Symmetry Control and Photoinduced Reactions

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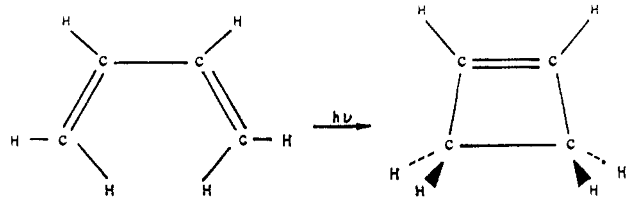
Abstract: The photochemical cyclization of butadiene to cyclobutene is used to illustrate certain problems connected with the application of the Woodward–Hoffmann rules to photoinduced concerted reactions. Energy levels for the ground states and excited states of butadiene, cyclobutene, and a large number of intermediate configurations have been calculated, thus enabling the establishment of potential surfaces, from which probable reaction paths for the thermal and photoinduced reactions can be determined. It appears that the thermal disrotatory process is improbable since this would require an activation energy of *ca.* 100 kcal/mole. Further, it turns out that the driving force for the photoinduced ring closure as a disrotatory process derives from a favorable symmetric excited state, whereas Woodward and Hoffmann consider an antisymmetric excited state.

The concept of orbital symmetry is most useful in helping to explain the stereoselectivity of a large number of thermal and photoinduced concerted reactions. The importance of orbital symmetry was first suggested in a paper by Havinga and Schlatmann.[2] This dealt with the opposite reaction paths for thermal and photoinduced ring closure of previtamin D, and mentioned that the symmetry characteristics of the highest occupied molecular orbital of the conjugated hexatriene system might be a factor contributing to the remarkable stereochemical difference.

The fact that symmetry is a general principle governing a large area of concerted reactions was first formulated in a number of papers by Woodward and Hoffmann.[3] They pointed out that in these reactions the symmetry of the highest occupied molecular orbital determines the stereochemistry of the products formed. A case in point is the electrocyclic conversion of butadiene to cyclobutene, which can occur in two ways—either as a conrotatory or as a disrotatory process. In order to stabilize the transition state of the reaction the terminal atoms have to rotate in such a way that a bonding interaction results in the highest occupied molecular orbital. Inspection of the Hückel molecular orbitals of butadiene indicates that the thermal reaction ought to be a conrotatory process and the photochemical reaction a disrotatory process, and this is in complete agreement with experimental findings.[4–7] The simple symmetry argument, furthermore, is supported by the results of quantum-chemical calculations using the extended Hückel theory.[3]

Woodward and Hoffmann's idea of orbital symmetry has been supplemented by Longuet-Higgins and Abrahamson.[8] They note that the orbitals of the reactant pass adiabatically into the orbitals of the product. Also, in the conrotatory mode of ring closure of butadiene the system preserves a twofold axis of symmetry throughout the reaction whereas in the disrotatory mode a plane of symmetry is maintained, it being supposed that the orbitals remain symmetric or antisymmetric with respect to the element of symmetry present. As a consequence it is possible to construct orbital and state correlation diagrams in order to follow the course of the reaction qualitatively, and the conclusions are in complete agreement with those of Woodward and Hoffmann. Another, but more quantitative, study for ground-state reactions has been described by Fukui.[9]

In spite of the general insight afforded by the Woodward–Hoffmann rules, however, many aspects of the reaction mechanisms still remain unexplained. In the case of thermal reactions the all-important role of the highest occupied molecular orbital has been justified by assuming this orbital to contain the two electrons most easily perturbed during the incipient reaction.[10,11] One may, however, wonder why the course of a photoinduced reaction is completely determined by the lowest antibonding molecular orbital, occupied in the first excited state by one electron only. A still more serious problem is illustrated by the photochemical cyclization of butadiene to cyclobutene. The energy scheme pertaining to this reaction, taken from Dauben,[12] is given in Figure 1. In discussing these data Dauben remarks, "When it is considered that in the ground state cyclobutene is about 20 kcal/mole less stable than butadiene, it is evident that the spectroscopic singlet of cyclobutene is about 50–60 kcal/mole higher in energy than the spectroscopic singlet of butadiene. Thus the formation of the spectroscopic singlet state of cyclobutene from a similar state of butadiene is not probable."



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[1] Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research N.V.).

[2] E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961).

[3] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2046, 4388 (1965).

[4] E. Vogel, *Ann.*, **615**, 14 (1958).

[5] K. M. Shumate, P. N. Neumann, and G. J. Fonken, *J. Am. Chem. Soc.*, **87**, 3996 (1965).

[6] R. Criegee and H. G. Reinhardt, *Chem. Ber.*, 101, 102 (1968).

[7] W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *J. Am. Chem. Soc.*, **88**, 2742 (1966).

[8] H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

[9] K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Jap.*, **40**, 2018 (1967).

[10] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).

[11] K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, 20, 722 (1952).

[12] W. G. Dauben, 13th Chemistry Conference of the Solvay Institute, "Reactivity of the Photoexcited Organic Molecule," Interscience Publishers, New York, N. Y., 1967, p 171.

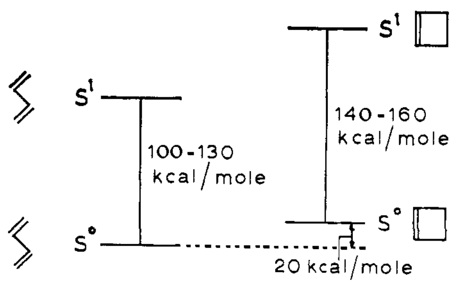

Figure 1. Energy scheme for the conversion of butadiene to cyclobutene.

