Ab Initio SCF and CI Study of the Electrocyclic Transformations of Cyclopropyl and Allyl Systems

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Abstract: *Ab initio* SCF and CI calculations employing a double ζ Gaussian basis have been carried out to deduce minimum energy surfaces for the electrocyclic transformations of the cyclopropyl cation, radical, and anion respectively to the corresponding allylic species. In each of the symmetry-forbidden interconversions, it is concluded that the ring-opening phase does not occur simultaneously with the actual CH_2 rotation. In the allowed disrotatory process of the cation, the methylene rotation begins very shortly after CC stretch is initiated and thereafter the two types of geometrical changes proceed in a synchronous fashion for virtually the entire reaction. Nevertheless, the calculations indicate that in the allowed (conrotatory) anion interconversion CH_2 rotation and ring opening again occur in well-separated phases, just as in fact was found before for the allowed thermochemical transformation of cyclobutene and butadiene. The different patterns of behavior in this respect are seen to be related to distinctions in the relative stabilities of the various ring compounds. The importance of CI in the calculations for the C_3H_5 systems is much smaller than has been noted in the earlier C_4H_6 study, with the result that the differences in the activation energies of the respective forbidden and allowed processes for both the cation and anion are calculated to be much greater than the corresponding difference in the cyclobutene–butadiene case. Analysis of a number of energy terms for the dis and con modes of the various C_3H_5 transformations suggests that the agreement between total and partial orbital energy sum potential curves is sometimes very poor, an observation which strongly suggests that the conservation of orbital symmetry principle's total reliance on the behavior of a few critical valence MO's in making its predictions can be unwarranted in a given case.

The thermochemical interconversions of the cyclopropyl cation, radical, and anion respectively with the corresponding isomeric allyl systems have been the subject of a great number of theoretical treatments in recent times, principally because the reacting species in question are among the simplest molecules known to participate in this type of electrocyclic process. Although the results of such calculations,[2-7] both semiempirical and *ab initio* alike, are in clear agreement with what is known experimentally regarding the stereospecific courses[8,9] preferred in each allyl–cyclopropyl interconversion, considerable variety is noted in their quantitative predictions regarding activation energies and details of geometrical changes undergone by the reacting species in the course of these processes. Of particular interest is the question of whether the effects of configuration interaction, universally ignored in the aforementioned calculations, are as significant in these cases as they have been found to be in the closely related reaction involving cyclobutene and butadiene, for which the activation energies obtained by single configurational treatments are found to be overestimated by some 50%.[10-12] By the same token, the relevance

of the main geometrical conclusion of the aforementioned C_4H_6 *ab initio* study, namely that the actual rotational phase in this reaction is accomplished with virtually no change in the distance between the carbon termini, is also a matter that requires further investigation for the description of the allyl–cyclopropyl isomerizations. In order to study these and other aspects of the theoretical treatment for such electrocyclic reactions, a rather large series of *ab initio* SCF and CI calculations has thus been carried out for the allyl–cyclopropyl species, with emphasis not only on the degree to which their isomerization reactions fall into a general pattern with other electrocyclic processes but also on specific details which distinguish at least some of these interconversions from their counterparts involving larger molecular systems.

I. Details of the Calculations and Preliminary Geometrical Considerations

The definition of the geometrical parameters to be used in the present study of the various C_3H_5 systems is given in Figure 1. As in previous work with the cyclobutene–butadiene system, the number of such geometrical quantities to be optimized along the various reaction paths is significantly reduced by making the assumption that an effective twofold symmetry is maintained throughout all stages of the isomerization process; in addition all CH bond lengths are held fixed at a normal equilibrium value for such quantities (1.085 Å). Otherwise all the geometrical variables defined in Figure 1 are given explicit consideration in the process of determining the minimum energy paths for the various cyclopropyl–allyl interconversions.

The energy minimizations are done by *ab initio* SCF

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(2) W. Kutzelnigg, *Tetrahedron Lett.*, 49, 4965 (1967).

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(4) (a) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 13, 365 (1969); (b) *ibid.*, 14, 370 (1969).

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(12) K. Hsu, R. J. Buenker, and S. D. Peyerimhoff, *J. Amer. Chem. Soc.*, 94, 5639 (1972).
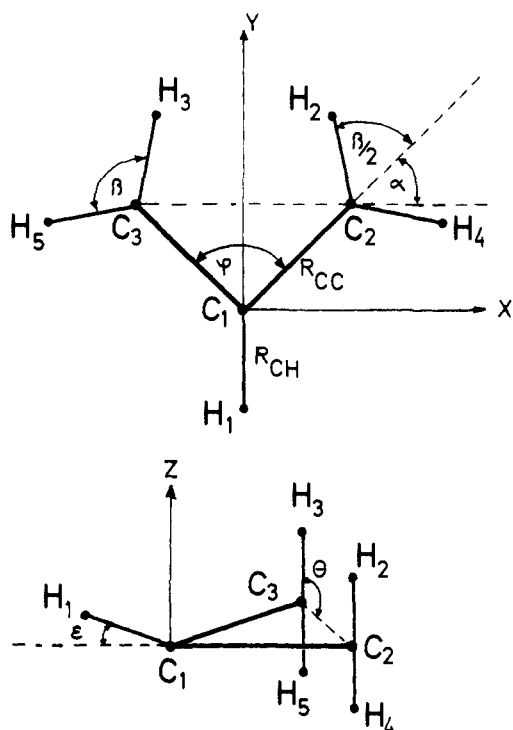
Figure 1. Definition of geometrical parameters used in the present study.

methods, supplemented with a limited configuration interaction treatment whenever it appears likely that multiconfigurational wave functions will be significantly more accurate in describing the various geometrical effects. The set of primitive Gaussian functions employed in the calculations is the same as that used earlier in connection with the cyclobutene–butadiene study,[10-12] namely Whitten's basis set for carbon[13] and hydrogen.[14] Nevertheless, in the present case the smaller size of the molecules under consideration allows one to conveniently employ a less restricted contraction than before, namely one which corresponds to essentially double ζ near-Hartree–Fock accuracy; in standard basis set notation the [10,5|5] primitive set has been contracted to a [4,2|1] set in the present calculations rather than to the [3,1|1] basis of single ζ type used in the aforementioned C_4H_6 study. The additional flexibility introduced by the double ζ groupings has earlier been found[15] to produce an energy lowering of 0.1729 hartree for the allyl cation, but the main advantage in extending the basis in this manner in the present study is the greater reliability it affords for the calculated results as they pertain to differences in energy and details of molecular geometry, a point which has been demonstrated in numerous investigations for molecules of similar size.[16,17]

Before searching for the details of the geometrical changes which occur in the course of any reaction, it is obviously quite important to have a good knowledge of

the equilibrium structures of the participants thereof. The relative lack of experimental data on this subject in the case of the allyl and cyclopropyl species makes this problem particularly critical in the present study. For example, the magnitude of the internal CC bond distance preferred by the species is unknown. In the allylic system a value of roughly 1.40 Å has been assumed in the past; this quantity is essentially equal to the experimental R_{CC} in benzene, which of course possesses a π system quite similar to what is found for the planar C_3H_5 species. Clark and Armstrong's calculations for the allyl cation[4] indeed substantiate this choice once their own estimates for the error in calculated bond lengths, due to their relatively small basis set, are taken into account. In the case of the corresponding cyclopropyl species, the analogous choice for R_{CC} has been based on the expected close relationship between these systems and a cyclopropane precursor. Calculations for the cyclopropyl cation using the double ζ basis discussed above, however, are in definite disagreement with the latter assumption as can be seen from Table I. The actual energy minimum is

Table I. Total SCF Energy of $C_3H_5^+$ for Different Values of R_{CC} ($\beta = 116°$, $\theta = 90°$, $\varphi = 80°$, $\alpha = 45°$)

R_{CC}, Å	E, hartrees
1.36	−116.03209
1.40	−116.03589
1.44	−116.03342
1.52	−116.01418
1.60	−115.98211

found to occur at 1.40 Å, that is, very nearly at the same value favored by the planar allyl species and at least 0.1 Å smaller than the equilibrium R_{CC} value in cyclopropane itself.

