The electron density maps are presented in Figures 5 and 6. The overall charge distributions in the fluorine–nitrogen and fluorine–oxygen bond regions of FNO and FON are somewhat similar, as are the densities in the nitrogen–oxygen bond regions. From the electron density maps, it is also observed, as was pointed out by Peyerimhoff and Buenker[17] for FNO, that both isomers appear to be molecules in which the fluorine atoms and the nitric oxide group retain a large measure of their individual identities. Surmising from the similarity of the population analyses of the fluorine and hydrogen derivatives that the bonding in F(NO) is primarily covalent, this result is then suggestive of a rather weak bond between fluorine and nitric oxide in both isomeric configurations. Peyerimhoff and Buenker noted that such a bonding description of FNO is supported by its rather long fluorine–nitrogen bond length; we see that this description seems also to apply to FON, whose calculated fluorine–oxygen bond length is ~0.1 Å longer than the anticipated value.[19] Parenthetically, it should be noted that Peyerimhoff and Buenker ascribed the molecular stability of FNO primarily to its highest occupied molecular orbital; however, our population analysis indicates that FNO's stability is due to a net contribution of several molecular orbitals and, in fact, the highest occupied orbital is predicted to be slightly fluorine–nitrogen antibonding. The same trend is observed for FON.

Acknowledgments. The computational aspects of this work were carried out in the computer center of the University of Connecticut which in part is supported by Grant No. GP-1819 from the National Science Foundation. One of the authors (J. P.) wishes to thank the National Science Foundation for fellowship support.

(19) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 229.

Analysis of Qualitative Theories for Electrocyclic Transformations Based on the Results of *Ab Initio* Self-Consistent-Field and Configuration-Interaction Calculations

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Abstract: Analysis of the conservation of orbital symmetry principle of Woodward and Hoffmann shows it to rest upon the implied agreement between the *signs* of differences in total and certain critical orbital energies calculated for two different rotational modes of a given electrocyclic transformation; emphasis is placed on the fact that the theory does not require exact equality between the two energy differences. In addition, it is pointed out that evaluation of the pertinent energy quantities should be made over the respective minimum-energy reaction paths for each rotational mode; in the case of the cyclobutene–*cis*-butadiene transformation SCF and CI calculations indicate, for example, that the rotational phase of the reaction is initiated only after an expanded cyclobutene structure has been formed and then continues to completion before further significant increase in terminal CC bond distance occurs. Very good agreement is found to exist between differences in total and critical orbital energies for the dis- and conrotatory modes in the aforementioned C_4H_6 isomerization when evaluated over the indicated reaction paths, and *nowhere* in these calculations or those of Clark and Armstrong for $C_3H_5^{\pm}$ systems is a violation of the requirement for equal signs of the two types of energy differences found, thereby substantiating the validity of the assumptions of the conservation of orbital symmetry principle, at least for the thermochemical processes. A similar stepwise mechanism for the photochemically induced isomerization of cyclobutene and *cis*-butadiene is suggested by additional calculations, and it is pointed out that for the prerotation conformations of the lowest excited states of these systems orbital symmetry is conserved for *both* rotational modes; prediction of the preferred rotational mode in this case is thus shown to be based on a secondary effect introduced by taking account of the role of configuration interaction in the description of these processes. General circumstances for which the aforementioned qualitative theory may be expected to lead to incorrect predictions are also discussed.

In a previous paper[1] the potential surface involved in the thermochemically induced electrocyclic transformation between *cis*-butadiene and cyclobutene was investigated in detail by means of *ab initio* SCF and CI calculations employing a moderately large AO basis set. This work has indicated that the particular isomerization reaction in question, and quite likely many others related to it, proceeds *via* a stepwise mechanism in which rotation of the methylene groups, in either the con- or the disrotatory mode, occurs only after an intermediate (not necessarily stable) structure with a partially destroyed ring of carbons has been formed. The key point in these findings is that the rotational phase of the reaction is not initiated until CC stretch (or contraction in the case of the open-chain isomer) deformation of the equilibrium form of the

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* Address correspondence to this author at the University of Nebraska.

(1) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, 93, 2117 (1971); hereafter referred to as part I.

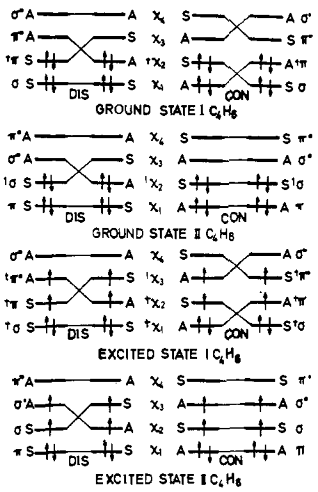

Figure 1. Orbital correlation diagrams for various electronic configurations of cyclobutene and *cis*-butadiene. In the figure, critical MO's are denoted by a dagger. Note that the only difference between the ground state I and ground state II cases (and also between the two excited states) is in their respective orbital energy orders for the cyclobutene geometry.

reactant species has taken place. These conclusions have been reached by calculation of the total energy of the system under systematic variation of the critical geometrical parameters.

The objective of the present paper is to discuss of what assistance the detailed information concerning the specific reaction surface for the electrocyclic transformation between cyclobutene and *cis*-butadiene can be for the understanding of existing qualitative theories[2-5] which predict the stereochemical course in such isomerization reactions in general; it will be of particular interest to see how the (calculated) stepwise mechanism bears on this question. Among the qualitative hypotheses to be investigated will be that of Woodward and Hoffmann[2] which states that the highest occupied orbital of the open-chain partner uniquely determines the preferred mode of rotation in electrocyclic transformations; the extension of this idea known as the conservation of orbital symmetry principle will also be discussed.

The method employed to investigate these questions involves examination of the aforementioned calculated results for cyclobutene and *cis*-butadiene, with particular emphasis on charge-density and orbital-energy data, since these properties play an important role in existing qualitative theories. In addition, previous calculations[6] on the allyl–cyclopropyl $C_3H_5^+$ systems, also capable of undergoing mutual electrocyclic transformations, will be considered in order to obtain a more general evaluation. Finally, although all the calculations discussed above are for the ground state only, attention will also be given to the reaction mechanism and functioning of qualitative theories relative to photochemical processes involving excited states of the aforementioned systems.