Many suggestions have been made concerning the actual reaction path of photoinduced cyclization reactions. Fonken[13] speculates that the excited singlet state might give rise, by internal conversion, to a highly vibrationally excited cyclobutene which then may revert thermally to butadiene or by collisional deactivation forms stable cyclobutene. Dauben[7] suggests that the spectroscopic singlet state of the diene decays to a "nonspectroscopic" excited singlet state which is stabilized by partial bond formation between C_1 and C_4 of the diene. Participation of the triplet state in this valence isomerization is not probable since Srinivasan[14] demonstrated that the photolysis of 2,3-dimethyl-1,3-butadiene in the vapor phase could not be quenched by oxygen or nitric oxide.

The situation is unsatisfactory from a theoretical point of view at least. In fact, from experiment one merely knows that the cyclization reaction of butadiene starts from an excited singlet state and terminates at the ground state of the product. Indeed, although the Woodward–Hoffmann rules predict the stereochemical course of the photoinduced reaction it is not clear why a reaction takes place at all. Two important questions, therefore, remain to be answered: what is the driving force of the reaction

$$S^1{}_{\text{butadiene}} \longrightarrow (?) \longrightarrow S^0{}_{\text{cyclobutene}}$$

and what is the actual path along which the molecule travels to the final state? It would also be highly interesting to know something about the nuclear configuration at the moment that the electronic ground state is reached. Indeed, little is known about such nuclear configurations in photochemical reactions in general.

It is the purpose of this paper to contribute to the solution of these problems through a discussion of the results of a series of quantum-chemical calculations on the valence isomerization of butadiene to cyclobutene.[15] In particular, energy levels have been calculated for the ground states and excited states of butadiene, cyclobutene, and a large number of intermediate configurations, thus enabling the establishment of potential surfaces which are a prerequisite to a discussion of the actual course of the reaction.

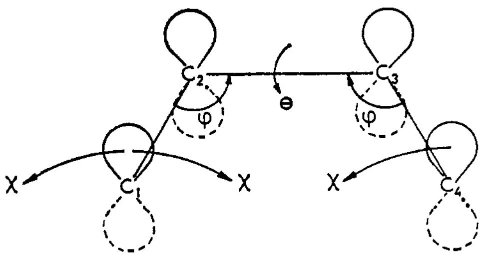

Figure 2. The three angles used as reaction parameters: φ is the angle directly related to the ring closure; it has been varied from 125 to 90° in steps of 5°; θ is a measure for the rotation about the bond between C_2 and C_3; it has been varied from -90 to $+90°$ in steps of 10°; χ describes the rotation of the p orbitals on C_1 and C_4; it has been varied from 0 to 90° in steps of 5°. In the conrotatory process the p orbitals are rotated in the same direction with conservation of a twofold axis of symmetry in the molecule. In the disrotatory process the rotations are in the opposite direction with conservation of a plane of symmetry for $\theta = 0°$.

Details of the Calculations

In order to gain an insight into the reaction paths of thermal and photoinduced electrocyclic reactions, a large number of nuclear configurations have to be considered. Even in a semiempirical approach it is impracticable to include all conceivable intermediate configurations, and so we have selected three angles which seem to us the most relevant reaction coordinates. These three angles, φ, χ, and θ, are detailed in Figure 2. Even using this simplified model the total number of configurations for which the energies have been calculated still comes to 4408.

The distances between the carbon atoms C_1–C_2, C_2–C_3, and C_3–C_4 have been kept constant, namely 1.34, 1.47, and 1.34 Å, respectively, and it has been assumed that the carbon atoms C_1 and C_4 retain their trigonal hybridization. These rather drastic simplifications make the model somewhat unrealistic in the neighborhood of cyclobutene.

It was assumed that there are three terms which are mainly responsible for the changes in the energies and that these three terms may be treated separately

$$E(\varphi, \chi, \theta) = E_{\text{electronic}} + E_{\text{angle}} + E_{\text{nonbonded}}$$

where $E_{\text{electronic}}$ represents the energy of four electrons as explained below, E_{angle} represents the angle strain energy on the atoms C_2 and C_3, and $E_{\text{nonbonded}}$ represents the energy due to the nonbonded interactions of hydrogen atoms.

$E_{\text{electronic}}$. During the reaction from butadiene to cyclobutene the two conjugated double bonds of butadiene pass gradually into the π bond between C_2 and C_3 and the σ bond between C_1 and C_4 of cyclobutene. It therefore seems reasonable to consider merely the energy of the four electrons involved in these bonds and to assume that the energy of all other electrons remains constant. The localized character of the electrons in the other bonds would support this assumption.

The energies of the four electrons in ground and excited states have been calculated using a valence bond (VB) method with orthogonalized atomic orbitals.[16] A method along these lines has been described in a number of papers by McWeeny.[17] In our treatment,

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(13) G. J. Fonken in "Organic Photochemistry I," O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1967, p 197.

(14) R. Srinivasan, *J. Am. Chem. Soc.*, **84**, 4141 (1962).

(15) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *Chem. Commun.*, 1235 (1968).

(16) W. Th. A. M. van der Lugt, Thesis, Leiden, 1968.

(17) R. McWeeny, *Proc. Roy. Soc.* (London), **A223**, 63, 306 (1954); **A227**, 288 (1955).