The calculated findings can be understood from a qualitative point of view quite easily on the basis of simple MO theory in general and application of Koopman's theorem in particular; in going from the cyclopropyl anion (which is isoelectronic with cyclopropane and is thus expected to also prefer a bond length of about 1.52 Å) to the corresponding cationic species, ionization occurs from the strongly R_{CC} antibonding $2b_1$ MO, thereby shortening the bond length considerably to about 1.40 Å. By the same reasoning, the bond length of the cyclopropyl radical is expected to fall roughly midway at about 1.46 Å. On the other hand, the orbital which becomes occupied in the transition from the allylic cation to the corresponding anion (the $1a_2$) is practically nonbonding, and thus the assumption of nearly constant R_{CC} throughout the allyl ionic series is much more realistic. A more general review of these points, particularly as they apply to the Mulliken–Walsh model of molecular geometry, has been given elsewhere.[18] In the present context, however, the key point is that the change in R_{CC} during the $C_3H_5^+$ isomerization is not nearly as great as has been assumed in earlier treatments of this reaction.[2-4] From Table I it is clear that the choice of a bond length of 1.52 Å for the cyclopropyl cation instead of the actual equilibrium value of 1.40 Å leads to an underestimation of the stability of the perpendicular ($\theta = 90°$; see Figure 1)

(13) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).
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(16) R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *J. Chem. Phys.*, **46**, 2029 (1967); S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **14**, 305 (1969).
(17) R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971).
(18) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, in press.
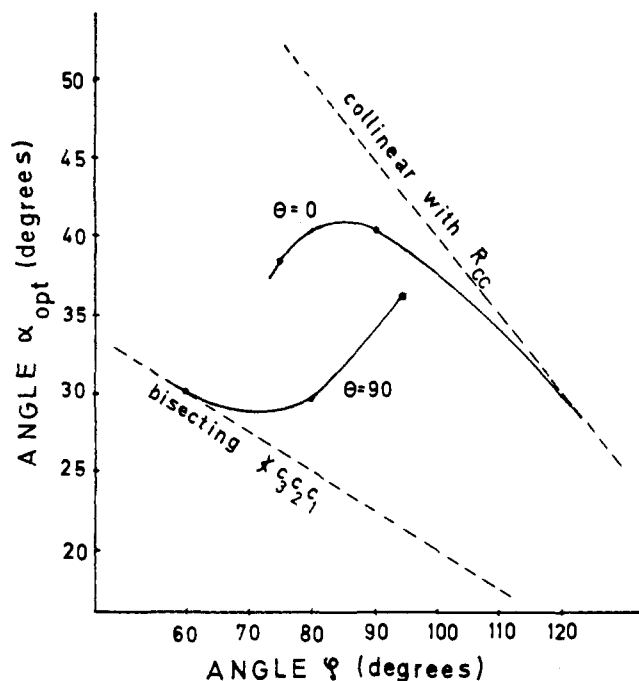
Figure 2. Variation of the optimum value of α as a function of the CCC angle φ for the allylic ($\theta = 0°$) and cyclopropyl ($\theta = 90°$) structures. For definitions see Figure 1.
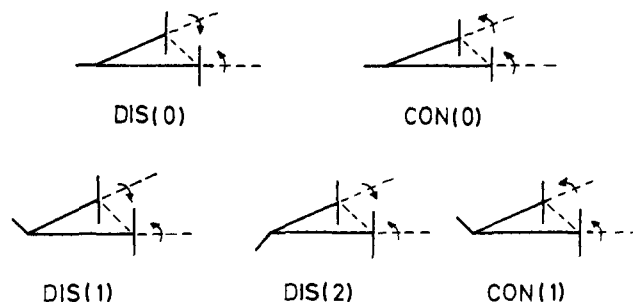

Figure 3. Definition of different reaction modes for the electrocyclic reaction between corresponding cyclopropyl and allyl systems.

isomer by some 13 kcal/mol relative to that of its allylic counterpart.

Similarly, calculations in which the methylene angles β (Figure 1) are varied indicate that the differences between these quantities in the allylic and cyclopropyl species are not as great as might have been thought. The equilibrium value for β in the allyl cation ($\theta = 0°$), for example, is found to be 116°, only slightly smaller than the corresponding quantity for cyclopropane. On the other hand, the CH_2 flapping angle α is found to exhibit a strong dependence on both the value of θ and the CCC internuclear angle φ, as can be judged from the results for $C_3H_5^+$ given in Table II. The occurrence of the energy minima in this table appears not surprisingly

Table II. Total SCF Energy of $C_3H_5^+$ as a Function of Angle α at Different Values of Angles φ and θ ($\beta = 116°$ and $R_{CC} = 1.40$ Å

φ^a	θ^a	α^a	E^b
120	0	20	−116.13614
		30	−116.14427
		40	−116.13342
90	0	25	−116.03847
		30	−116.05740
		35	−116.06955
		45	−116.07086
		55	−116.03422
75	0	25	−115.90861
		35	−115.93356
		45	−115.92382
		55	−115.84469
95	90	25	−115.99896
		30	−116.00062
		40	−116.00165
80	90	25	−116.04169
		30	−116.04231
		35	−116.04151
		45	−116.03589
		55	−116.02309

^{a} Angles are in degrees; for definition see Figure 1. ^{b} In hartrees.

to be dictated largely by steric effects, an observation made in similar calculations for the C_3H_5 systems reported earlier.[15] In the allyl cation ($\theta = 0°$), for example, the $\angle$HCH bisector (Figure 1) tends to be collinear with the adjacent CC bond for large values of φ, but as the distance between the terminal carbons decreases the methylene groups show an obvious tendency to bend out of each other's way; that is, α_{opt} differs by increasingly wider margins from the values corresponding to collinearity of the $\angle$HCH bisector with the CC bond (see Figure 2). Roughly the same type of effect is observed for the cyclopropyl cation ($\theta = 90°$), with the CH_2 groups gradually bending away from each other as φ decreases, as α_{opt} ultimately approaches values corresponding to collinearity between the $\angle$HCH bisector and that of $\angle C_3C_2C_1$ (Figure 2). Similar results are expected for the cyclopropyl and allyl radicals and anions, respectively, in view of the basically steric nature of this effect.

In summary, this preliminary study of the interrelationship of the various geometrical variables introduced in Figure 1 suggests that in the study of the interconversions between corresponding cyclopropyl and allyl species account must be taken not only of how rotation of the CH_2 groups and opening of the cyclopropyl ring occur but also of how the optimum values of α and R_{CC} vary during the course of the reactions. In what follows it will simply be assumed that for a given value of θ and φ the optimum values for R_{CC} and α can be determined accurately on the basis of linear interpolations between relevant limiting values obtained for these quantities thus far. In addition, variations in the central CH bending angle ϵ (Figure 1) will also require explicit consideration (section IV), but values for R_{CH} and β will simply be assumed to remain constant for all possible modes of the various C_3H_5 electrocyclic transformations under discussion.

II. Calculation of Minimum Energy Surfaces for $C_3H_5^+$ ($\epsilon = 0°$)

Because of the possibility that the central CH bond in the C_3H_5 skeleton (Figure 1) may not remain in the plane of carbon atoms throughout the entire reactive process, it is possible to distinguish five distinct transformation modes (as indicated in Figure 3) by which the interconversion between the various cyclopropyl and allyl counterparts can occur. Initially, attention will be confined only to the dis(0) and con(0) modes for which the central CH bond is constrained to lie in the plane of the three carbons at all times. From typical Woodward–Hoffmann correlation diagrams[9] for these