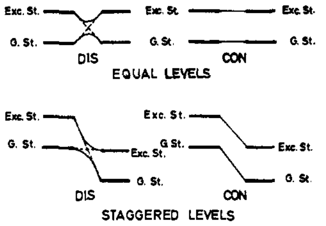

Figure 2. Schematic electronic state correlation diagrams showing different effects of CI treatments. The dotted connecting lines in the figure correspond to SCF results, the solid to CI data.

Relationship between Qualitative Theory and Quantitative Calculation

(A) Definition of Critical Orbital. Originally it was proposed by Woodward and Hoffmann[2] that prediction of the preferred rotational mode in a given electrocyclic transformation is possible strictly on the basis of whether the highest occupied MO of the open-chain isomer is bonding or antibonding between the terminal carbon atoms. At least three objections to the validity of such a simple hypothesis present themselves, however. First of all, emphasis on a property of the open-chain partner, to the exclusion of considerations of the ringed system, seems inconsistent with the known reversibility of such reactions; thus, while the highest occupied MO in *cis*-butadiene is indeed antibonding between the terminal carbons, the opposite is true for cyclobutene, whose least stable occupied MO is the π orbital, clearly a bonding species, albeit practically nonbonding between the termini.

The second objection is more technical in nature and revolves around certain ambiguities encountered in *plotting* the highest occupied orbital energy as a function of the rotational angle θ, at least as long as the Hartree–Fock method is employed in the calculations. The difficulty arises because the orbital in question (for C_4H_6) correlates with an *occupied* MO of cyclobutene if the reaction proceeds in the experimentally preferred conrotatory mode, but with an *unoccupied* species for the disrotatory process; the well-known overestimation of the energy gap between occupied and unoccupied MO's in the Hartree–Fock method thus leaves it open to question which of several possible orbital energy plots is most consistently associated with that referred to in the qualitative theory.

Finally, the suggestion that only *one* orbital is actually critical in determining the course of such a complex reaction, involving systems with many more than one pair of electrons, clearly requires some quantitative verification, whether reference is made to the highest occupied MO of the open-chain isomer or to any other single species, whatever its characteristics. The other orbital energy terms, not to mention the nuclear and electronic repulsion contributions to the total molecular energy, are too large and complex to be ignored without some sort of *a priori* justification.

Yet the empirical observations demonstrate that almost without exception the foregoing "one-orbital" theory does indeed predict the correct stereochemical route for electrocyclic transformations. Closer examination of the subject shows, however, that it is only coincidental that the critical or reaction-determining MO is the highest occupied species. Its distinctive

(2) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

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

(4) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

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

(6) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).

characteristics lie rather in the fact, as brought out by Longuet-Higgins and Abrahamson[3] and by Woodward and Hoffmann[4,5] in their formulation of the conservation of orbital symmetry principle, that it correlates with an occupied MO of the other isomer in the stereospecifically preferred case, but with an unoccupied species for the unpreferred mode; more generally, in the fact that its orbital occupation merely is altered during the transformation in one of the modes but not in the other. It is intuitively quite reasonable then to expect that the process in which a given MO remains occupied throughout the reaction is energetically preferred to one in which the same orbital is converted continuously into an unoccupied species.

Defining the reaction-determining characteristics of the critical orbital in this manner not only establishes the one-orbital theory on firmer energetic grounds, but also removes the objections raised against the former definition with respect to its apparent disregard for the inherent reversibility of electrocyclic transformations; the latter point is emphasized in the sample correlation diagrams of Figure 1. In these examples it is seen that the critical property is exhibited equally well by MO's of the ringed system as by those of the open-chain isomer. Furthermore, it is not at all remarkable that MO's with the critical property are generally the highest occupied species (for both products); there is, however, nothing in principle which prevents a situation in which the highest occupied MO does not possess the critical characteristic, while some other orbital does. The examples of Figure 1 demonstrate that in a given case there may be more than one MO in the reaction-determining category; also, that there may be none at all.

Of course all of this argumentation contains nothing which is essentially different from the considerations of the conservation of orbital symmetry principle, but rather merely places emphasis on the fact that it too is basically a one-orbital theory. Thus, while it overcomes the first two objections by incorporating reversibility and correlation properties of the critical MO (or MO's) in its formulation, it still requires quantitative justification of its apparent disregard of energy terms other than the critical orbital energy. In addition, its prevailing emphasis on the equilibrium values of the orbital energies in question is not obviously consistent with the result of the aforementioned *ab initio* calculations which indicate, at least for the prototype cyclobutene-*cis*-butadiene reaction, that actual rotation occurs only for structures well removed from either of the equilibrium forms. Clearly, each of these questions is worthy of further examination, with particular reference to existing quantitative calculations.

(B) Relation between Critical MO Energy and Total Energy. The rigorously correct method of determining whether the disrotatory or the conrotatory mode is favored in a given process utilizes of course a comparison of the total energies of the system in question in various nuclear conformations. For practical reasons, theoretical treatments must rely upon total energy values other than the *exact* energies; in the treatment that follows the total energy is assumed to be obtained in two steps, by first carrying out an SCF calculation solving the Hartree–Fock equations, and secondly by following this result with a configuration-interaction (CI) calculation. The existence of a critical MO actually makes the CI method indispensable in the treatment of the less favorable rotational mode, as has been pointed out by Longuet-Higgins and Abrahamson.[3]

Formally a convenient energy expression[7-9] for the SCF part of the treatment is

$$E_{\mathrm{SCF}} = \sum_i N_i \epsilon_i + V_{\mathrm{N}} - E_{\mathrm{rep}} \qquad (1)$$

where ϵ_i is the canonical orbital energy of the ith MO, N_i its occupation number, V_{N} the nuclear repulsion, and E_{rep} the total electronic repulsion. The total energy E_{T} is then defined as

$$E_{\mathrm{T}} = E_{\mathrm{SCF}} + E_{\mathrm{CI}} \qquad (2)$$

where E_{CI} is the energy *lowering* relative to the SCF value obtained by introducing the CI; it is an inherently negative quantity according to the variation principle, since the SCF wave function is the leading term in the CI expansion.

