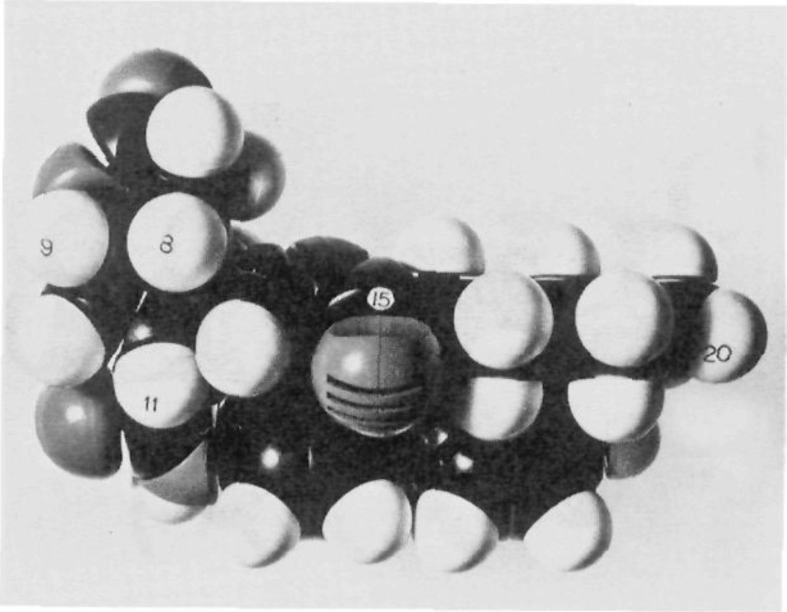

Figure 2. CPK model of I, R = $p\text{-}C_6H_5C_6H_4NHCO$, with s-cis arrangement of the $\Delta^{13(14)}$-en-15-one unit, antiplanar H–C(12)–C(13)–H unit, maximum contact between enone chain (extended C_5H_{11}) and *p*-phenylphenylcarbamoyl group. In this conformation the O–CO–N–C part of the urethane function is planar and the C–O–CO–N part is nonplanar, corresponding to amide delocalization in preference to ester delocalization. The s-cis enone unit contacts four adjacent carbons of the NHC_6H_4 unit. Numerals refer to carbon position.

1.0, $CHCl_3$), was carried out from the alcohol I, R = H, by reaction with the readily available *p*-phenylphenyl isocyanate, mp 58–58.5°[8] (1.2 equiv), in dry tetrahydrofuran (4 ml/g of isocyanate) and triethylamine (1.2 equiv) at 25° for 3 hr (yield, >90%). For reduction the *p*-phenylphenylurethane I in tetrahydrofuran–ether (1:4, 40 ml/g of I) at *ca.* −130°[9] was treated dropwise with a 0.23 *M* solution in tetrahydrofuran of the reagent IV[1a] (*ca.* 30 ml/g of I), reaction was continued for 4 hr at −130° and 2 hr at −115° (ethanol–liquid nitrogen bath), and the product was isolated by extraction after quenching of the reaction mixture with methanol and 1 *N*-hydrochloric acid. The total yield of II,[7] R = $p\text{-}C_6H_5C_6H_4NHCO$, was quantitative, and the ratio of 15*S* to 15*R* isomers in several runs was 92/8. For the synthesis of prostaglandins it was found to be expedient to utilize the product II directly and to remove the small amount of 15*R* by-product at the stage of prostaglandin $F_{2\alpha}$ or E_2 where the separation of 15*S* and 15*R* diastereomers is extremely simple. The conversion of II, R = $p\text{-}C_6H_5C_6H_4NHCO$, to the required diol II [R = H,[1a] oil, $[\alpha]^{23}D$ −7.1° (*c* 1.1, $CHCl_3$)] was accomplished in >90% yield by hydrolysis using 1 *M* aqueous lithium hydroxide at 120° for 72 hr, extraction of the basic reaction mixture at 0° with ether–ethyl acetate (1:1) to remove neutral and basic components, and relactonization by the addition of ethyl chloroformate (2 equiv) to the aqueous phase which had been neutralized with carbon dioxide.[10]

The highly selective reduction of I, R = $p\text{-}C_6H_5C_6H_4\text{-}NHCO$, could also be carried out with thexyl di-*sec*-butylborohydride (88/12) and tri-*sec*-butylborohydride[11] (89/11).