Figure 5. Optimum value of the rotational angle θ as a function of the ring-opening angle φ for the electrocyclic conversion of $C_3H_5{}^+$ in the con(0) and dis(0) modes.
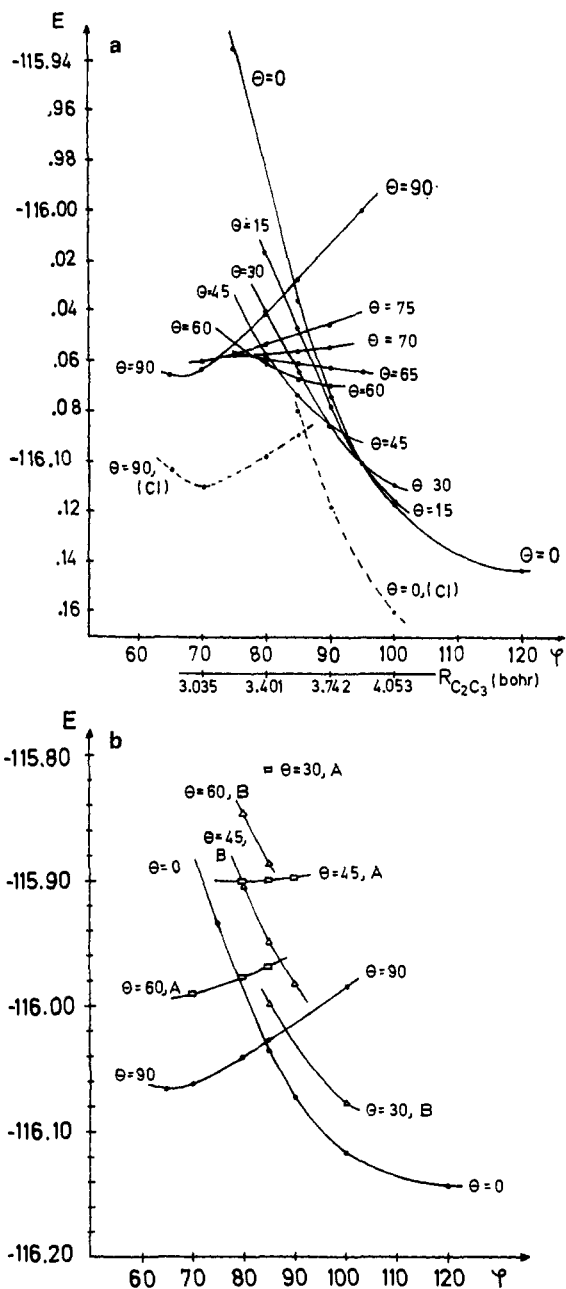

Figure 4. Potential curves (E in hartrees) for $C_3H_5{}^+$ conformations in the disrotatory mode (a) and in the conrotatory mode (b) for different rotational angles θ. The lower curves are obtained via CI calculations.

two transformation modes for each of the cyclopropyl-allyl pairs, it is concluded that the disrotatory mode is an allowed process only for the cation, while the conrotatory one is only allowed for the anion; from this point of view neither rotational mode represents a symmetry-allowed process for the free radical transformation.

Knowledge of the preferred rotational mode alone, however, is not at all sufficient to specify the dynamic path actually followed by the reaction. More details about the actual minimum energy surfaces are obtained from SCF calculations on $C_3H_5{}^+$ in the aforementioned double ζ basis. The resulting potential surface data for the allowed dis(0) mode are collected in Figure 4a in the form of a series of potential curves for the ring-opening process occurring for various constant θ
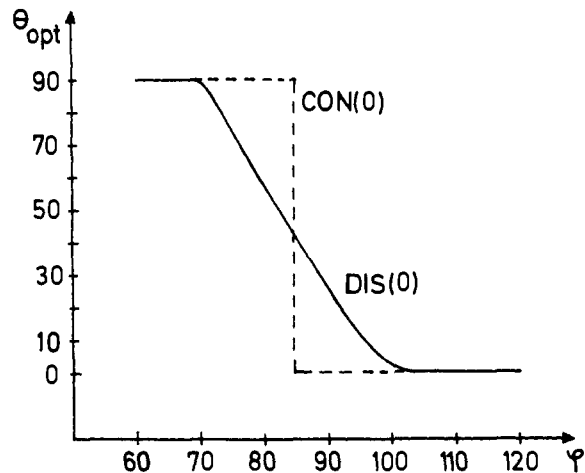
values.[19] The figure shows clearly that the $\theta = 0$ and 90° species are not the lowest in energy throughout the entire reaction, in contrast to what has been observed in the analogous diagram for the cyclobutene-butadiene electrocyclic transformation.[10] In the present case these two potential curves cross each other at an energy which is considerably *higher* than that obtained for some partially rotated CH_2 conformations at the same value of φ (approximately 85°), whereas in the C_4H_6 reaction the analogous crossing point between the $\theta = 0$ and 90° potential curves is *lower* than the energy corresponding to *any other value* of θ at this point in the ring-opening process (for both dis- and conrotatory modes). Thus, while the analogous ab initio calculations for the cyclobutene-butadiene thermochemical interconversion predict that the rotational phase of the reaction does not occur simultaneously with the bond-breaking process,[20] the conclusion that must be drawn from Figure 4a is clearly that in the electrocyclic transformation of $C_3H_5{}^+$ the bond-breaking and rotational phases occur synchronously in the dis(0) mode (at least between $\varphi = 70$ and 100°).

If the same theoretical treatment is employed to study the forbidden con(0) mode for the $C_3H_5{}^+$ transformation it is found, however, that a nonsynchronous mechanism is favored, as can be seen from the pertinent potential curves shown in Figure 4b. In contrast to the dis(0) case, it appears that partially rotated structures are nowhere more stable than the corresponding conformations with the CH_2 groups either coplanar or perpendicular to the plane of carbon atoms. These results can be summarized quite succinctly in terms of a plot of the optimum value of the rotational angle as a function of φ for these two transformation modes (Figure 5), from which it is seen that while the optimum value of θ changes relatively slowly with ring opening

(19) For each set of θ and φ values the corresponding choice for angle α is made on the basis of linear interpolations of the data in Table II. Also in these calculations R is held fixed at 1.40 Å throughout the entire transformation process.

(20) Quite similar behavior, namely a reaction occurring in successive steps of bond stretching and CH_2 rotation, has also been observed by Horsley, et al.,[21] for the geometrical isomerization of cyclopropane in an ab initio calculation employing a minimal STO basis set.

(21) J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, J. Amer. Chem. Soc., 94, 279 (1972); Pure Appl. Chem., Suppl. 1969, 1, 197 (1971).

in the dis(0) mode a much more abrupt transition from the perpendicular to the planar CH_2 conformations is predicted for the con(0) case (C_2 symmetry maintained throughout).

Qualitatively, such a dynamical mechanism for the two reaction modes appears to be quite consistent with the conservation of the orbital symmetry principle.[9] The fact that conrotation of the CH_2 groups is accomplished only by a relatively large increase in energy in comparison to the allowed disrotatory process makes it easily understandable that in the former case the actual methylene rotation is delayed until the planar $C_3H_5{}^+$ system becomes isoenergetic with the corresponding perpendicular conformer (as a result of deformation of the cyclopropyl ring). Nevertheless, such argumentation does not explain the difference found in the *ab initio* results for the *allowed* rotational modes of $C_3H_5{}^+$ and C_4H_6, respectively, with regard to the manner in which ring opening and methylene rotation are accomplished. An understanding of the underlying basis for this difference seems especially important since MINDO calculations have predicted that bond breaking and CH_2 rotation occur synchronously in the allowed thermochemical isomerizations of *both* cyclopropyl cation[5] *and* cyclobutene.[22] A closer investigation of this point will be deferred, however, until the effects of out-of-plane motion of the central CH bond in $C_3H_5{}^+$ and the importance of configuration mixing in the present theoretical treatment are discussed, since both of these factors have proven to be of considerable quantitative significance in the earlier calculations for the C_4H_6 isomerization;[10,12] in addition, analogous calculations for the C_3H_5 radicals and anions, respectively, would also seem to have bearing on this point.