Since the qualitative theories place emphasis on the critical orbital, with its distinguishing correlation property, it is useful to separate out the energy contribution of this species and rewrite eq 2 in the following manner

$$E_{\mathrm{T}} = \sum_{\mathrm{c}} N_{\mathrm{c}} \epsilon_{\mathrm{c}} + E' + E_{\mathrm{CI}} \qquad (2')$$

where the sum is only over critical MO's (normally, of course, the sum contains but one term) and E' is simply the sum of the remaining terms in E_{SCF} as defined in eq 1. Finally, since prediction of the preferred stereochemical process is always based on a *comparison* of the total energies for the two (or more) possible rotational modes, only *differences* for the various quantities in eq 2′ between modes are of real interest; hence, another expression which calls attention to the energy differences ΔE is

$$\Delta E_{\mathrm{T}} = \Delta \sum_{\mathrm{c}} N_{\mathrm{c}} \epsilon_{\mathrm{c}} + \Delta E' + \Delta E_{\mathrm{CI}} \qquad (3)$$

Ordinarily, the sign of ΔE_{T} does not change with variation of the rotational angle θ, *i.e.*, one mode of transformation is energetically preferred over the entire region; more generally, however, that process is favored which possesses the lower energy maximum (potential barrier) for the rotational potential surface. The energy differences in eq 3 must be evaluated over the respective *minimum-energy* reaction surfaces for each rotational mode; evaluation over higher energy paths can lead to a prediction of an erroneous sign for ΔE_{T}.

In order for a "critical-orbital theory" to predict the preferred rotational mode in a given electrocyclic transformation, it is only necessary that the sign of $\Delta\epsilon_{\mathrm{c}}$ (or the sum thereof in the general case) be the same as that of ΔE_{T} over the required range of θ; it is not necessary, however, that the difference in total energies be *equal* to $\Delta\Sigma_{\mathrm{c}} N_{\mathrm{c}} \epsilon_{\mathrm{c}}$. The sign of $\Delta\epsilon_{\mathrm{c}} = \epsilon_{\mathrm{c}}(\mathrm{dis}) - \epsilon_{\mathrm{c}}(\mathrm{con})$ is generally quite simply predicted; from the definition of the critical orbital, it is clear that the preferred mode is that for which correlation is with an occupied MO of the other isomer rather than with an unoccupied species of this structure (in accordance with the conservation of orbital symmetry principle).

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(7) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill, New York, N. Y., 1963.

(8) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, 45, 3682 (1966).

(9) S. D. Peyerimhoff and R. J. Buenker, *ibid.*, 47, 1953 (1967).

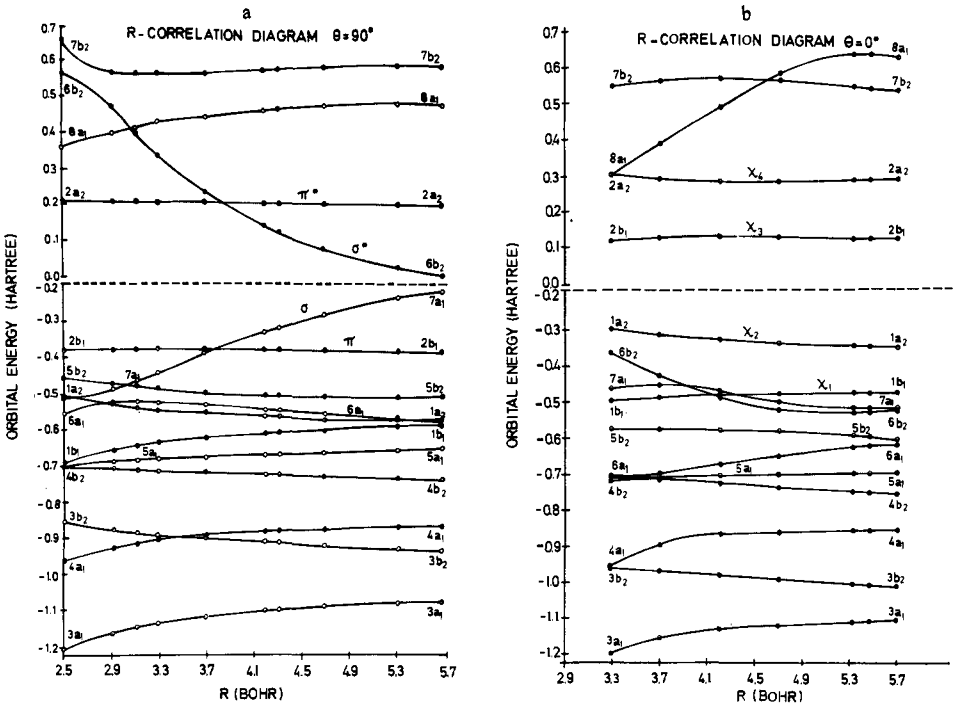

Figure 3. Variation of orbital energies with the terminal CC bond distance R for C_4H_6 conformations having $\theta = 90°$, perpendicular CH_2 groups (a) and $\theta = 0°$, planar CH_2 groups (b).

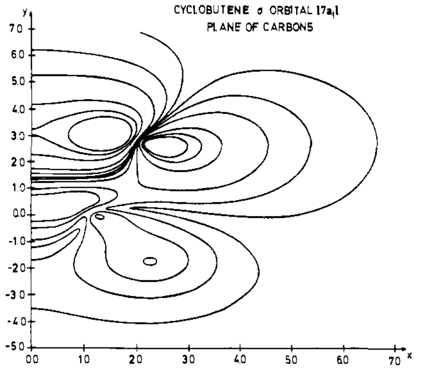

Figure 4. Charge-density contours for the $7a_1(\sigma)$MO of cyclobutene in the plane of the carbon atoms; there is reflection symmetry across the y axis. The carbon atoms in the figure are located at (1.26, 0.0) and (2.1, 2.75), respectively (not the equilibrium conformation).