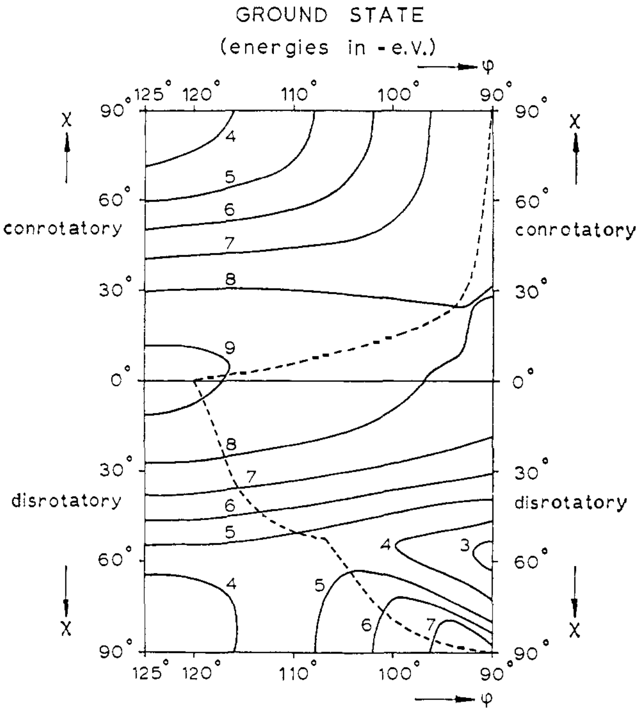

Figure 3. Potential surfaces for the ground state.

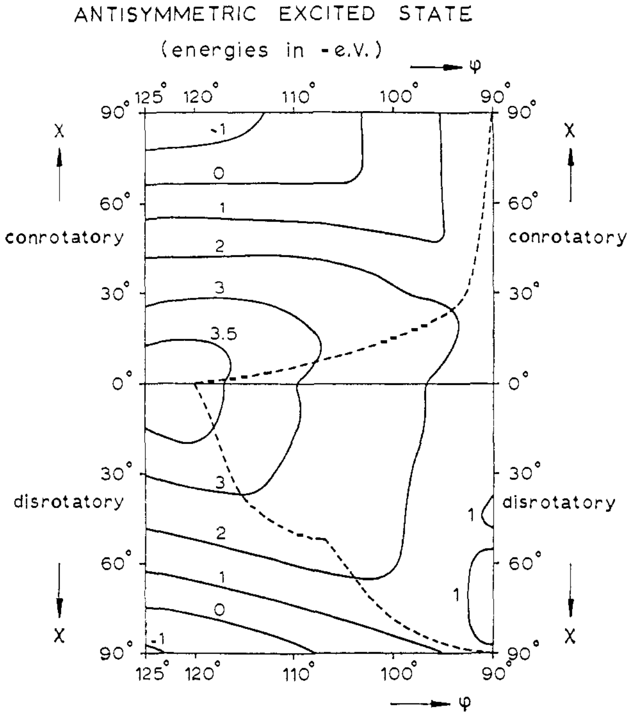

Figure 4. Potential surfaces for the antisymmetric excited state.

however, we have consistently applied the approximations and adjustments introduced by Pariser and Parr[18] and by Pople[19] in the molecular orbital (MO) theory. Since the problem is a four-electron–four-orbital problem, complete VB calculations involve 20 singlet structures (covalent and ionic structures), all of which were included in each calculation. It turns out that the energies of the covalent structures are equal within the approximations used and this energy has been chosen as the zero on the energy scale. As regards the semiempirical parameters, the electronic repulsion integrals have been calculated from the formulas of Pariser and Parr,[18] and the resonance integrals have been determined with the aid of the formula $\beta_{pq} = -10.4 \times S_{pq}$ eV, where S_{pq} is the overlap integral between the orbitals on the atoms p and q. In this connection it should be noted that since in our model the carbon atoms C_1 and C_4 retain a trigonal hybridization the σ bond in cyclobutene is formed from two p_σ orbitals.

The same results can of course be obtained from complete MO calculations, but there are two reasons why we prefer the VB procedure. In the first place, the reactions of butadiene to cyclobutene and *vice versa* are valence isomerizations, which can be considered as a change of the ground state of the molecule from one covalent valence bond structure to the other. For this reason alone, therefore, it seems worthwhile to interpret the results of the calculations in terms of valence bond structures. A second reason, however, is that for complete calculations the VB method is much more practical than the MO method where all singly and higher excited configurations are included.[16] The results of MO calculations which include only singly excited configurations are unreliable as regards the photochemical reaction, as will become clear later.

E_{angle}. The strain associated with the deviation of the bond angle from equilibrium on the carbon atoms C_2 and C_3 has been calculated from a formula given by Gleicher and Schleyer.[20]

$E_{\text{nonbonded}}$. This contribution to the energy is due to the interaction of "nonbonded" atoms. In calculating this term, only the two hydrogen atoms bonded to carbon atoms C_1 and C_4 and close together in *cis*-butadiene have been taken into account. This contribution, too, has been calculated from a formula given by Gleicher and Schleyer,[20] although this formula has had to be adapted to fit our model, in which the hybridization is artificially kept constant. Without the adaptation the two hydrogen atoms appear to be too close to one another in cyclobutene when the latter is formed in a disrotatory process. Actually the hybridization of carbon atoms C_1 and C_4 changes in such a way that the hydrogen atoms bend away from each other. Consequently we have multiplied the formula by a factor of $(90° - \chi)/90°$, with the result that the nonbonded interaction decreases to zero on formation of cyclobutene when χ is 90°.