III. Out-of-Plane Motion of the Central CH Bond in $C_3H_5{}^+$

Aside from fundamental considerations of ascertaining the minimum energy path in the electrocyclic transformations under discussion, the main interest in the out-of-plane bending motion of the central CH bond in the various C_3H_5 systems arises from the fact that under actual experimental conditions the incipient cyclopropyl species is formed from a cyclopropane derivative (such as a tosylate) in which neither the leaving group nor the adjacent hydrogen atom lies in the plane of carbons. Thus, Kutzelnigg[2] has pointed out that even though EHT calculations indicate that a cyclopropyl cation *in statu nascendi* after decomposition of such a derivative (with $\epsilon = 57°$, see Figure 1) is some 6 kcal/mol *less stable* than in the corresponding conformation with the CH bond lying in the CCC plane ($\epsilon = 0°$), the fact remains that the actual reaction mechanism undoubtedly involves the former (nonequilibrium) species in the initial stages of the transformation to the allyl cation. The essential accuracy of the latter assertion is borne out by *ab initio* calculations using the present double ζ basis in which the SCF energy is varied as a function of the out-of-plane bending angle ϵ for various combinations of θ and φ (see Figure 6). In fact, reference to the curve for $\theta = 90°$ and $\varphi = 70°$ (the calculated equilibrium values of the two quantities for
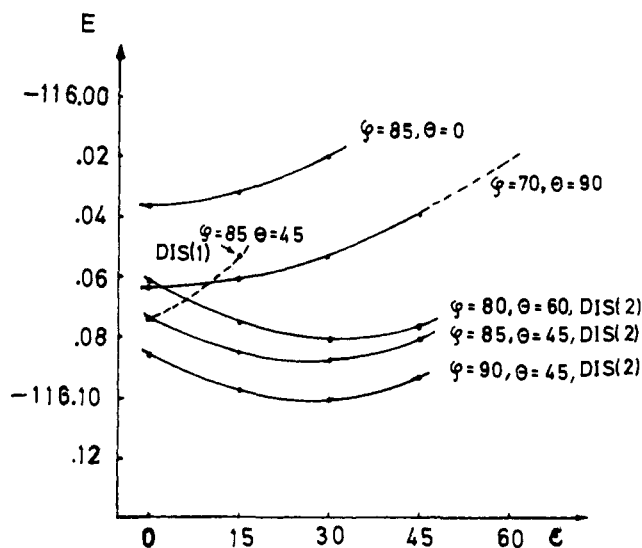
(22) M. J. S. Dewar, lecture at the "Symposium on Computation of Reaction Paths and Reaction Mechanisms," Paris, Sept 11–14, 1972.

Figure 6. Total energy E (in hartrees) as a function of ϵ (see Figure 1) for a number of $C_3H_5{}^+$ conformations with different values of φ and θ in the dis(2) and dis(1) rotational modes.

the cyclopropyl cation, see Figures 4a,b) shows that the increase in energy in going from the most stable to the *ex statu nascendi* form of the cation in question is somewhat underestimated in the aforementioned EHT calculations, with the actual difference being somewhere in the 10–15 kcal/mol range.

The present calculations indicate, however, that as the CH_2 groups begin to rotate the foregoing decided preference for an in-plane central CH bond is quickly removed. In the dis(2) mode at $\theta = 60°$, for example, the SCF energy is found to be minimal for $\epsilon = 40°$ (at least for $\varphi = 80°$), and this behavior is mirrored in calculations for which θ is fixed at a value of $45°$ (Figure 6). As the rotation approaches completion, this effect apparently reverses itself, with a completely planar allyl cation being favored, but it is clear from these results and indeed those of Clark and Armstrong before[4a] that out-of-plane bending of the central CH bond occurs along *the minimum energy path* for this reaction as well as for its counterpart involving the cyclopropyl cation *in statu nascendi*. This point is emphasized in Figure 7 by means of a comparison of the dis(2) and dis(0) potential curves from beginning to end of the $C_3H_5{}^+$ interconversion; in both cases, the optimum value of θ is chosen at each φ value, as determined by the present SCF calculations. The maximum separation[23] between the dis(2) and dis(0) potential curves is approximately 10 kcal/mol, occurring for $\varphi = 85°$. Only one calculation has been carried out for the dis(1) mode (for $\varphi = 85°$, $\theta = 45°$, and $\epsilon = 15°$; see Figure 6), but the results indicate that this conformation is even less stable than the dis(0) structure (by more than 10 kcal/mol in this instance) and thus is of little importance in the cation transformation, again in qualitative agreement with Clark and Armstrong's *ab initio* SCF results for this system.[4a] No calculations for the con(1) mode

(23) The nonequilibrium reaction path originating with the cyclopropyl cation *ex statu nascendi* is actually somewhat arbitrary (for example, the CH bond might well assume a planar conformation immediately after the leaving group departs without further change in either φ or θ), and thus the corresponding potential curve shown in Figure 7 (denoted by a dashed line) should be considered merely as one of many such relatively high energy routes to the transition state for this reaction.
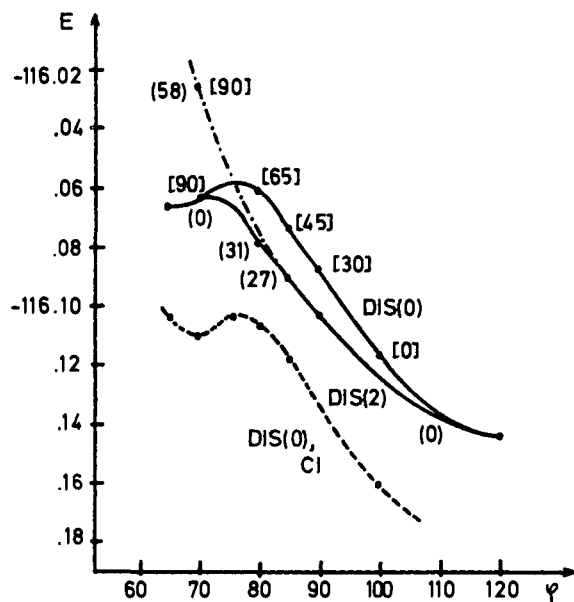
Figure 7. Comparison of dis(2) and dis(0) potential curves for the electrocyclic transformation between the cyclopropyl and allyl cations. The optimum values of θ are given in brackets, those of ϵ in parentheses. The (– · –) line refers to the transformation with the cyclopropyl cation initially *in statu nascendi*, i.e., $\epsilon = 58°$ is assumed in the neighborhood of $\varphi = 60°$. The dashed line refers to the corresponding CI curve for the dis(0) process.

of the cationic reaction have been carried out in the present study in view of the essential forbiddenness of all conrotatory processes involving the $C_3H_5^+$ ground state.

In summary, the favored rotational mode for the transformation from the cyclopropyl to the allyl cation is of dis(2) type, with bond breaking, CH_2 rotation, CH out-of-plane bending, and CH_2 wagging (as indicated by the change in α_{opt} in Figure 2) occurring simultaneously over a broad range of the minimum energy pathway; the results of Table I suggest, however, that the C_2–C_3 distance remains relatively constant in the neighborhood of 1.40 Å for the entire $C_3H_5^+$ isomerization. The occurrence of out-of-plane bending of the central CH bond even along the course of the minimum energy path for this reaction has its analog in the cyclobutene–butadiene interconversion in the form of torsional motion which develops at the onset of rotation of the methylene groups[12] in this case, but again the synchronous occurrence of ring opening and CH_2 rotation in the $C_3H_5^+$ reaction definitely distinguishes this process from that which has been indicated in the *ab initio* calculations for the otherwise closely related C_4H_6 systems.

IV. Importance of CI in the Theoretical Treatment

As mentioned in the introductory section the SCF method by itself does not yield a satisfactory estimate for the activation energy in the cyclobutene–butadiene thermochemical interconversion reaction, primarily because conformations assumed in the neighborhood of the transition state (for which the ring is almost completely destroyed) are much less satisfactorily represented by a single configurational wave function than is either of the isomeric C_4H_6 species in their respective equilibrium geometries. The latter difficulty is easily overcome by means of configuration interaction (CI),

a procedure which is also quite effective in improving the quite unrealistic SCF description[24] of the forbidden (disrotatory) reaction path for the C_4H_6 electrocyclic transformation; thus, the difference in activation energy for the two rotational modes in C_4H_6 is reduced from 50 kcal/mol in the SCF treatment to only 14 kcal/mol after a limited CI is introduced. In the present context the obvious question is whether the same type of deficiencies in the SCF treatment are also present in the calculations for the various C_3H_5 systems.

