (g) (h) conversion of Dewar benzene and of its 1-chloro and 1,4-dichloro derivatives to benzenes, (i) (j) (h) conversion of bicyclo[2.1.0.]pentene and its 1- and 2-methyl derivatives to cyclopentadienes.

In (a-e) we followed the reaction by rotating one methylene group, using as reaction coordinate the angle of twist (ϕ_1) of the HCH plane from its initial orientation orthogonal to the ring. For each value of ϕ_1 the geometry was calculated by minimizing the energy with respect to all other geometrical variables, no assumptions of symmetry, etc., being made. If no constraints were applied, the reaction naturally followed the corresponding "allowed" path. To study "forbidden" processes we applied only the condition that the other methylene group must not rotate in the "wrong" direction from its initial orientation orthogonal to the ring (twist angle, ϕ_2 , zero).

Under these conditions all five reactions behaved in a similar way. In each case ϕ_2 remained close to 0° until the transition state was passed. In each case the value of ϕ_1 at the transition state was in the range $40-50^\circ$. In each case the HOMO/LUMO crossing characteristic of forbidden reactions⁹ occurred only after the transition state was passed. The reactions were thus quite "normal" processes, involving the formation of an intermediate homomeric⁹ with the reactant. The intermediate then passes over to the product with negligible activation, the orbital crossing occurring during this downhill phase. The calculated difference in activation energy between the "allowed" conrotatory and "forbidden" disrotatory openings of cyclobutene (16.6 kcal/mol) was in good agreement with a recent experimental estimate (~ 15 kcal/mol).¹⁰

The remaining reactions can take place only in a disrotatory manner and so could be studied without imposing any restraints. The rearrangements (f-h) of Dewar benzene and its chloro derivatives resembled (a-e), each transition state having an unsymmetrical structure in which one bridgehead methine had rotated only a little while the other had approached planarity with the other carbon atoms. The HOMO/LUMO crossing again occurred after the transition state had been passed. The only reactions where symmetry was retained were the openings of the three bicyclopentenes (i, j, h). Here the geometrical constraints are very strong. The transition states corresponded to the HOMO/LUMO crossings.

Regardless of their validity these results show that one certainly cannot assume symmetrical intermediates in reactions of this kind. All previous calculations in this area² must therefore be disregarded, including our own.³ Indeed, it seems clear that calculations of reaction paths in which such assumptions are made are chemically worthless; an assumption concerning the geometry of the transition state of a reaction is tantamount to an assumption concerning its mechanism. There is little point in studying the mechanism of a reaction by a procedure which prejudges the result. If calculations of this kind are to be of any chemical value, they must be based on procedures in which the geometry is completely optimized.

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

(10) J. I. Brauman and W. G. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972).

The validity of our present conclusions rests on that of MINDO/3. Detailed MINDO/3 calculations, with complete geometry optimization, have now been carried out for 14 electrocyclic reactions for which experimental data have been reported. The calculated activation energies nearly all agree with experiment to within 5 kcal/mol.¹¹ The only serious deviation was in the case of cyclobutene where our calculated activation energy is too large by 13.0 kcal/mol. This error is, however, no greater than that (12.8 kcal/mol) from a very detailed *ab initio* SCF-CI treatment²ⁱ⁻¹ and much less than that from the same treatment without CI (39.0 kcal/mol¹⁶). No other procedure has been tested with anything like this degree of rigor, let alone survived such tests.

Our results for reactions a-e can be understood easily in terms of orbital isomerism.^{9,17}

During a "forbidden" electrocyclic reaction, the system has to pass through a biradical intermediate corresponding to the HOMO/LUMO crossing. The most direct path from reactant to product leads through an intermediate biradical which is of very high energy, being antiaromatic.¹⁸ The most stable state of such a biradical will be one derived from the cyclic reactant by rotating one methylene group only, since any rotation of the second methylene will give rise to an unfavorable cyclic conjugation. The lowest point in the biradical barrier will therefore be that corresponding, in the symbols used above, to a 90° , 0° configuration (*i.e.*, $\phi_1 = 90^\circ$, $\phi_2 = 0^\circ$). The "best" reaction path will be one in which the reactant approaches this ideal structure as closely as possible before trying to cross the barrier. This can be achieved by rotating one methylene group only, the other retaining its original position ($\phi_2 = 0^\circ$). As the first methylene rotates, the original C-C σ -bond weakens and a new C-C π -bond forms. At some point, in the general vicinity of $\phi_1 = 45^\circ$, the formation of the new π -bond will begin to outweigh weakening of the old σ -bond so the energy will begin to decrease with further increase in ϕ_1 . At this point any rotation of the second methylene will still increase the energy since π interactions between it and the adjacent sp^2 carbon are still antibonding. The transition state for the overall reaction will therefore correspond to the maximum ($\sim 45^\circ$, 0°) since the path from this to the 90° , 0° configuration is downhill.