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E. J. Corey,* Konrad B. Becker, Ravi K. Varma
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138
Received September 8, 1972

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[8] M. J. van Gelderen, *Recl. Trav. Chim. Pays-Bas*, **52**, 969 (1933).

[9] Cooling bath: *n*-pentane–liquid nitrogen; see R. E. Rondeau, *J. Chem. Eng. Data*, **11**, 124 (1966).

[10] This procedure for lactonization was developed in collaboration with Dr. A. Venkateswarlu in these laboratories.

[11] See H. C. Brown and S. Krishnamurthy, *J. Amer. Chem. Soc.*, **94**, 7159 (1972).

Symmetry Selection Rules for Transition States

Sir:

The transition state for a chemical reaction is the lowest possible potential energy barrier (assuming one exists) between reactants and products. At the transition state there must exist directions along which the potential energy decreases as the atoms are displaced toward reactants or products. In other words, the curvature of the potential energy along such a direction must be negative. The unit vector leading from the transition state toward products along the direction of most negative curvature we define as the *transition vector*. It can be shown that this is the eigenvector of the force constant matrix **F** corresponding to the lowest eigenvalue, that this eigenvalue is negative, and that **F** can have no other negative eigenvalues.[1] Moreover, the transition vector, like all eigenvectors of **F**, must belong to one of the irreducible representations of the point group of the transition state.[2]

The purpose of this communication is to demonstrate the existence of selection rules governing the symmetry properties of the transition vector and, in fact, for a broad class of reactions, governing the structural symmetry of the transition state itself. These selection rules, presented in the form of three theorems, follow from group theoretical and geometric considerations alone. Consequently, they are valid for any potential surface which shows symmetry properly, whether it be numerically exact or approximate. The theorems are as follows.

1. *The transition vector cannot belong to a degenerate representation of the point group of the transition state.*
2. The transition vector must be symmetric with respect to a symmetry operation of the transition state which leaves reactants or products unchanged.
3. The transition vector must be antisymmetric with respect to a symmetry operation of the transition state which converts reactants into products.

The first theorem follows immediately from the requirement that at the transition state **F** must have one and only one negative eigenvalue.[3] The proofs of the

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[1] J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968); see also J. N. Murrell and G. L. Pratt, *ibid.*, **66**, 1680 (1970). We have assumed that the potential surface is quadratic in the vicinity of the transition state, *i.e.*, that the transition vector does not correspond to a zero eigenvalue of the force constant matrix **F**. Aside from pure translations and rotations, it is unlikely that the first and second derivatives of the potential energy will simultaneously vanish along an eigenvector of **F**. This argument is essentially the same as that which underlies the noncrossing rule. K. R. Naqvi and W. B. Brown, *Int. J. Quantum Chem.*, **6**, 271 (1972).

[2] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, pp 106–107.

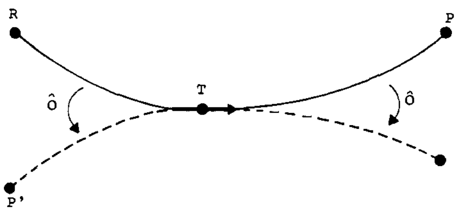

Figure 1. Illustration of proof of theorem 3.

second and third theorems are similar to one another and proceed by *reductio ad absurdum*. Here we outline the proof of theorem 3.