To investigate this matter a series of limited CI calculations has been carried out for $C_3H_5^+$ in various nuclear conformations associated with the dis(0) and con(0) reaction paths. All the electronic configurations in this treatment are constructed from the ground state SCF-MO's for each geometry considered; the eight most stable SCF-MO's are always held doubly occupied whereas the remaining six valence electrons of the system are distributed among the other three occupied orbitals plus 12 other virtual species, which in turn are chosen on the basis of their ability to introduce valence-shell correlation into the electronic wave function (very diffuse orbitals are excluded from the treatment, for example). Furthermore, care is taken that the proper MO correlation is maintained throughout all stages of the reaction being considered. Finally, the resulting set of configurations is further restricted to include only those which differ by at most a double excitation from the ground state configuration and which are capable of lowering the energy of same by at least 5×10^{-5} hartree in a 2×2 CI.[25] The orders of the secular equations actually solved fall in the range of 125 to 150 symmetry adapted multideterminantal functions (SAF's); this treatment is roughly equivalent to that used earlier in the cyclobutene–butadiene calculations.[10,12]

The total energies resulting from the CI treatment for $C_3H_5^+$ nuclear conformations with perpendicular and planar ($\theta = 90$ and $0°$, respectively) arrangements of the methylene groups are plotted in Figure 4a along with the corresponding SCF results. From these data it is clear that the CI treatment effects only rather minor changes in the shapes of the latter two potential curves relative to their SCF counterparts; the steepness of the curves is somewhat altered and the equilibrium value of φ is increased slightly for both the cyclopropyl and allyl cations, but no really significant changes are apparent. This overall evaluation is reinforced by the finding that the energy difference between the equilibrium forms of the two isomeric cations is 48.5 kcal/mol (with allyl more stable, of course) in the SCF calculations and only about 1.5 kcal less in the CI treatment, whereas in the case of the C_4H_6 isomers a change of 13 kcal in the analogous quantity is observed upon introduction of CI; indeed, without CI one is led to erroneously predict that cyclobutene is the more stable of the latter two isomeric species.

The CI potential curve for the optimum dis(0) reaction pathway of $C_3H_5^+$ is given for comparison with

(24) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, **87**, 2045 (1965).

(25) More details on the general subject of configuration selection may be found in S. D. Peyerimhoff and R. J. Buenker, *Chem. Phys. Lett.*, **16**, 235 (1972), and also in a more comprehensive article by the authors dealing with such techniques, "Individualized Configuration Selection in CI Calculations with Subsequent Energy Extrapolation," submitted for publication.

the corresponding SCF data in Figure 7. Again the indication is that the CI method has very little effect on the shape of the minimum energy surface in question, with the calculated activation energy for this process changing by less than 1 kcal/mol (to only 4 kcal/mol). The main reason for this small magnitude in the change of the latter quantity lies quite obviously in the fact that in this instance the activated complex is very similar in structure to the equilibrium form of the cyclopropyl cation itself (Figure 7), a circumstance which is not at all unexpected in view of the Hammond principle and the aforementioned high exothermicity of this process. Again this situation is quite different from the case of the C_4H_6 process, for which the activation energy of the allowed conrotatory interconversion is significantly reduced as a result of the CI.

Indeed, the relative ineffectiveness of the CI method for the various $C_3H_5^+$ reaction surfaces is even carried over into the description of the symmetry-forbidden (conrotatory) electrocyclic process, despite the existence of the characteristic energy crossing in the SCF treatment[24] for this reaction mode. The con(0) activation energy (see Figure 8) is decreased by only 7 kcal/mol upon introduction of CI to a value of 79 kcal/mol, still over 75 kcal/mol greater than the corresponding quantity for the dis(0) mode; in the case of the C_4H_6 isomers, the analogous CI treatment leads to a much larger decrease in E_{act} for the corresponding (disrotatory) forbidden processes and, perhaps even more significantly, to a 36 kcal decrease in the difference between the con and dis barrier heights to a value of only 14 kcal/mol.[26]

In conclusion, the present calculations indicate that CI or correlation effects are not at all as significant in the theoretical description of the various thermochemical electrocyclic transformation modes of the $C_3H_5^+$ isomers as they are in the analogous study of the C_4H_6 isomerization processes. Consequently, the SCF or single configurational method should be quite satisfactory for the treatment of the $C_3H_5^+$ reaction surfaces, whereas the same is not at all true for the description of the corresponding C_4H_6 species. Far from lessening the need to consider the influence of CI in calculations of this genre, these results show clearly that failure to account for such theoretical effects in general will inevitably result in an erratic description of both the similarities and dissimilarities which exist within a large series of such chemical reactions.

V. Thermochemical Interconversions of C_3H_5 and $C_3H_5^-$

A. Calculated Potential Curves. The results of the present investigations can be carried over to the study of the corresponding radical and anion species with almost no additional computational effort *via* Koopmans' theorem.[28] As long as the MO's of the cation A^+ possess very nearly the same constitution as

(26) The large distinctions in these results are easily understood with reference to the magnitude of the interaction matrix elements between the two pertinent configurations used to describe the forbidden process in each case; in C_4H_6 the matrix element in question is quite large, namely the exchange integral $K(\sigma,\sigma^*)$,[27] while for $C_3H_5^+$ the analogous quantity $K(\sigma,\pi^*)$ is very much smaller.

(27) For the transition state of this reaction the orbital energy order is no longer the same as for cyclobutene at equilibrium.

(28) T. A. Koopmans, *Physica (Utrecht)*, **1**, 104 (1933); C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).
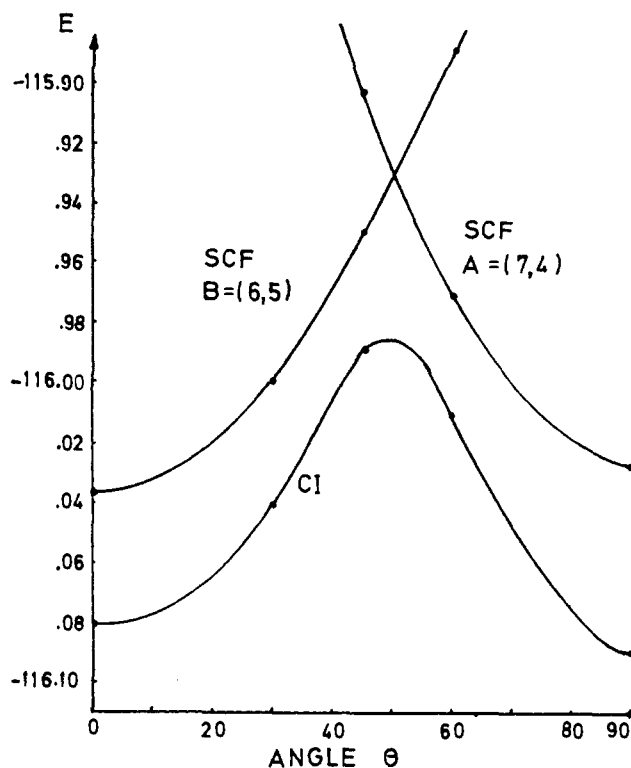

Figure 8. Rotational phase of the conrotatory process in $C_3H_5^+$ ($\varphi = 85°$); the CI energies as well as the SCF energies for the two ^1A states involved are plotted as a function of the CH_2 rotational angle θ. [The notation (7,4) indicates that 7 MO's of a type and 4 of b symmetry are occupied.]

those of the radical A, Koopmans' theorem in the form of

$$E_T(A) = E_T(A^+) + \epsilon(LUMO,A^+) \qquad (1)$$

can be used to obtain a very good approximation to the total energy $E_T(A)$ of the radical strictly on the basis of the SCF results for A^+ itself, including the orbital energy ϵ of the lowest unoccupied MO in the cation. Aside from a small expansion in the electronic charge distribution due to the addition of an electron to a positive ion, very little difference in the MO composition of $C_3H_5^+$ and C_3H_5, respectively, is in fact expected; indeed, despite the fact that the LUMO of the cation is a virtual orbital, it should satisfy the Koopmans' theorem assumption quite well since it is still calculated in the field of a positive ion and thus does not tend to become an unrealistically diffuse species in the Hartree–Fock limit in contrast to the case for its counterparts in neutral systems. Furthermore, since *the errors* introduced through the use of eq 1 *are very likely to be nearly the same for each nuclear conformation* considered, application of Koopmans' theorem is especially warranted in the present study in which the interest lies mainly in the overall *shapes* of the calculated potential curves and not so much upon their relative spacing with respect to one another. Further ramifications of this *differential* approach to the use of Koopmans' theorem may be found elsewhere.[18]