The interaction matrix of the 20 valence bond structures was constructed and diagonalized for each of the 4408 combinations of φ, χ, and θ. The distance between the two hydrogen atoms was calculated by elementary analytical geometry and the three energy terms were added. A special Fortran program was written in order to perform the calculations on the computer at the University of Leiden, an IBM 360-50.

Potential Surfaces and Reaction Paths

From the treatment of the 4408 nuclear configurations the energies of their ground states and excited states are obtained as functions of the angles φ, χ, and θ. In

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(18) R. Pariser and R. G. Parr, *J. Chem. Phys.*, 21, 466, 767 (1953).

(19) J. A. Pople, *Trans. Faraday Soc.*, 49, 1275 (1953).

(20) G. J. Gleicher and P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 582 (1967).

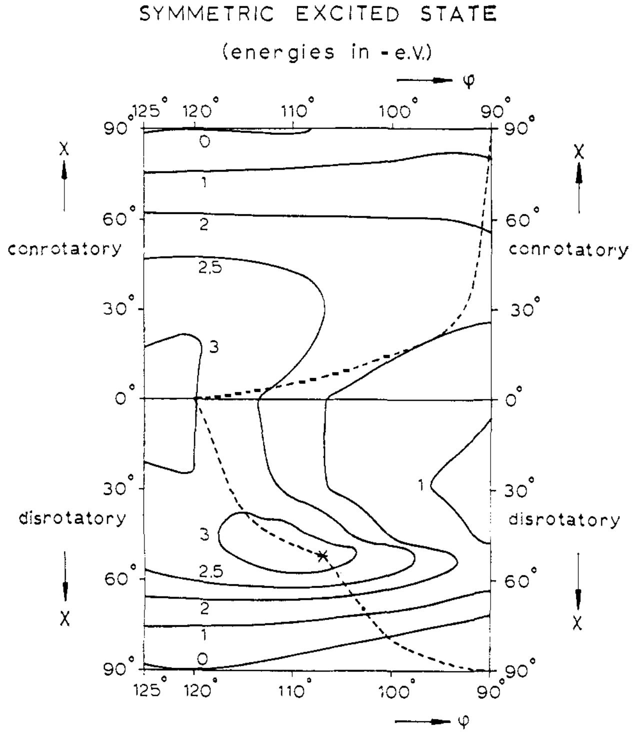

Figure 5. Potential surfaces for the symmetric excited state. The asterisk marks the configuration with the lowest energy.

order to cope with the vast array of numbers thus involved, the angle θ was eliminated as an independent variable as follows: for each combination of φ and χ the value of θ which gives the lowest energy for that combination was selected independently for the ground state and excited states. Two-dimensional graphs of the energy as a function of φ and χ can then be made for each state.

The first two excited states of butadiene differ little in energy since there is an antisymmetric excited state at 5.4 eV and a symmetric one at 6.1 eV above the ground state. The remaining 17 calculated excited states are at least 2 eV higher in energy, however. Representations of the potential surfaces for the ground state and the two lowest excited states are shown in Figures 3–5.

The Thermal Reaction. Let us first take the isomerization of butadiene to cyclobutene in the ground state. In fact, the course of the thermal reaction is in the opposite direction since butadiene is more stable than cyclobutene. It is, however, better to start from butadiene because our model makes the calculations more accurate in the region of the diene. The actual direction of the reaction is simply a question of thermodynamic relations which need not concern us here.

It is evident from Figure 3 that the disrotatory process of ring closure is impossible. On the reaction path with the lowest activation energy, the energy steadily increases from −9.11 to −4.77 eV in the transition state, which means that an activation energy of *ca.* 100 kcal/mole is required. In the conrotatory process, however, we find no activation energy at all. This absence of a barrier along the path of minimum energy would mean that cyclobutene is unstable, but, as already pointed out, the results of the calculations are rather inaccurate for low values of φ. The activation energy found experimentally for the formation of butadiene from cyclobutene is 32.5 kcal/mole,[6] whereas the activation energy for the forbidden disrotatory μ ring opening of cyclobutene was estimated at approximately 4 kcal/mole.[21]

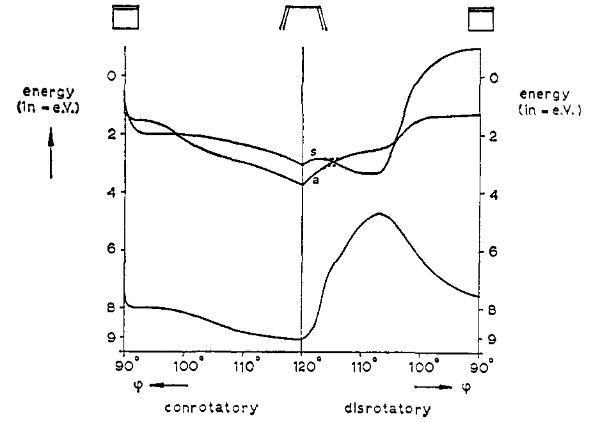

Figure 6. The energies of the ground state and two excited states during the reactions.

A probable reaction path for the ground-state reaction as a conrotatory process is indicated in Figure 3 by a dotted line, and this path is also given in Figures 4 and 5. A clearer picture of this section through the potential surfaces, however, is given in Figure 6, on the left-hand side, where the energy is shown as a function of the angle φ.