The solid line in Figure 1 represents a path leading from reactants R through the transition state T to the products P. The path is chosen so that the energy at each point leading up to T is less than that at T itself. For simplicity we also require that the path follow the transition vector for a small but finite distance on each side of T. Let $\hat{O}$ be some symmetry operator[4] of the transition state which converts reactants R into products P′ that differ from P by no more than free translations and rotations of isolated molecules. The application of $\hat{O}$ to the original path will convert each point into an energetically equivalent point on a path (dashed line in Figure 1) joining P′ and T. (The point T representing the transition state is, by definition, invariant under $\hat{O}$.) Let us suppose that in contradiction to theorem 3, the transition vector was symmetric under $\hat{O}$. It is evident from Figure 1 that if this were the case, then one could proceed from R to P′ to P by crossing from the solid path to the dashed path where they meet at the arrow. At no point would the energy be as high as that of the transition state. Since this contradicts the supposition that T is the lowest barrier, the transition vector cannot be symmetric. Since by theorem 1 it cannot belong to a degenerate representation, it can only be antisymmetric. This completes the proof.

There are many reactions which possess some symmetry and thus to which one or more of the theorems can be applied. Here we restrict ourselves to a few rather striking examples. Consider the simple isotopic exchange reaction $X_1X_2 + X_3X_4 \rightarrow X_1X_4 + X_2X_3$ (*e.g.*, $H_2 + D_2 \rightarrow 2HD$). Among the symmetric structures proposed for the transition state are the tetrahedral (point group T_d), centered equilateral triangle (D_{3h}) and square-planar (D_{4h}) configurations.[5] The T_d structure is illustrated in Figure 2. The arrows in the figure *do not* represent the transition vector but rather the displacements of the atoms to reactants or products. These arrows are the objects of the symmetry operations. The atomic labels remain unchanged.[4] In the case shown, the improper rotation $\hat{S}_4$ converts the reactant arrows (a) into a product set (b). Theorem 3 requires, therefore, that the transition vector be antisymmetric under $\hat{S}_4$. Inspection of the character table for the point group T_d reveals that only the species A_2 and T_2 behave in this way. The T_2 representation is eliminated as the species of the transition vector by theorem 1, and standard group theoretical techniques can be used to show that A_2 is not available to the internal coordinates of this system. We conclude, then, that the tetrahedral transition state is forbidden. Even if the A_2 species were available, the transition state would still be forbidden. This is because there are, in addition to the $\hat{S}_4$ operation, four distinct $\hat{C}_3$ operations which convert reactants into products, and the character table shows that A_2 is *symmetric* under these operations. There are, incidentally, four more $\hat{C}_3$ operations which convert reactants into the alternative products $X_1X_3 + X_2X_4$. It follows that the tetrahedral transition state is forbidden for this reaction as well. By similar arguments, we can eliminate the D_{3h} transition state for these reactions. The square-planar structure, on the other hand, is "allowed"; if it is the transition state, the theorems imply that the transition vector belongs to the B_{1g} representation.

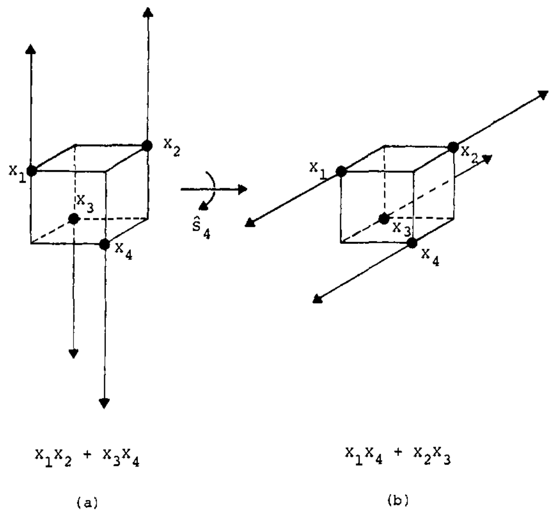

Figure 2. Conversion of reactants into products by the tetrahedral operation S_4.