The Dewar benzene reactions (f-h) follow the same pattern except that here the geometrical constraints prevent the molecule from adopting a (90° , 0°) configuration. In the bicyclopentenes (i-k) the con-

(11) Reactions (error in activation energy, kcal/mol): f^{12a} (4); g^{12a} (5); h^{12a} (5); i^{12a} (1); j^{12a} (2); h^{12a} (4); electrocyclic openings of bicyclobutane^{12b} (0), endo (7), and exo (7) dimers of cyclobutadiene¹⁵ and of bicyclo[4.2.0]octatriene¹³ (4); Cope rearrangement¹⁴ of 1,5-hexadiene *via* chair (2) and boat (2) transition states; Diels-Alder reaction of ethylene with butadiene^{12b} (1); dissociation of cyclobutane into ethylene^{12b} (1).

(12) M. J. S. Dewar and S. Kirschner, (a) *J. Chem. Soc., Chem. Commun.*, in press; (b) *J. Amer. Chem. Soc.*, in press.

(13) M. J. S. Dewar, A. C. Griffin, and S. Kirschner, *J. Amer. Chem. Soc.*, in press.

(14) M. J. S. Dewar and L. E. Wade, to be submitted for publication.

(15) R. S. Case, M. J. S. Dewar, S. Kirschner, R. Pettit, and W. Sleiger, *J. Amer. Chem. Soc.*, in press.

(16) Reported by Dr. S. D. Peyerimhoff at the CECAM Colloquium on "Calculation of Reaction Paths and Reaction Mechanisms," Paris, Sept 1972.

(17) M. J. S. Dewar, S. Kirschner, H. C. Kollmar, and L. E. Wade, *J. Amer. Chem. Soc.*, **96**, 5242 (1974).

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

straints become so extreme that the reaction is forced to follow an unfavorable symmetrical path.

These arguments imply that the transition state of any "forbidden" electrocyclic reaction should be unsymmetrical unless symmetry is enforced by severe geometrical constraints and that in general the transition state of such a reaction will precede the HOMO-LUMO crossing.¹⁹ Biradical intermediates should not therefore play any mechanistic role in such reactions, except as transition states in the exceptional cases where symmetry is enforced.

(19) Bauld, *et al.*,²⁰ have suggested that "forbidden" electrocyclic reactions take place *via* unsymmetrical transition state; which in our terminology would be described as biradicals. It is of course well recognized that other "forbidden" pericyclic reactions take place *via* unsymmetrical transition states so the same would also be expected of "forbidden" electrocyclic reactions. However, the present discussion shows that the latter do show a novel feature; *i.e.*, the transition states occur *before* the biradical intermediate is reached.

(20) N. L. Bauld, F. R. Farr, and C. S. I-Chang, *Tetrahedron Lett.*, 2443 (1972).

Michael J. S. Dewar,* Steven Kirschner

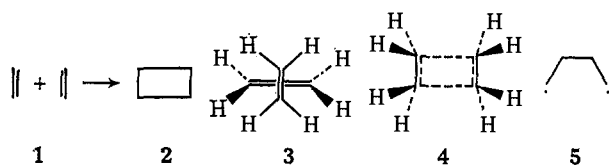
Department of Chemistry, The University of Texas at Austin
Austin, Texas 78712

Received December 1, 1973

Dimerization of Ethylene to Cyclobutane¹

Sir:

The dimerization of ethylene (**1**) to cyclobutane (**2**) and the reverse conversion of **2** to **1** have been the subjects of much recent discussion.²⁻⁹ The mechanisms which have been considered are first an "allowed" reaction proceeding with inversion about one double bond *via* a skew transition state **3**, secondly, a "forbidden" reaction proceeding *via* an antiaromatic rectangular transition state **4**, and thirdly, a reaction involving the biradical **5** as a stable intermediate. The latter mechanism has been favored by Benson⁵⁻⁷ on the grounds that the observed activation energy for conversion of **2** to **1** is greater than the estimated difference in energy between **2** and **5**.