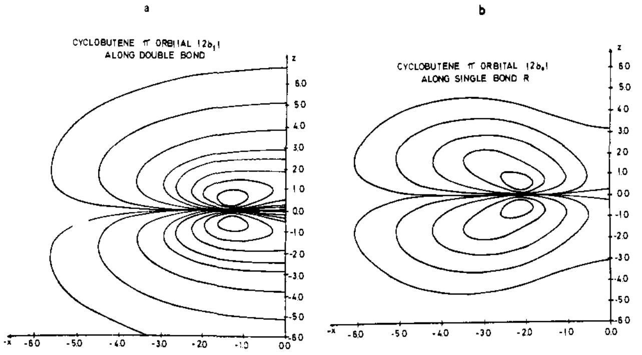

Figure 5. Charge-density contours for the $2b_1(\pi)$ MO of cyclobutene in planes containing the CC double bond (a) and the terminal CC bond R (b).

The other terms in eq 3 are clearly nonvanishing in the general case; indeed, the sign of ΔE_{CI} is almost certain to be opposite to that of the critical-orbital energy difference, since the CI treatment invariably is more effective for the unpreferred rotational mode whose SCF potential curve consists of two distinct branches.[1,3] Ordinarily, the absolute magnitude of ΔE_{CI} will be considerably smaller than that of $\Delta\Sigma_c N_c \epsilon_c$, so that the latter term of the two still determines the sign of their sum. This circumstance has in fact been assumed in the treatment of Longuet-Higgins and Abrahamson but, as can be seen from Figure 2, counterexamples for this behavior are possible, particularly if the energy levels of one reactant are substantially higher than those of the other. Especially when the effect of $\Delta E'$ is also taken into account, it is not out of the question that these considerations could cause the qualitative theory to incorrectly predict the preferred rotational mode. The effect of $\Delta E'$ in turn is not at all as subject to generalization as those of the other energy differences in eq 3 and thus will be considered in the context of the calculated results obtained for specific systems.

Quantitative Results for the Thermochemical Process

Since the calculated data have indicated that either the cyclobutene ring is partially destroyed (the terminal CC distances R increase by roughly 1.5 bohrs) or the chain of carbons in *cis*-butadiene is partially closed (R decreases by about 1.0 bohr relative to its equilibrium value) before rotation of the methylene groups is actually initiated, consideration should be given to the variation of orbital energies with R. This information is contained in Figures 3a, b for $\theta = 90°$ (perpendicular CH_2 groups) and $\theta = 0°$ (planar CH_2 groups), respectively; details of the other geometrical parameter values for which these data have been calculated are contained in part I.

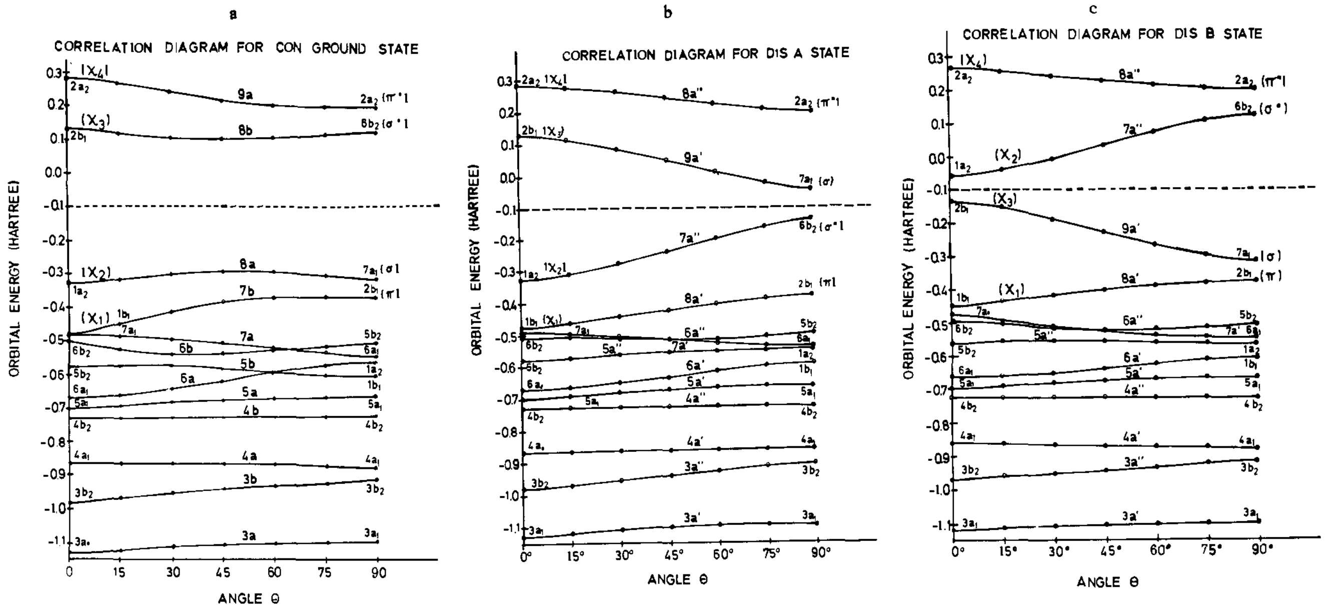

Figure 6. Variation of orbital energies with the rotation angle θ (with R held fixed at the prerotation point) in (a) the ground state for conrotation, (b) the dis-A, and (c) the dis-B states for disrotation.

The higher stability of the $\sigma(7a_1)$ MO at small distances arises from its strongly bonding character along R, as can be seen from its calculated charge-density contours contained in Figure 4; the contours for the $\sigma^*(6b_2)$ species at 90° show it to be strongly antibonding along R, hence the opposite behavior in its energy curve. Both of these orbitals are localized along the R bond, although clearly not completely so.[5] More detailed discussion of these and other MO's of general C_4H_n systems can be found in earlier work.[10] By contrast, the orbital energies of the π and π^* MO's for the 90° structure, and of all π orbitals ($\chi_1 - \chi_4$) of the 0° species, are relatively independent of R. In the case of the π and π^* orbitals, the explanation for this behavior clearly rests on the localization of these MO's along the CC double bond of cyclobutene. The charge-density contours of the $\pi(2b_1)$ MO contained in Figures 5a, b along the double bond and R, respectively, emphasize, however, that the localization is not complete for the π orbitals either, a fact which is reflected somewhat in Figure 3a.