Since the value of the angle θ was selected independently for the ground state and the excited states, related points in the Figures 3, 4, and 5 (equal values of φ and χ) correspond in general to different values of θ. In Figure 6, however, the values of the angles χ and θ are the same for equal φ. The values of the angles φ, χ, and θ and of the energies of the ground and the two excited states along this probable conrotatory reaction path are given in Table I.

Table I. The Values of the Angles φ, χ, and θ and of the Energies of the Ground State and of the Two Excited States along a Probable Reaction Path for the Thermal Conrotatory Process[a]

Angles, deg			Energies, −eV		
φ	χ	θ	Ground state	Sym excited state	Antisym excited state
120	0	20	9.11	2.92	3.56
115	0	30	8.95	2.63	3.31
110	5	40	8.79	2.37	2.94
105	10	40	8.55	2.18	2.66
100	15	40	8.28	2.03	2.19
95	20	40	8.06	1.97	1.50
90	90	0	7.52	0.79	1.28

[a] These data have been used in Figure 6.

Although this reaction path is rather uncertain, due to the absence of a potential barrier, the behavior of the angles χ and θ is noteworthy. The initial decrease in φ causes only a small rotation of the p orbitals on C_1 and C_4, so that the conjugation with the p orbitals on C_2 and C_3, respectively, is maintained to a large extent. The angle θ changes considerably since a large rotation about the bond between C_2 and C_3 is required in order

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(21) J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).

to obtain a positive overlap between C$_1$ and C$_4$ for the highest occupied molecular orbital. The value of 40° for this rotation in the transition state is in good agreement with the experimentally estimated value of 45° for phenyl-substituted dienes.[22]

The Photoinduced Reaction. When *cis*-butadiene is irradiated with uv light, the molecule is excited into the antisymmetric excited state ("a"). The transition to this state is allowed and has, according to our calculations, an oscillator strength of 0.31. The transition to the symmetric excited state ("s"), on the other hand, is forbidden. At the same time Figure 4 shows that the potential surfaces of "a" do not reveal any driving force, either for a conrotatory or for a disrotatory process of ring closure, since the energy increases with changing φ and χ and the steepness in both directions is nearly the same.[23]

However, an explanation for the preference of butadiene for a disrotatory mode of ring closure on irradiation with light is found in Figure 5, where the shape of the potential surfaces of the symmetric excited state is shown. A probable reaction path for a disrotatory ring closure from the antisymmetric excited state has also been indicated in Figures 3, 4, and 5 by a dotted line, and this section through the potential surfaces is given on the right-hand side of Figure 6.[24]

The essential thing here is that at $\varphi \cong 116°$ in the disrotatory direction the antisymmetric and symmetric energy levels intersect. But this accidental degeneracy can be lifted by nuclear configurations which deviate from twofold symmetry, and in that case the levels will no longer cross. Nuclear vibrations cause a molecule in "a" to pass adiabatically into "s," as shown in Figure 6 by the dotted line. In this way the molecular electronic state "a" is converted into "s," in which a disrotatory deformation can proceed. The nuclear configuration will then change in such a way that the electronic energy corresponds to the well[25] in "s" at a value of $\varphi = 107°$, $\chi = 50°$, and $\theta = 0°$. Vibrational energy thus obtained will be distributed over the whole molecule or dissipated by collisions with other molecules.

As a result the molecule is captured in the energy well, from where it is assumed to reach the lower potential surface of the ground state. The mechanism of such a transition is not yet known and is related to radiationless processes in molecules. It may very well be, however, that collisions with other molecules are essential for the return to the electronic ground state.

On reaching the electronic ground state the molecule is in a nuclear configuration corresponding to the disrotatory transition state between butadiene and cyclobutene. The reaction can now proceed in one of two directions: either cyclobutene is formed or butadiene is re-formed. This also explains why butadiene can be re-formed without fluorescence or phosphorescence, as has been observed experimentally in liquid solutions.

Some interesting data along this probable disrotatory reaction path starting from the antisymmetric excited state are given in Table II.

Table II. The Values of the Angles φ, χ, and θ and of the Energies of the Ground State and of Two Excited States along a Probable Reaction Path, Starting from the Antisymmetric Excited State, for the Photoinduced Disrotatory Process[a]

Angles, deg			Energies, −eV		
φ	χ	θ	Ground state	Sym excited state	Antisym excited state
120	0	0	9.08	3.02	3.69
115	40	0	6.54	3.03	2.90
110	50	0	5.11	3.28	2.59
107	50	0	4.73	3.31	2.53
105	60	0	4.85	2.64	2.32
100	80	0	6.25	−0.13	1.36
95	85	0	7.15	−0.83	1.37
90	90	0	7.52	−1.34	1.28

[a] These data have been used in Figure 6.

The behavior of the angles χ and θ here is different from that in the thermal conrotatory process in that there is no rotation about the bond between C$_2$ and C$_3$. On the other hand, the nonbonded interaction between the two hydrogen atoms forces a rotation of the p orbitals on C$_1$ and C$_4$.

Concerning the importance of the three terms included in the calculations of the energies, it appears that the contribution of the electronic energy is responsible for the general shape of the potential surfaces. The position of the states in relation to each other is completely determined by this term. The nonbonded interaction was included in our model in order to avoid having too short a distance between the hydrogen atoms, and the angle strain energy was included in order to scale the energies of butadiene and cyclobutene with respect to each other. Recently the strain energy of cyclobutene has been found experimentally to be 29 kcal/mole,[26] which rather fortunately happens to be in good agreement with the value of 31 kcal/mole used in our calculation. In Figure 7 we have given the contribution of the electronic energy and it is clear that conclusions to be drawn from this figure are essentially the same as those to be drawn from Figure 6.