The potential curves obtained from eq 1 by adding the LUMO orbital energy curve to the corresponding species for the $C_3H_5^+$ total energy are shown in Figure 9a for the dis(0) process of the radical; there are always two choices for the LUMO since the disrotatory mode
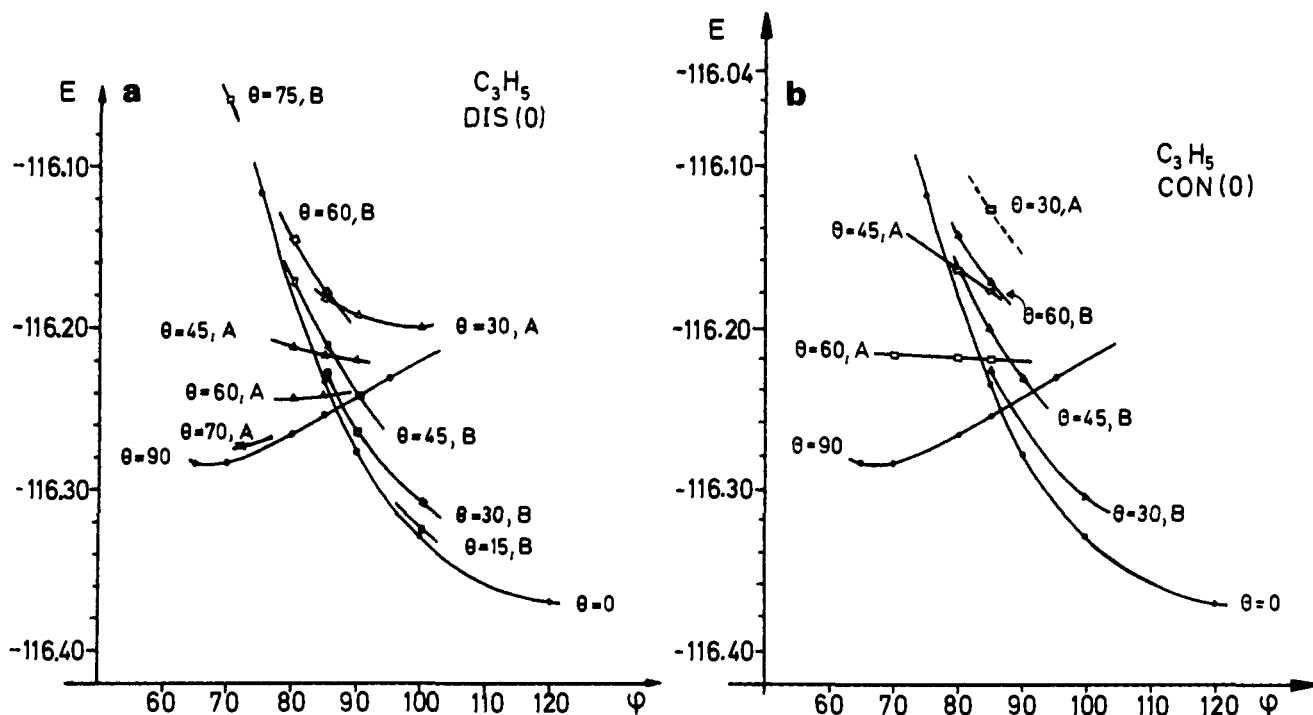
Figure 9. Potential curves obtained *via* Koopmans' theorem for $C_3H_5\cdot$ conformations assumed in the disrotatory mode (a) and in the conrotatory mode (b) for different rotational angles θ (energy values in hartrees). State A refers to the configuration in which the $2b_1$ MO is singly occupied; in B states the $1a_2$ MO contains the extra electron.

is not symmetry allowed and hence the occurrence of two electronic states (designated A and B) in this case. From these data it is apparent that addition of the extra electron has destroyed the synchronous nature of the bond-breaking and rotational phases previously observed for this reaction mode in $C_3H_5^+$; the fact that the crossing of the $\theta = 0$ and 90° potential curves in this diagram occurs at an energy which is *lower* than that associated with any partially rotated nuclear conformation at this stage of the ring-opening process again indicates that the actual CH_2 rotation occurs over a relatively narrow range of φ, just as in the forbidden con(0) mode of the cation and in both allowed and forbidden thermochemical transformations of the aforementioned C_4H_6 species. A very similar result is also evident in the case of the (also forbidden) con(0) interconversion of the C_3H_5 radicals, as can be seen from the relevant potential curves presented in Figure 9b, thereby providing another example of a *forbidden* process in which CH_2 rotation and ring opening do not occur synchronously.

These results of course do not in themselves rule out the possibility that some synchronous motion does occur in the free radical interconversion as a result of out-of-plane motion of the central CH bond. On the other hand, the calculations indicate that the dis(0) mode is not as unfavored for the $C_3H_5\cdot$ systems relative to the dis(2) counterpart as is the case for $C_3H_5^+$. In any event the present results do agree with those of Boche and Szeimies (and also those of Dewar[5]) in the important respect that the dis mode is unequivocally favored over the con type for these systems; more quantitative details of these calculations will be discussed later.

Potential curves for the $C_3H_5^-$ systems can also be obtained *via* eq 1 simply by substituting the radical for A^+ therein and of course the anion for A.[29] This suc-

cessive application of Koopmans' theorem then leads to the potential curves shown in Figure 10 for the con(0) and dis(0) modes, respectively, for the $C_3H_5^-$ interconversion. Just as before in the case of the free radicals it is found that *both* types of rotational processes occur over a very narrow range of φ. Indeed this aspect of the calculation is reinforced when out-of-plane distortion of the central CH bond is taken into account since such geometrical changes are much more important for perpendicular conformations of the anion than for partially rotated structures of this system. The equilibrium form of the cyclopropyl anion (with $\epsilon = 55°$) is calculated to be 12 kcal/mol more stable than its counterpart with $\epsilon = 0°$, whereas the energy lowerings observed in bending the CH bond out of the CCC plane for the anionic transition state are virtually of negligible magnitude (the equilibrium form of the allyl anion is definitely planar). The preferred path for the anion is clearly con(1), for which of course conservation of orbital symmetry is maintained, while the next most stable process appears to be dis(1), at least on the strength of the data given in Table III.

In summary then, the only electrocyclic reaction of the C_3H_5 systems which is predicted in the *ab initio* calculations to be characterized by *synchronous* methylene rotation and ring opening is *the allowed disrotatory process of the cation*. This result is in distinct contrast