The most important consequence of the behavior of the various orbital energies with variation of R is the change in order which occurs for the 90° structure with expansion of its ring of carbons. Specifically, the order is different for the prerotation conformation (R = 4.32 bohrs, SCF result) than for the equilibrium structure (R = 2.92 bohrs); both the π and σ, and π^* and σ^* pairs are interchanged during the conversion between these two structures. This result does not affect the application of the conservation of orbital symmetry principle to the *ground-state* case because there is no accompanying change in total electronic configuration (*i.e.*, there is no interchange between occupied and unoccupied species) and thus there is no essential distinction in the two ground-state correlation diagrams of Figure 1. As pointed out earlier by Feler,[11] however, the change in orbital energy order may affect the excited-state interpretation.

Variation of orbital energies with the rotational angle θ for the con- and disrotatory modes is shown in Figures 6a–c; these data are calculated at the prerotation value of R, as discussed in part I. Two figures are necessary for the disrotatory transformation mode because of the change in ground-state electronic configuration which occurs as θ varies from 0 to 90°. In the dis-A case (Figure 6b), the critical MO is $\chi_2(1a_2)$ at 0°, which correlates in the conrotatory mode with 8a (ultimately denoted by $7a_1$ or σ at 90°) but with 7a'' in the disrotatory process (correlating with $6b_2$ or σ^* at 90°). For dis-B (Figure 6c), the critical MO is $7a_1(\sigma)$ at 90°, correlating again with 8a and $1a_2(\chi_2)$ in the conrotatory mode, but with 9a' and $2b_1(\chi_3)$ under disrotation (see Figure 1, ground state II case). In Figure 6a it can be seen that the critical orbital energy (8a) is relatively independent of θ, but in Figures 6b, c the corresponding quantities (for 7a'' and 9a', respectively) are found to increase rather sharply from their minimum values; consequently, the critical orbital is responsible for a definite tendency favoring conrotation.

The more quantitative aspects of these results and how they relate to eq 3 can be depicted by plotting $N_c\Delta\epsilon_c$ as a function of the rotation angle θ for comparison with the analogous data for $\Delta E_{\mathrm{SCF}} = \Delta E_{\mathrm{T}} - \Delta E_{\mathrm{CI}}$ and $\Delta E'$ (Figure 7). Two sets of curves, dis-A and dis-B, are necessary in order to compare the conrotatory data with those of each of the disrotatory states. From this figure it is clear that the ΔE_{SCF} curve is approximated quite closely by the corresponding $N_c\Delta\epsilon_c$ result; $\Delta E'$ is of opposite sign to $N_c\Delta\epsilon_c$ at every point of the rotation, but considerably smaller in absolute magnitude. Thus the one-orbital quantity $N_c\Delta\epsilon_c$ determines the sign of ΔE_{SCF}, and the quantitative agreement between the two curves in the calculations for cyclobutene and *cis*-butadiene is actually much better than would be required to ensure the success of the qualitative theory.[12]

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(10) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, 48, 354 (1968).

(11) G. Feler, *Theor. Chim. Acta*, 12, 412 (1968).

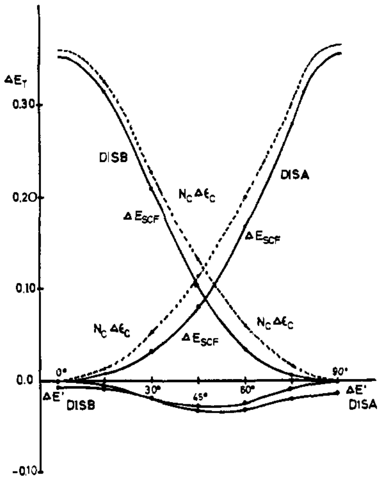

Figure 7. Variation of energy differences as defined in eq 3, comparing dis-A and dis-B data with corresponding results for the conrotatory ground state. (Note that the differences at 0° vanish only in the dis-A comparison, while those at 90° do so only for the dis-B results.) For coordinates employed see Table IV of part I.

A similar analysis has been made by Clark and Armstrong[13] with respect to their results for the $C_3H_5^\pm$ electrocyclic transformation but, interestingly enough, these authors have reached a far different conclusion in their work, namely that $N_c\Delta\epsilon_c$ is not closely related to ΔE_{SCF}. In examining their arguments, however, two points should be noted. First, in spite of their negative conclusion, nowhere in their calculated results is it found that $\Delta\epsilon_c$ is opposite in sign to that of ΔE_{SCF}. Granted, the quantitative agreement between $2\Delta\epsilon_c$ and the difference in total SCF energy is not as good as has been found in the present C_4H_6 data (Figure 7) for the analogous comparison, but, as has been pointed out in part B of the previous section, the only criterion which may be validly considered in assessing the reliability of the conservation of orbital symmetry principle is the agreement between *signs* of the two energy differences, a relationship which is of course much more easily satisfied than that of exact equality. The sign of the difference for the sum of *all* occupied energies has been shown to be different from that of ΔE_{SCF} in numerous comparisons for $C_3H_5^-$, emphasizing quite strongly that $N_c\Delta\epsilon_c$ is the proper quantity to employ in the qualitative theory.

The second point to be made with respect to Clark and Armstrong's refutation of the qualitative "one-orbital" theory is that the quantitative calculations employed in their work have assumed a linear (not stepwise) reaction mechanism for the $C_3H_5^\pm$ systems. Examination of Figure 2 of ref 6, which shows the allyl ion ground-state potential curve intersecting with that of the cyclopropyl cation counterpart for a CCC angle of roughly 90°, suggests that the conditions accompanying the $C_3H_5^\pm$ transformations are quite comparable to those found in the C_4H_6 process. It thus seems very probable that the actual rotation in these reactions also occurs over a narrow range of the CC terminal bond distance; since the conservation of orbital symmetry principle need only be valid over the true reaction path or a good approximation thereof, observations relative to another path may be misleading.