We have studied these processes in detail, using the MINDO/3 semiempirical SCF MO method.¹⁰ The path of lowest energy was found to be *via* structures

(1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and by 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) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(3) L. M. Stephenson, J. H. Gibson, and J. I. Brauman, *J. Amer. Chem. Soc.*, **95**, 2849 (1973).

(4) R. Hoffmann, S. Swaminathan, B. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(5) S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961).

(6) S. W. Benson and M. F. O'Neal, *J. Phys. Chem.*, **72**, 1866 (1968).

(7) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968 Section 3.10.

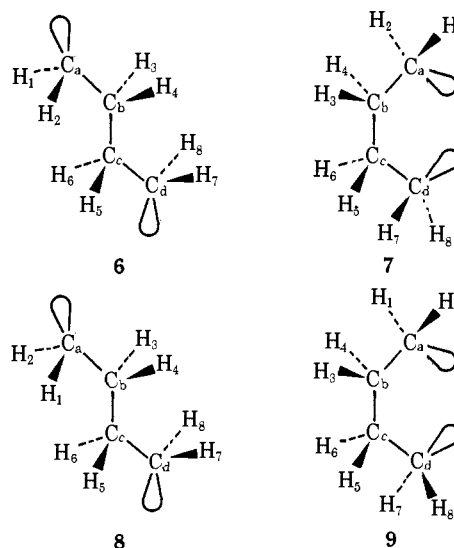
(8) G. R. Freeman, *Can. J. Chem.*, **44**, 245 (1966).

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

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

analogous to **5**. In view of the biradical-like nature of such intermediates, CI with the lowest doubly excited configuration was included.¹¹ The potential surface had the "two-valley" structure typical of forbidden pericyclic reactions.¹² The surface is divided in two by a ridge corresponding to the biradical intermediates, separating the lumomeric species on either side of it.¹³ In the vicinity of the transition state, the system exists as one of two biradicaloid¹⁴ structures, **6** and **7**. In **6**, which is homomeric with **1**, the radical centers are coupled hyperconjugatively *via* the intervening C-C σ : σ bond,¹⁴ while in **7**, which is homomeric with **2**, the coupling is across space.¹⁴ In each case the "radical" centers are nonplanar, as in the analogous biradicaloids derived from bicyclo[2.2.0]hexane.¹⁴ The biradicaloid **6** is most stable, as indicated, in a *trans* conformation while **7** is most stable in *cis*. Neither biradicaloid is a stable species but there is a ridge in the potential surface for conversion of **2** to **1** at *ca.* 60 kcal/mol above **2**. The conversion of **7** to **6**, and hence **1**, involves rotation about the central bond and inversion of both terminal methylene groups. The reaction involves a HOMO-LUMO crossing, *i.e.*, is "forbidden," and so requires activation. The overall activation energy for conversion of **2** to **1** (62 kcal/mol) agrees well with experiment (62.5 kcal/mol⁷).

Simple dimerization of ethylene in this way *via* **6** and **7** would give a cyclobutane in which the geometry of both ethylene units is retained. In order to get inversion of one methylene moiety, it is necessary to rotate one of the terminal methylene groups in **6**, *e.g.*, CH₁H₂, about 180° to form, *e.g.*, **8**. This is a "forbidden" process, precisely analogous to the corresponding rotation of one terminal methylene in 1,3-butadiene, though the activation energy here will naturally be much smaller since the AO's of the two terminal carbon atoms are coupled much less strongly in **6** than in butadiene. "Forbidden" inversion of **8** to **9** can then lead to the



isomeric cyclobutane. The amount of **9** formed, and

(11) *Cf.* R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9107 (1972).

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

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

(14) M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Amer. Chem. Soc.*, **96**, 5242 (1974).