In the case of the $H_2 + D_2 \rightarrow 2HD$ exchange, it is likely that the T_d and D_{3h} transition states could have been eliminated on the basis of the Jahn–Teller theorem since the relevant electronic states are probably degenerate.[3,5] In other cases it may be difficult to decide whether or not such a degeneracy exists without computation. The theorems presented here, however, will generally make such a computation unnecessary. A

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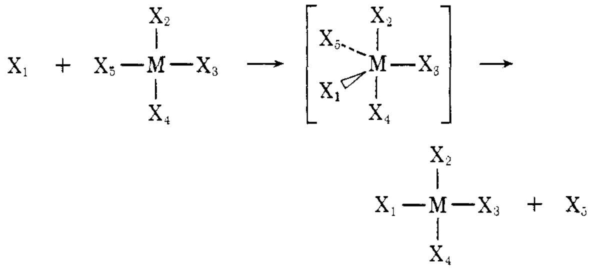
(3) If the force constant matrix were to have a degenerate negative eigenvalue, then the transition state would resemble a hilltop, clearly not the lowest barrier between any two points. Transition states possessing a Jahn–Teller instability due to electronic degeneracy can be eliminated on similar grounds. The surface in this case differs from that just discussed only in that the top of the hill is sharpened into a peak rather than being rounded. See G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand-Reinhold, New York, N. Y., 1966, p 40 ff; and J. N. Murrell, *J. Chem. Soc., Chem. Commun.*, 1044 (1972).

(4) The mathematical effect of a symmetry operation on a molecular configuration is to "rotate" the entire molecule in space and then permute the nuclei back to the vicinity of their original positions. When applied to a symmetrical configuration, it leaves the structure unchanged; when applied to a distorted configuration, it changes it into a *different*, yet equivalent, distorted configuration. Pictorially this is equivalent to a rotation of the displacement vectors leading from the symmetric to the distorted configuration without changing the atomic labels (see Figure 2 for an example). This point is not always made clear in elementary treatments. For further discussion, see R. McWeeny, "Symmetry, An Introduction to Group Theory and Its Applications," Macmillan, New York, N. Y., 1963, pp 144–145.

(5) *E.g.*, C. W. Wilson, Jr., and W. A. Goddard, *J. Chem. Phys.*, 51, 716 (1969).

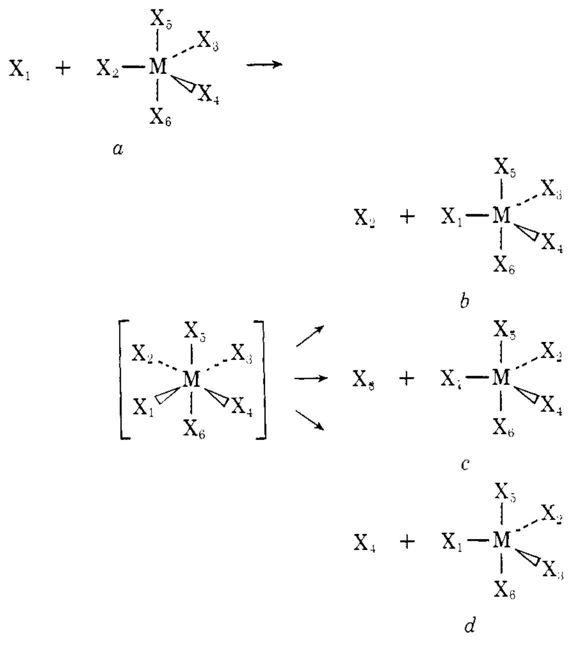
structure which is forbidden by our theorems will not be made allowed by additional instabilities.