A third remark in this connection concerns the significance Clark and Armstrong have attached to the inner-shell orbital energies in their analysis, since these quantities are observed to vary rather sharply with rotation of the methylene groups. For an adequate evaluation of the significance of these changes, however, it must be kept in mind that the inner-shell *orbitals themselves* are, for all practical purposes, independent of the rotational angle,[14] and thus any change in their orbital energies can only be a reflection of changes in the *valence* charge distribution; indeed, relatively large changes in inner-shell orbital energies are to be expected (from the one-orbital theory) because of the changes in certain (critical) valence MO's occurring during the electrocyclic transformation. It is also of interest that the variation of 1s orbital energies invariably is found to be opposite in direction to that of the $V_N - E_{rep}$ term in E_{SCF} (see eq 1).[15] Because of this cancellation and the practical dilemma of predicting even qualitatively the direction of change in the 1s orbital energies, there seems to be no question that the most satisfactory partitioning of the total energy for purposes of developing a qualitative theory is indeed that of eq 3, gathering such unwieldly quantities as core orbital energies and total electronic repulsion into one term, denoted herein by E', and concentrating instead on the orbital energies of the critical MO's.

In summary then, all the quantitative calculations at hand find that $\Delta E'$, though certainly not of vanishing magnitude, is a minor term in the equation for ΔE_T; the criterion for the validity of the conservation of orbital symmetry, namely that the sign of $N_c\Delta\epsilon_c$ (or sum thereof if there is more than one critical MO) is everywhere the same as that of ΔE_T in eq 3, holds in every case. Nevertheless, the $\Delta E'$ term *can* lead to erroneous predictions on the part of the qualitative theory (as also can ΔE_{CI}), especially in cases where there are no critical orbitals (Figure 1, excited state II case) or even where there are two or more such species with conflicting tendencies.[16]

Photochemical Process

The photochemical mechanism for the electrocyclic transformation of cyclobutene and butadiene appears to be much more complicated than that of the corresponding thermochemical process. Different products in widely varying quantum yields are known to result,

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(12) The SCF method greatly overestimates the difference between the disrotatory and conrotatory barrier heights; the CI method is necessary to greatly reduce this discrepancy. In part I, the magnitude of the barrier in the conrotatory mode has been calculated (with CI) to be 1.95 eV, 0.59 eV lower than the corresponding value for disrotation (calculated with respect to the cyclobutene equilibrium conformation) as compared to an experimental value of approximately 1.4 eV.

(13) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 13, 3651 (1969); 14, 370 (1969).

(14) Detailed evidence for this statement has been reported with regard to F_2O and O_3 calculations[8,9] and has also been observed in $C_3H_5^\pm$ studies.[6]

(15) Such cancellation effects have been observed without major exception in all calculations in this laboratory; they are also found to exist in the data of Clark and Armstrong, and are in fact supported by a more general analysis of the factors involved.[8]

(16) In this connection the examples of Li_2O and LiOH[8] relative to the functioning of Walsh's rules[17] are certainly applicable; in these cases the $V_N - E_{rep}$ term varies unusually strongly because of the ionic character of these systems and, as a result, despite the fact that they possess the same number of valence electrons as does water, they are known to possess linear equilibrium geometries.[18,19]

(17) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

(18) A. Büchler, J. Stauffer, W. Klemperer, and L. Wharton, *J. Chem. Phys.*, 39, 2299 (1963).

(19) D. White, K. S. Seshadri, D. F. Deves, D. E. Mann, and M. J. Leneusky, *ibid.*, 39, 2463 (1963).

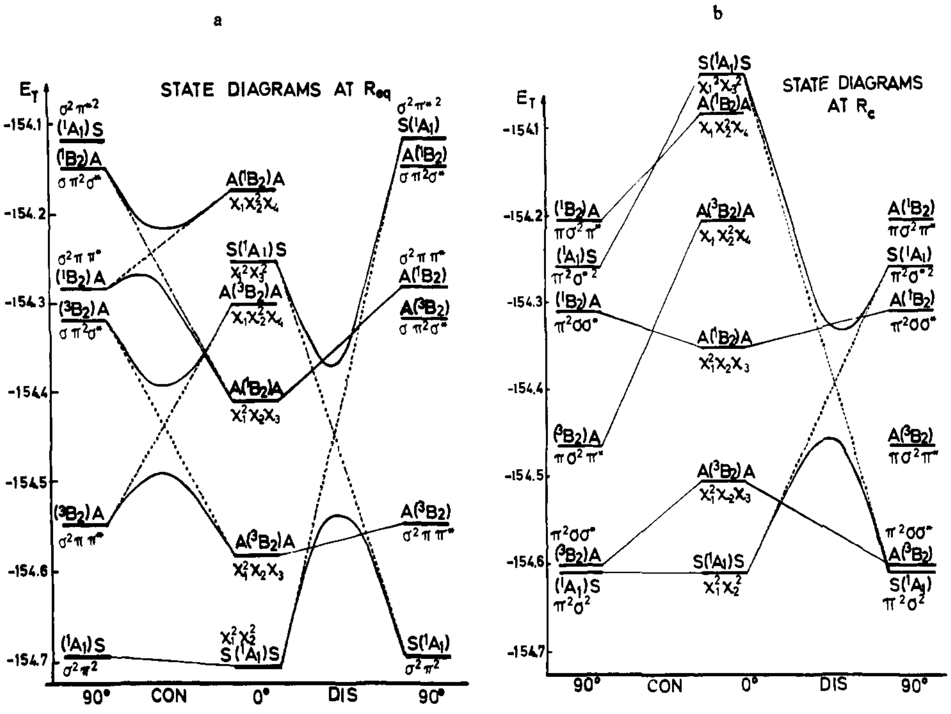

Figure 8. Electronic state correlation diagrams for various low-energy species of cyclobutene and *cis*-butadiene for (a) their respective equilibrium conformations and (b) their respective associated prerotation conformations. (In each case various $^3A_2$ and $^1A_2$ states are omitted for clarity even though they are sometimes lower in energy than certain of the species shown explicitly in the figures.)