(29) Since the orbital energies used in eq 1 should be obtained in the field of the radical, A^+ in this case, the successive application of Koopmans' theorem leads to reliable information for the anion only if the additional assumption holds that the orbital energy curves of the LUMO in eq 1 have essentially the same shape for both radical and cation; alternatively, it requires that the repulsive interaction term between the two electrons contained in this orbital for $C_3H_5^-$ does not vary significantly with motion of the nuclei. It should also be pointed out again that the main interest in this case is only in the *variation* of the total energy of the $C_3H_5^-$ species with geometrical changes and not on *absolute* energy values, for which this method is not at all satisfactory.
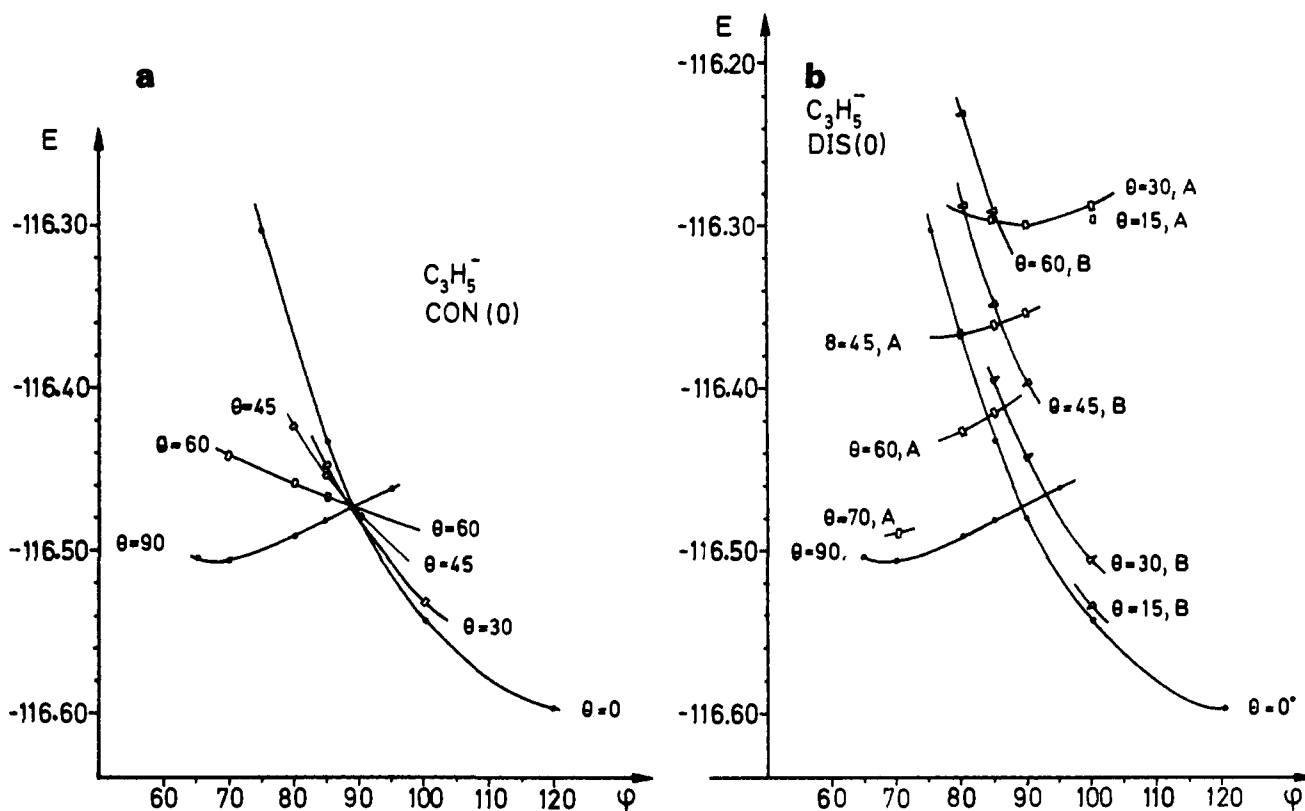
Figure 10. Potential curves obtained *via* Koopmans' theorem for the con(0) mode (a) and the dis(0) mode (b) of the $C_3H_5^-$ interconversion at different values of the rotational angle θ. The state designated by A occupies the $2b_1$-$8a'$ (π) MO while the B state refers to the configuration with the $1a_2$-$5a''$ (χ_2) species doubly occupied.

Table III. Total Energy E_T (hartrees) of the C_3H_5 Radical and Anion in Various Disrotatory Conformations ($\varphi = 85°$ and $\theta = 45°$ in all cases) Obtained *via* Koopmans' Theorem (eq 1) from the Corresponding SCF Total and Lowest Unoccupied Orbital Energies ϵ_i of $C_3H_5^+$

	Dis(2) $\epsilon = 15°$	Dis(1) $\epsilon = 15°$	Dis(0) $\epsilon = 0°$
$E_T(C_3H_5^+)$	−116.08516	−116.05367	−116.07429
$\epsilon_i(8a')$	−0.13418	−0.16213	−0.14401
$E_T(C_3H_5\cdot)$	−116.21934	−116.21580	−116.21830
$E_T(C_3H_5^-)$	−116.35352	−116.37793	−116.36231

to what has been reported by Dewar on the basis of MINDO calculations,[5,22] namely that *all* allowed processes investigated, not only for the various C_3H_5 species but also for the cyclobutene–butadiene pair, occur synchronously in this respect. Thus, while there is at least qualitative agreement between the two theoretical methods that all the forbidden processes of these various systems are nonsynchronous in this sense, the *ab initio* techniques are seen to be much more discriminating than the semiempirical in the case of the allowed processes. As mentioned in section II it is easily understandable that the rotational phase in forbidden reactions should be delayed as long as possible, but there is certainly no compelling reason to believe that the *converse* of this statement is true for symmetry-allowed interconversions, simply because in many cases there are clearly other features (increased ring strain, for example) which inhibit CH_2 rotation irrespective of whether orbital symmetry is conserved or not. The fact that MINDO calculations predict that in all allowed processes ring opening and CH_2 rotation occur syn-

chronously indicates that such semiempirical treatments do not find that *any* of the cyclic species under discussion react adversely to the increased strain inevitably produced by the methylene rotation; but given the well-known tendency of the MINDO method to underestimate ring strain effects[7,30,31] in general, there is good reason to conclude that such findings merely represent an artifact of the semiempirical calculations themselves rather than an accurate estimation of the true experimental situation.

B. Relation between *ab initio* Calculations and Conservation of Orbital Symmetry Principle. The relative magnitudes of the energy barriers which are encountered when the actual CH_2 rotation occurs in these reactions are easily interpretable in terms of the conservation of orbital symmetry principle. Thus, while only very small barriers to rotation are calculated for the allowed processes, those found for their forbidden counterparts are quite sizable (as much as 60 kcal). Also somewhat predictably the sizes of the barriers in the case of both (forbidden) free radical processes are calculated to be only about half as great as for the corresponding forbidden rotational modes of the cation and anion. The success of the conservation of orbital symmetry principle in predicting the relative stabilities of the various interconversion processes can be rationalized in terms of SCF theory, as has been pointed out previously;[11] the energy difference between corresponding disrotatory and conrotatory conformations, which is clearly the key quan-

(30) A. R. Gregory, 6th Jerusalem Symposium on Chemical and Biochemical Reactivity, 1973, in press.
(31) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, 5, 402 (1972).
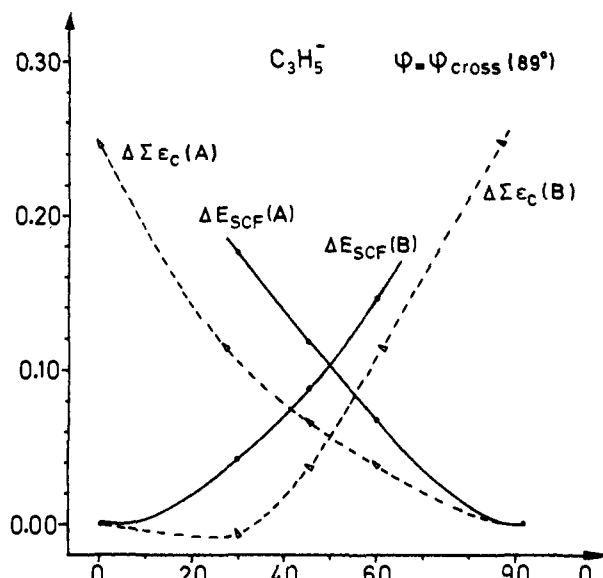
Figure 11. Comparison of energy differences between the two transformation modes (eq 2) in the rotational phase of the $C_3H_5^-$ interconversion. (Two states A and B are necessary.)

Figure 12. Comparison of energy differences between the two transformation modes (eq 2) in the rotational phase of the C_3H_5 interconversion. (Two states A and B are necessary.)

tity in such discussions, can be given approximately by

$$\Delta E_T \cong \Delta \sum N_c \epsilon_c \qquad (2)$$

where N_c and ϵ_c are occupation numbers and canonical orbital energies, respectively, for all those (critical) MO's *which undergo a change in occupation* in the forbidden process. The sign of ΔE_T of course determines which rotational mode is preferred, but to a good extent the same information can be obtained from the partial orbital energy sum on the right-hand side of eq 2. Plots of both these quantities ($\Delta E \equiv E_{dis} - E_{con}$) for $C_3H_5^-$ as a function of θ are given in Figure 11, and from these it is clear that the partial orbital energy sum indeed succeeds quite well in predicting the greater stability of the conrotatory mode (two sets of curves are required because of the two different states pertinent in the forbidden disrotatory case). In other words, all the other terms in the total energy expression for these species have very little influence on the choice of the preferred rotational mode in this reaction.