One may doubt whether butadiene in "a" can in fact reach the intersection with "s," since an activation energy of ~14 kcal/mole is required, which is much too large for a photochemical reaction to proceed in a time comparable to the lifetime. The calculated value for this activation energy depends, however, on the parametrization used in the calculations and, in addition, will be made smaller by the inclusion of asymmetric nuclear configurations. A rotation of the p orbital of C$_1$ by 20° and of C$_4$ by 60°, for example, lowers the activation energy by 4 kcal/mole.

Theoretical Analysis

The reaction of butadiene to cyclobutene can be considered as a change of the ground state of the molecule from one covalent valence bond structure into the other.

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(22) Reported by H. H. Freedman at the Symposium on Valence Isomerization in Karlsruhe, 1968.

(23) In their first paper in 1965, Woodward and Hoffmann[3] mention in support of their symmetry arguments some results of extended Hückel calculations. These indicate a clear preference for disrotatory twisting in the first excited, antisymmetric state. From our calculations it follows that these results are incorrect, probably because state energies are obtained in the extended Hückel theory by simple summation of orbital energies.

(24) It should be mentioned that "s" terminates in different states of cyclobutene in the two processes.

(25) Since the precise position of the well is required for a sound discussion, the calculations were extended by varying φ from 115 to 105° in steps of 1° and χ from 35 to 55° in steps of 2.5°.

(26) J. F. Oth, private communication.

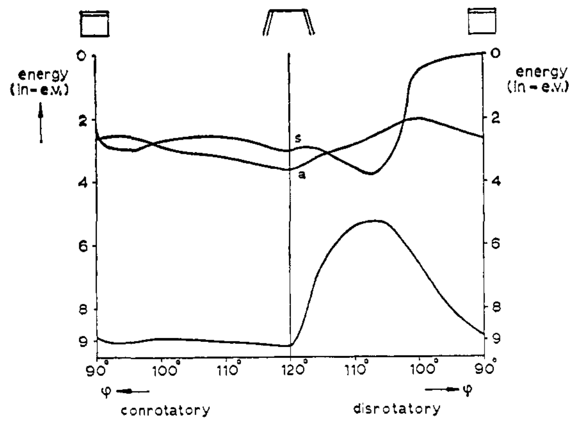
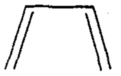


Figure 7. The electronic energy of the ground state and two excited states during the reactions.

It seems, therefore, worthwhile calculating the contributions of the valence bond structures along the reaction paths of the thermal conrotatory and the photoinduced disrotatory processes.

We are primarily interested here in the weights of the covalent structures (CS) A and B. Unfortunately, however, contributions of CS based on orthogonalized atomic orbitals are generally small. In order to obtain a clearer picture we have added to the weights of the CS those of the related polar structures: a singly polar structure is related to the CS from which the polar structure can be obtained by one charge shift, and so on. A more detailed discussion on this procedure has been given elsewhere.[16] The total contributions of the covalent structures A and B thus obtained along the reaction paths are given in Table III for the thermal conrotatory process and in Table IV for the photoinduced disrotatory process.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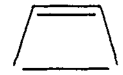
B

Table III. The Contributions of the Covalent Structures A and B during the Thermal Conrotatory Process, Expressed as Percentages

Angles, deg			Contributions of A and B, %: Ground state		Sym excited state		Antisym excited state	
φ	χ	θ	A	B	A	B	A	B
120	0	20	88	12	11	89	55	45
115	0	30	88	12	12	88	55	45
110	5	40	88	12	14	86	55	45
105	10	40	84	16	16	84	52	48
100	15	40	80	20	21	79	52	48
95	20	40	75	25	28	72	49	51
90	90	0	4	96	78	22	18	82

The figures in Table III are in agreement with the idea regarding the transition state of the thermal process mentioned earlier. Until the reaction is nearly finished the p orbitals on C_1 and C_4 are parallel to those on C_2 and C_3, maintaining the conjugation C_1–C_2 and C_3–C_4, *i.e.*, the molecule persists in the valence bond structure A.

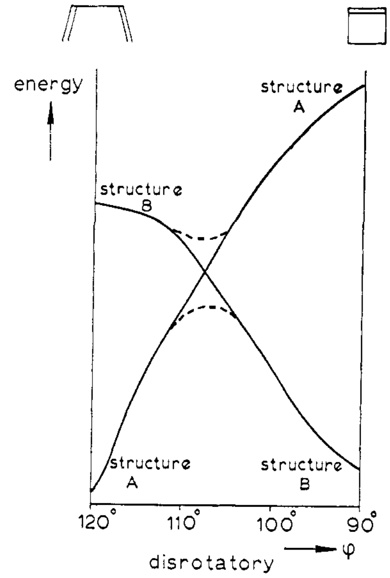

Figure 8. A simplified picture of the energies of the ground state and the symmetric excited state in terms of the covalent valence bond structures for the disrotatory process.

The contributions of the covalent structures in the disrotatory process, in Table IV, are especially interesting for the behavior of the wave functions corresponding to the ground state and the symmetric excited state. Following the reaction path, we see that the electronic ground state related to the nuclear configurations between butadiene and the transition state can be represented by the covalent structure A, whereas for the configurations between the transition state and cyclobutene structure B strongly dominates. The situation in the symmetric excited state, on the other hand, is precisely the opposite.