depending on the specific experimental conditions[20,21] accompanying the reaction, and various mechanisms, not all of which are consistent with the Woodward–Hoffmann scheme (which postulates direct conversion between corresponding *excited electronic* states of each system), have been invoked to explain these data.[20,22,23] The direct vapor-phase photolysis is generally believed to involve the first excited singlet of butadiene, but not that of cyclobutene.[20,22,23] A recent four-electron valence-bond calculation by van der Lugt and Oosterhoff,[24] on the other hand, has led to the prediction that the *second* excited singlet of butadiene results from the initial excitation; at the same time, participation of triplet states (either the first or the second) cannot be entirely ruled out on the basis of present experimental evidence, although such species are generally thought to play a role only in sensitized processes.

Since the main objective of the present study is to utilize existing quantitative data for the evaluation of the conservation of orbital symmetry principle, in what follows attention will be restricted to photochemical mechanisms which are consistent with this general scheme. At present, such data are more readily accessible for triplet excited states (with comparable accuracy to that obtained for the ground state) than for singlets,[25] and thus discussion will be further restricted to triplet species, especially since there is good reason to expect that the potential surface for a given excited singlet will be nearly parallel to that of its corresponding triplet. In particular, the following analysis is centered upon the effect a stepwise mechanism has on the application of the conservation of orbital symmetry principle in this case; the mechanism in question may of course be different from that actually operative in the direct photolysis, and this matter clearly requires further investigation.

The change in orbital stability order for the 90° structures upon *R* stretch (Figure 3a) apparently has a major effect with respect to a process involving the lowest excited states of these systems, although it does not alter the overall prediction of the qualitative theory for the ground-state species; the significance of this phenomenon with regard to the conservation of orbital symmetry principle can perhaps be best understood with reference to the electronic state correlation diagrams given in Figures 8a, b for the equilibrium and prerotation structures, respectively. For the equilibrium structures (Figure 8a), one finds the same correlation pattern as that described earlier by Longuet-Higgins and Abrahamson,[3] with the first SCF excited states crossing in the conrotatory mode but not in the disrotatory process (the corresponding orbital correlation diagram is that of excited state I in Figure 1). The extraordinarily large splitting found to exist between corresponding triplet and singlet states is an interesting quantitative aspect of Figures 8a, b, especially since in the usual qualitative treatment, as in ref 3, no distinction based on the multiplicity of states is taken into account. For the prerotation conformations (Figure 8b), the lowest two $^3B_2$ states switch positions, thereby leading to a situation in which there is no crossing of the lowest triplet states for either reaction mode; hence, no critical MO can be identified (as pointed out schemati-

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(25) From experience with ethylene, it appears that addition of diffuse functions to the AO basis set is necessary for a reliable description of the $\pi \rightarrow \pi^*$ excited singlet states.

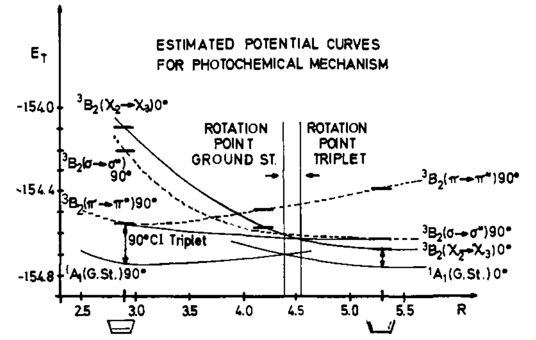

Figure 9. Estimated SCF and CI potential curves for the lowest lying triplets (as well as the corresponding CI ground states) of the C_4H_6 systems for R stretch for both $\theta = 90°$ and $\theta = 0°$. (The crossing points of corresponding 0° and 90° potential curves are associated in the figure with the values of R for which the rotational phase of various electrocyclic processes occurs.)

cally in the excited state II diagram in Figure 1) and no prediction either way of the preferred direction of rotation is forthcoming from application of the qualitative theory. The question thus presents itself as to which of the two state correlation diagrams in Figures 8a, b corresponds to the experimental conditions; indeed, it is not immediately clear that either diagram represents the real situation, since the calculations on which they are based employ only optimum geometrical parameters for the *ground state*, which likely differ significantly from the corresponding values for the excited states. In determining the reaction mechanism and/or the reaction path for the photochemical process, it is thus once again necessary to know the details of the potential surfaces of the C_4H_6 systems, in this case in their excited states.

Although a complete set of the necessary calculations has not yet been carried out, the data of Figures 8a, b plus those of some additional exploratory calculations allow for the construction of a useful estimate of what the lowest geometrically optimized potential curves look like, at least for the lowest energy $^3B_2$ species; this information is contained in Figure 9. The most interesting feature of this plot is the crossing of the two 90° $^3B_2$ potential curves at approximately $R = 3.7$ bohrs. Since the two corresponding SCF states ($\pi \to \pi^*$ and $\sigma \to \sigma^*$, respectively) possess the same symmetry, it is clear that once again CI is necessary before a satisfactory representation of the lowest 90° triplet is possible. An estimated $^3B_2$ CI potential curve (shown as a solid line in Figure 9) is therefore also included in the diagram.

The resulting 90° CI curve intersects in turn with the potential curve of the lowest 0° triplet. Comparison with the corresponding ground-state data shows that if the excited-state data are at least qualitatively correct, one would also expect a stepwise mechanism in this photochemical process. Again, as in the ground-state case, large energy separation between the 90 and 0° structures at most values of R seems to prevent any methylene rotation from occurring until a terminal bond distance in the neighborhood of 4.5 bohrs, the crossing point of the estimated optimal 0 and 90° potential curves, is attained by the system, in which case rotation can proceed with relative ease.