Because the minimum energy pathways are considerably different for the two $C_3H_5^+$ modes, there are not enough calculated data available to make the analogous comparison for the cation; on the other hand, such an analysis can be carried through for the free radical species, for which of course the qualitative application of the conservation of orbital symmetry principle merely leads to the conclusion that neither rotational mode is allowed. A plot of the pertinent energy differences (in this case $\Delta E \equiv E_{con} - E_{dis}$) given in Figure 12 again shows that the partial orbital energy sum predicts the correct stability ordering ($\Delta E > 0$), but it is obvious that the quantitative agreement (eq 2) is quite poor. Results such as these would therefore seem to emphasize that while qualitative arguments based on the conservation of orbital symmetry are very often reliable indicators of which process is favored in a given reaction, their failure to consider the effects of *all* electrons and particularly their reliance on a strictly single configuration approach does not rule out the occurrence of exceptions in a given case.[31]
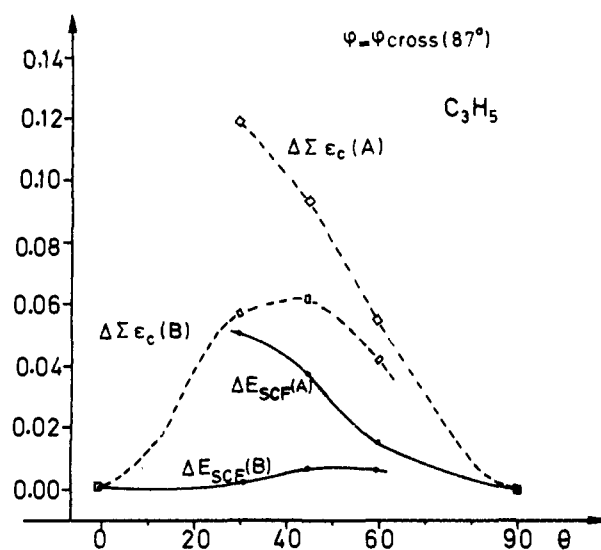
C. Comparison of Calculated Activation Energies. Although the present calculations for the C_3H_5 radical and anion systems have not specifically considered CI effects, the results discussed in section IV for the corresponding cation suggest that very little change in the shapes of the resultant potential curves occurs upon improving the theoretical treatment in this manner. Indeed, since the key electronic states (A and B) involved in the free radical reaction actually possess different *total symmetry* for both rotational modes, at least as long as a nontrivial symmetry element is retained,[32] the possibility of any significant change in the relative stabilities of either transition state as a result of CI seems especially remote.

From a geometrical point of view a more serious deficiency in the calculations discussed so far for the radical and anion is the assumption of a constant R_{CC} value throughout the transformation process. The actual equilibrium R_{CC} value for the cyclopropyl radical is some 0.06 Å greater than the assumed value (1.40 Å), whereas no such significant difference is expected for the allyl radical; nevertheless, the change in the exothermicity of this reaction introduced by accounting for this fact is expected to be only about 2 kcal/mol. The error introduced by this assumption of constant R_{CC} is greater for the comparison of the anion stabilities (approximately 12 kcal/mole) since the assumed R_{CC} value for the cyclopropyl species is too small by 0.12 Å.

When these considerations are taken into account, one obtains a set of energy values for each of the C_3H_5 processes which are compared in Table IV with previous estimates for these quantities by other authors.[33]

(32) This point has been missed by Boche and Szeimies[6,7] in their discussion of the supposed importance of CI in the description of the free radical reaction surfaces.

(33) The results of previous *ab initio* calculations by Clark and Armstrong for the $C_3H_5^+$ and $C_3H_5^-$ electrocyclic reactions[4] are not included in the table primarily because in their work a search for the minimum energy path was not actually carried through; instead, it is assumed that all parameters which are different in the initial and final species simply vary linearly throughout the course of these reactions. As indicated in section I, it seems clear that the structures assumed for the cyclopropyl species in general are not really optimal, a fact which in all probability has led to overestimations of the exothermicities in these reactions and by the same token to underestimations of the corresponding activation energies (at least in their 37 GF basis).

Table IV. Pertinent Energy Differences (kcal/mol) for Various Allyl–Cyclopropyl Interconversion Processes

		E(allyl) − E(cyclopropyl)	E(dis max) − E(cyclopropyl)	E(con max) − E(cyclopropyl)
$C_3H_5^+$	SCF	−48.8	4.7 dis(0)	86.3 con(0)
			1.6 dis(2)	
	CI	−47.7	4.4 dis(0)	78.5 con(0)
			1.3 dis(2)	
	MINDO[5]		7.4	38
C_3H_5	Koopmans'	−52	43 dis(0)	55[a] con(0)
	theorem		35 dis(2)	
	Semiempirical[7]		31.8, 30.1 dis(2)[b]	40.7, 37.5 con(1)
	MINDO[5]		24.7	52.3
$C_3H_5^-$	Koopmans'	−31	107 dis(0)	43[a] con(0)
	theorem		$ca.$ 97[c] dis(1)	
	MINDO[5]		65.7	30.7

[a] The favored mode is presumably con(1), for which no calculations have been carried out. [b] Note that the definitions of the dis(1) and dis(2) processes are reversed in ref 7 relative to those in the present study and also in ref 2. [c] Since only one calculation has been carried out for the dis(1) mode (see Table III), it is difficult to estimate this quantity more accurately.

The present *ab initio* treatment predicts that the dis(2) cation process occurs with by far the smallest activation energy of any of the interconversions considered. Interestingly enough it finds the dis(2) activation energy for the free radical isomerization to be of essentially the same magnitude as that of the (allowed) con(1) anionic process, despite the fact that orbital symmetry is not conserved for the former reaction; the calculated free radical activation energy is in good agreement with an earlier estimate[34] of 25 kcal/mol for this quantity based on experimental findings. In general, the present *ab initio* results are seen to predict much greater stability differences between corresponding allowed and forbidden processes in $C_3H_5^+$ and $C_3H_5^-$ than are indicated in the semiempirical (MINDO) method; in this respect the agreement with Clark and Armstong's earlier *ab initio* results obtained using a small AO basis set is much better, despite the rather limited geometry search undertaken in the latter study.

VI. Conclusion

Quantitative results of the present *ab initio* investigation of the electrocyclic transformations undergone by the C_3H_5 systems support the qualitative predictions of the conservation of orbital symmetry principle with regard to the preferred mode of reaction in each instance. A comparison with a similar study of cyclobutene–butadiene interconversion processes indicates further that the minimum energy pathways for the *forbidden* modes of such thermochemical reactions have certain common features regardless of the detailed electronic structure of the systems involved; specifically, the calculations distinguish three separate phases of the reaction in each case: the first is the ring-opening phase, which in turn is followed by the actual CH_2 rotation, and then upon completion of this stage by further separation of the terminal carbons until the equilibrium form of the linear isomer is finally attained. The situation for the symmetry-allowed processes depends much more heavily on details of the molecular structure of such systems, however; if the ringed structure is relatively stable it tends to oppose rotation of the methylene groups and hence the CH_2 rotational phase also occurs only *after* a ring-opening phase has transpired,

but if by contrast the ringed species is only marginally stable (as in the case of the cyclopropyl cation) it is possible for the ring-breaking and CH_2 rotation phases to occur in a much more synchronous fashion. Additional distortions, such as torsion of the C_4 ring in C_4H_6 or out-of-plane bending of the central CH bond in $C_3H_5^+$ structures (which are not important in either the initial or the final stages of such isomerization processes), may also produce a lowering in the activation barriers for these reactions without altering the aforementioned conclusions regarding the minimum energy pathways followed in each case.

The effects of including CI in the *ab initio* treatment have been shown to be much less important for the reactions of the various C_3H_5 species than they are for the cyclobutene–butadiene interconversion. This result emphasizes the selectivity of the CI method, particularly with regard to the degree to which it produces a decrease in the activation energy of symmetry-forbidden processes. Since qualitative rules such as the conservation of orbital symmetry principle essentially ignore correlation effects, in general there is certainly danger that such large distinctions between different types of electrocyclic reactions will be overlooked in applying these simplified techniques. Indeed, even when CI effects are relatively small the example of the C_3H_5 radical interconversions illustrates quite clearly that symmetry-forbidden processes can proceed with activation energies which are comparable to or even lower than those characterizing allowed processes for closely related species (such as for $C_3H_5^-$, for example). When these factors are taken together with the existence of certain competing steric effects which occur in given experimental situations,[31,35] there is ample reason to conclude that a certain degree of caution must be exercised in applying the conservation of orbital symmetry principle and related qualitative theories to determine the preferred mode in a particular electrocyclic transformation.

(34) G. Greig and J. C. J. Thynne, *Trans. Faraday Soc.*, **62**, 3338 (1966); **63**, 1369 (1967).

(35) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).