Table IV. The Contributions of the Covalent Structures A and B during the Photoinduced Disrotatory Process, Expressed as Percentages

Angles, deg			Contributions of A and B, %: Ground state		Sym excited state		Antisym excited state	
φ	χ	θ	A	B	A	B	A	B
120	0	0	88	12	12	88	55	45
115	40	0	84	16	11	89	55	45
110	50	0	71	29	25	75	55	45
107	50	0	65	35	30	70	54	46
105	60	0	11	89	90	10	54	46
100	80	0	4	96	100	0	53	47
95	85	0	4	96	100	0	44	56
90	90	0	4	96	100	0	18	82

This interpretation in terms of valence bond structures is surprisingly simple. As the nuclear configuration changes from butadiene to cyclobutene, the energy of the covalent structure A steadily increases while the energy of structure B decreases. At the intersection the interaction between the structures has a pronounced effect and the degeneracy is lifted as shown in Figure 8. In this way the ground state and the symmetric excited state pass over adiabatically from one covalent valence bond structure into the other as a result of the noncrossing rule.

It is instructive to compare the potential surfaces for the disrotatory ring closure with the simple correlation diagrams given by Longuet-Higgins and Abrahamson.[8] The diagram pertaining to the disrotatory mode for the interconversion of butadiene and cyclobutene also reveals a potential well in a symmetric excited state. Concerning this well their qualitative conclusions are in agreement with the results of our calculations. We would like to stress, however, one dissimilarity of great importance. Our calculations show, in contrast with the qualitative diagram of Longuet-Higgins, *that the energy of the symmetric excited state during the photoinduced reaction reaches a lower value than the energy of the antisymmetric excited state.* A solution to the problem, originally posed by Dauben and mentioned in the beginning of this article, is found by taking the symmetric excited state into account.

A complete molecular orbital calculation for the nuclear configuration corresponding to the well in the symmetric excited state reveals that the doubly excited configuration $|\psi_1\bar{\psi}_1\psi_3\bar{\psi}_3|$ makes a 65% contribution to this state. Similar calculations to those described here, moreover, have also been performed on the triplet states, including all 15 triplet valence bond structures.[27] But a driving force for a cyclization reaction starting from an excited triplet state of butadiene has not been found, and such a reaction is therefore not expected. This is easily explained by the fact that the well in the symmetric excited singlet state is due to the configuration $|\psi_1\bar{\psi}_1\psi_3\bar{\psi}_3|$, while a corresponding triplet configuration does not exist.

General Conclusions

Since the interpretation of thermal and photoinduced electrocyclic reactions in terms of orbital symmetries by Woodward and Hoffmann, many authors have given alternative explanations for the opposite reaction paths.[28] In all cases, however, only the antisymmetric excited state has been considered as being responsible for the photoinduced reaction of butadiene, resulting in a stereochemistry opposite to that of the thermal reaction.

From our calculations it follows that in discussing the direction of the photochemical reaction it is not sufficient to consider the antisymmetric excited state only, since this state is scarcely relevant to the explanation of the course of the photoinduced reaction.[29] In fact, the driving force for the reaction is due to the presence of a nearby symmetric excited state which has a potential well in the same nuclear configuration in which the ground state has a high potential barrier. It is because the well in the symmetric excited state is situated above the potential barrier in the ground state that the direction of the photoinduced reaction will be opposite to that of the thermal reaction.

The results thus suggest the following statement, which would seem to us to be generally applicable.

If a conrotatory (disrotatory) process is unfavorable in the ground state it implies the presence of a high potential barrier. From general principles it follows that there will be another potential surface of the same symmetry which has a well not far above this barrier. The photoinduced reaction may profit from this energy well to bring about ring closure or opening by a conrotatory (disrotatory) process opposite to the reaction in the ground state.

Our potential curves may also be used to explain some other photochemical phenomena. First, the presence of a well in potential energy surfaces of excited states offers an explanation for photochemical transformations in the chemistry of vitamin D and related substances. On irradiation of previtamin D (P), lumisterol (L) and ergosterol (E) are obtained by conrotatory processes. Also, irradiation of L or E yields P as primary product, but a direct conversion of L to E or E to L has not been observed.[30,31] It follows from these observations that the formation of an excited P molecule from an excited L (E) molecule can be excluded. This conclusion certainly is in agreement with the picture obtained from our calculations concerning the reaction paths of this kind of photoinduced valence isomerization. According to this an excited L (E) molecule will be captured in a potential well corresponding to a nuclear configuration between L (E) and P, and from there the molecule will reach the electronic ground state, resulting in the formation of L (E) or P, whereas formation of E (L) does not occur.

A second phenomenon for which the well in the symmetric excited state offers an explanation is the absence of fluorescence and phosphorescence of dienes and trienes in liquid solutions. Fluorescence has only been observed in a few cases in glasses at low temperature.[30] Our picture suggests that in liquid solutions a molecule in the antisymmetric excited state very rapidly reaches the well in the symmetric excited state before interconversion to the ground state with emission of light has occurred.