In spite of the lack of quantitative data for all curves in Figure 9, some consequences with respect to the theory of photochemically induced electrocyclic transformations can be drawn from those aspects of the figure which appear to be at least qualitatively correct. It seems clear, for example, that the prescriptions of the conservation of orbital symmetry principle can be meaningfully applied only for structures possessing values of R in the neighborhood of the crossing point in Figure 9. Under these conditions, however, it would appear that the excited state II diagram of Figure 1 (corresponding to the electronic state diagram of Figure 8b) is more pertinent than its equilibrium counterpart, but, as noted by Feler,[10] in this case the qualitative theory is incapable of predicting the preferred mode of rotation.

The experimental data indicate that the photochemical (unsensitized) process is also stereospecific, with the disrotatory mode being favored. The most plausible explanation for this behavior, which is still consistent with Figure 9, merely takes account of the fact that the 90° wave function at the crossing point is neither purely a $\sigma \to \sigma^*$ species nor a $\pi \to \pi^*$ species, but rather a CI mixture of both. In this case, both sets of rules are simultaneously operative, weighted in rough proportion to the squares of the respective CI expansion coefficients. Consequently, despite the fact that correlation with the $\sigma \to \sigma^*$ excited state leads to *no* conclusion on the basis of the qualitative theory, the secondary influence of the 90° $\pi \to \pi^*$ state does lead to the prediction of preferred disrotation, in agreement with experiment.

Conclusions

The conservation of orbital symmetry principle predicts differences in *total energies* for two different reaction modes on the basis of the corresponding differences between certain *critical orbital energies*. The definition of these reaction-determining MO's in turn, which specifies that such a species correlate with an occupied MO of the product of the transformation in the preferred rotational process but with an unoccupied orbital in the other, allows for a straightforward prediction of the *sign* of their orbital energy difference. Since the choice of the experimental process actually followed in a given reaction is ultimately based on the total energy difference, the conservation or orbital symmetry principle can be said to rest on the assumption that the signs of these two energy differences are the same; clearly, it does not require that the quantities themselves be equal. The results of calculations on cyclobutene and *cis*-butadiene in both ground and excited states, plus those of Clark and Armstrong for the $C_3H_5^+$ systems, suggest strongly that this relationship between signs of energy differences, although clearly not required by the exact quantum-mechanical theory, can be expected to hold extremely well in practice. Nevertheless, additional energy terms such as other orbital energies, the nuclear and electronic repulsion, and the CI lowering relative to the SCF result obviously could produce an exception to the rule in a given case, especially since the CI energy difference is virtually certain to be of opposite sign to that of the critical orbital energy difference.

In spite of these considerations, the observed agreement between the differences in total and critical orbital energies does not in itself guarantee the success of the qualitative theory, for it is still necessary to obtain these theoretical quantities for the *reaction path actually followed* in a given process. Calculating these results over higher energy paths can and has led to prediction of a different stereochemical route than that favored experimentally; clearly, only energy comparisons for the minimum-energy paths available to each rotational mode are of experimental consequence. Examples of the importance of this point can be found in the present C_4H_6 calculations, which have indicated that the actual rotation in this isomerization occurs only over a very narrow range of the terminal CC bond distance, that is, for structures with a considerably expanded cyclobutene ring. The effect of taking into account these details of the reaction path is to cause a change in the designation of the critical MO for the 90° structure in the thermochemical process (albeit no change in the prediction of the preferred rotational mode) and, more significantly, to eliminate all critical species for the photochemically induced transformation. Thus, the qualitative theory is seen to be somewhat ambiguous with regard to predictions of the preferred photochemical rotational mode, indicating that the total energy difference between the potential maxima of dis- and conrotatory processes is much smaller in absolute magnitude in the reaction involving the lowest excited states of these systems than for their ground states.

In summary, there seem to be two rather well-defined areas in which one can expect to find that conservation of orbital symmetry is violated. In the first area, exceptions might occur because one product is much more stable than the other; staggered energy levels could well lead to a situation in which the total energy difference does not take its sign from that of the critical orbital energy term. In the second case, exceptions might be expected to arise because a change in electronic configuration occurs as one product is converted into its prerotation conformation; clearly, such situations are not so much exceptions to the qualitative theory as they are evidence of its incorrect application. Acquiring an accurate picture of the reaction mechanisms operative in each type of electrocyclic transformation should all but eliminate such pitfalls, and this objective should therefore be the goal of quantum mechanical calculations in the near future.

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Studies on Diffusion and Diffusion-Controlled Reactions Involving Alkyl Radicals in Solution

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Abstract: The method of photochemical space intermittency (PCSI) has been used to measure diffusion coefficients of propyl, pentyl, dodecyl, and octadecyl radicals in solution. The measured diffusion coefficients are smaller than would have been predicted for the parent hydrocarbons. In combination with the Smoluchowski equation, these diffusion coefficients yield calculated rate constants for radical combination–disproportionation which are in good agreement with experimental values for all but the octadecyl radical. The unusually small diffusion coefficient of the pentyl radical indicates that a certain portion of its lifetime is spent in a state such that its translational mobility is inhibited.

Diffusion coefficients of very reactive species are difficult to determine by classical methods because of the very short lifetimes involved. In fact, it was not until a few years ago that Noyes and his coworkers carried out diffusion measurements on the reactive iodine atom in solution using the method known as photochemical space intermittency (PCSI).[2,3] Apparently the only other reported use of the PCSI method is that of Davies and North,[4] who performed some diffusion measurements on the polystyryl radical in solution.

The diffusive behavior of free radicals in solution is obviously of interest to kineticists concerned with the rates of supposedly diffusion-controlled processes. For instance, conclusions about whether or not certain radical–radical reactions are really diffusion controlled have been necessarily based upon the assumption that the frictional force of a radical species may be calculated using Stokes'[5] law or that a free radical, R·, and its parent, RH, have the same diffusion coefficient in a given medium.[6] It is desirable to test these ideas experimentally.

The PCSI method involves the photochemical production of free radicals in a spatially nonhomogeneous fashion. This may be accomplished by irradiating the reaction mixture through a space-intermittency pattern so that illuminated and dark regions exist in a regular

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