As a practical matter, we wish to point out that in all point groups containing a three-, five-, or sevenfold axis, the nondegenerate representations are symmetric with respect to rotations about this axis. Thus, from theorems 1 and 3, no structure for which rotation about this axis converts reactants into products can be a transition state. The T_d and D_{3h} structures discussed above fall into this category. Another example would be the trigonal-bipyramid structure for the substitution (1). Although this structure cannot be the transition


(1)

state, it could be a metastable intermediate (for which F would have no negative eigenvalues). There is some evidence to indicate that this is in fact the case in at least one example.[6]

The case of an evenfold axis is more complex. In reaction 2, for example, there are three distinct prod-


(2)

uct sets b, c, and d which can arise from reactants a *via* the D_{4h} (or C_{4v}) structure as the transition state. The transition state is "allowed" for the reactions a → b and a → d. This is because there exists a nondegenerate representation (B_{1g}) which is antisymmetric under the operations which convert a into b or d and symmetric under the operations which leave a unchanged. On the other hand, it is "forbidden" for the reaction a → c since every nondegenerate representation is symmetric under the operation $\hat{C}_4^2$ which concerts a into c. Moreover, from the proof of theorem 3, it follows that if the D_{4h} structure is indeed the transition state for a → b, then there must exist a *lower energy* transition state (of different symmetry) for the reaction a → c.

From this last example it should be clear that any of the "forbidden" structures discussed above could be stationary points with a single, nondegenerate, negative eigenvalue of F. Theorem 3 eliminated them as transition states only for the reactants and products under consideration.

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James W. McIver, Jr.*
Department of Chemistry, State University of New York at Buffalo
Buffalo, New York 14214

Richard E. Stanton
Department of Chemistry, Canisius College
Buffalo, New York 14208

Received June 1, 1972

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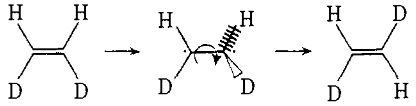
(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, p 379.

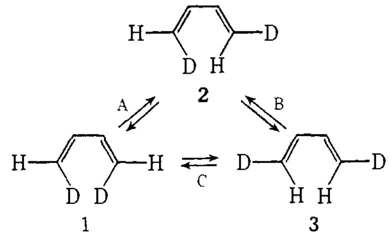
Thermal Cis–Trans Isomerization of Butadiene

Sir:

Many cis–trans isomerization reactions are now believed to proceed *via* a twisting mechanism which includes as a midpoint a species which has been termed a 1,2 diradical.[1] We wish to report that a portion of the



thermal cis–trans isomerization reactions of the 1,4-dideuterio-1,3-butadienes[2] also proceeds by such a mechanism, paths A and B, below, but that a *correlated double isomerization*, path C, appears to dominate the reaction mechanism.[6]



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[1] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 72.

[2] The *trans,trans*- and *cis,cis*-dideuteriobutadienes were prepared in good yield from the *trans,trans*-[3] and *cis,cis*-dichlorobutadienes[4] (pure by vpc) *via* Zn–Cu couple reduction in refluxing dioxane–D_2O. The details of these procedures will be reported elsewhere. The *cis,-trans*-dideuteriobutadiene could also be prepared from the corresponding dichlorobutadiene,[4] or more conveniently by the method of Fleming.[5] The structures and deuterium contents were confirmed by nmr and mass spectral measurements. The analysis of the pyrolysis products was most conveniently accomplished by a least-squares fit to five Raman lines, at 1171, 1216, 1226, 2260, and 2280 cm^{-1}.

[3] R. Huisgen, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **75**, 585 (1966). Pure *trans,trans*-dichlorobutadiene was obtained after two recrystallizations from pentane.

[4] Prepared and purified according to the method of P. D. Bartlett and G. E. H. Wallbillich, *J. Amer. Chem. Soc.*, **91**, 409 (1969).

[5] I. Fleming and E. Wildsmith, *J. Chem. Soc. D*, 223 (1970).

[6] A discussion of this possibility has appeared: J. I. Brauman and W. C. Archie, Jr., *J. Amer. Chem. Soc.*, **94**, 4262 (1972).