At present we cannot judge whether our results are also applicable to the interpretation of other types of photoinduced reactions. Many examples are known where the course of a photochemical process is different from that of the thermal process; different reactions like this are observed, for instance, in heterolytic photosubstitution reactions in aromatic compounds.[32] Furthermore, there are experimental and theoretical indications that a photochemical reaction may start from the second electronically excited state.[33] However, it has been assumed in most cases that the reaction starts from the first excited state because of its longer lifetime. As a consequence the reaction is usually discussed in terms of static electron densities, dynamic localization energies, and similar quantities related to the first excited state, whereas from our calculations it follows that interpretations along these lines should be regarded with caution. It is possible that in a number of photoinduced reactions the driving force is determined by the behavior of the potential surface of a higher excited state. It is also conceivable that after excitation of a molecule into a higher excited state the

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(27) The calculations have been performed by R. J. van Santen.

(28) (a) K. Fukui, *Bull. Chem. Soc. Jap.*, **39**, 498 (1966); (b) H. E. Zimmermann, *J. Am. Chem. Soc.*, **88**, 1564 (1966); (c) M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

(29) The transition to the antisymmetric excited state may, because of its high oscillator strength, play a part in the absorption of light required for a photochemical process.

(30) E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, 11, 276 (1960).

(31) G. M. Sanders, Thesis, Leiden, 1967.

(32) E. Havinga, 13th Chemistry Conference of the Solvay Institute, Interscience Publishers, New York, N. Y., 1967, p 201.

(33) H. M. Buck, W. Th. A. M. van der Lugt, and L. J. Oosterhoff, *Tetrahedron, Suppl.*, **2**, 173 (1963).

reaction starts from this state (because of the shape of the potential surface) before radiationless conversion to the first excited state has occurred. If this is the case, then any discussion in terms of the properties of the first excited state will be inadequate. But before a sound discussion of these reactions is possible, extensive studies of photochemical transformations using monochromatic light are essential.

Photolytic Rearrangement and Halogen-Dependent Photocylization of Halophenylnaphthalenes. II[1]

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Abstract: Photolysis of 1-(*o*-chlorophenyl)naphthalene proceeds with unusual efficiency to give a high yield of fluoranthene under a wide variety of conditions, while 1-(*o*-iodophenyl)naphthalene gives a variety of rearrangement and solvolytic products but virtually no fluoranthene. The bromo derivative exhibits intermediate behavior. The above chloro compound produces fluoranthene in somewhat better yield and quantum yield in more polar solvents. Treatment of the iodo compound with thermally generated phenyl radicals produces substantial quantities of fluoranthene. 1-(*o*-Iodophenyl)naphthalene and 1-iodo-8-phenylnaphthalene are photochemically interconvertible and their chloro and bromo analogs behave similarly. 1-*o*-Chlorophenyl-5-methoxynaphthalene produces only a slightly higher ratio of fluoranthene derivative to other products than does 1-(*o*-chlorophenyl)naphthalene. The results are all consistent with a mechanism where the initial photochemical step is a homolytic cleavage to give an aromatic radical and a halogen atom. The radical may undergo several reactions, but the product distribution is controlled by the reactivity of the halogen coradical.

In contrast to the large number of photocyclization reactions of aromatic compounds which have been found to produce a six-membered ring, reports of five-membered rings formed under these conditions are rare. Linschitz and Grellmann and Bowen and Eland[2] noted the photocyclodehydrogenation of diphenylamines which produced carbazoles. The former group found spectroscopic evidence for a dihydrocarbazole intermediate. Grellmann and Tauer[3] more recently reported several other photolytic heterocyclic ring closures where the newly formed five-membered ring contained six π electrons. Kampmeier and Evans[4] reported a photolytic cyclization reaction of 2-iodo-2′-thiomethoxybiphenyl which resulted in dibenzothiophene formation. Their evidence indicated that the ring-closure step was a nonphotochemical reaction of the photochemically produced radical species.

Reports of photochemical generation of five-membered rings containing five π electrons are even less common. An early study[5] indicated that irradiation of the trityl radical produces 9,9′-diphenyl-9,9′-difluorenyl and triphenylmethane. Badoche[6] found that 9-iodo-10,11,12-triphenyltetracene gave 9,10-*o*-phenylene-11,12-diphenyltetracene, when irradiated. The mechanistic details of these reactions have gone unexplored.

In contrast to the photocyclization of aromatics, five-membered ring formation frequently occurs on irradiation of dienes.[7]

We have examined the photochemical behavior of the 1-(*o*-halophenyl)naphthalenes and related compounds as part of an effort to understand the requirements for photolytic generation of five-membered rings in aromatic systems. Our interest in a detailed study was aroused by the initial observation[1] that 1-(*o*-chlorophenyl)naphthalene photocyclized to fluoranthene in high yield, while 1-(*o*-iodophenyl)naphthalene did not.

Results

Synthesis and Spectroscopy. 1-(*o*-Chlorophenyl)naphthalene (**1**, X = Cl), 1-(*o*-chlorophenyl)-5-methoxynaphthalene (**6**), and 1-(*p*-chlorophenyl)naphthalene were prepared by the method of Johnson and Waters.[8] The bromo and iodo compounds **1** (X = Br and I) were synthesized as described in the Experimental Section. 9-(*o*-Chlorophenyl)anthracene[9] was made by heating a mixture of anthracene, *o*-chloroaniline, and amyl nitrite in benzene.

The compound 1-iodo-8-phenylnaphthalene (**7**) was prepared in several steps from the known 1-bromo-8-nitronaphthalene.[10] Attempts to prepare the analogous chloro and bromo compounds *via* the same route failed.

The ultraviolet absorption spectra were obtained in methanol. The band maxima and their extinction coefficients are reported in Table I. The compounds

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