manageable. Parametric methods were barely mentioned, the important preprocessing step was only lightly treated, and only one method for each approach was demonstrated. If sufficient interest is stimulated, these points will be treated in greater detail.

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The Role of Ring Torsion in the Electrocyclic Transformation between Cyclobutene and Butadiene. A Theoretical Study

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Abstract: *Ab initio* SCF and CI calculations are reported which consider the effects of ring torsion (out-of-plane deformations) upon the reaction mechanism of the thermochemically induced electrocyclic transformation between cyclobutene and butadiene. It is found that conformations with both CH_2 groups perpendicular to the plane of the four carbons are strongly resistant to out-of-plane ring deformations but that structures with planar methylene groups are subject to a significant amount of such torsional displacements. The major effect of ring torsion upon the mechanism of this reaction is to decrease the CC distance R at which CH_2 rotation becomes favored relative to the corresponding value for a constrained reaction path in which torsion is not allowed; nevertheless the main conclusion of previous calculations is left unaltered, namely, that the rotational phase of this process occurs over a very narrow range of R. The calculations also indicate that formation of *trans*-butadiene, the ultimate product of the reaction, involves the cis isomer as an intermediate rather than direct conversion as a result of *simultaneous* CH_2 rotation and ring torsion.

In a previous communication[2] *ab initio* SCF and CI potential surfaces for the C_4H_6 isomers of cyclobutene and *cis*-butadiene were reported with the aim of providing detailed information about the minimum energy path followed by these systems in a thermochemically induced electrocyclic transformation. According to this study a partial opening of the cyclobutene ring occurs prior to any rotation of the methylene groups; at a certain separation of the carbon termini rotation becomes energetically likely and only after the complete rotation has occurred is further CC stretch to the *cis*-butadiene product favored.

The calculation of a reaction surface of this nature requires a sufficiently detailed examination of the energy dependence of *each* of the geometrical parameters. Because of the large number of these quantities, however, it becomes a matter of practical necessity, regardless of the method of calculation employed, to forego the complete optimization of each of these parameters and rather to assume certain fixed relationships for some of those species which do not appear to play a critical role in the process as a whole. Thus optimal values for the CH bond lengths and the HCH angles have been assumed in I, and C_2 or C_s symmetry of the nuclear framework is maintained throughout. With these assumptions the geometry search was then carried out in a four-dimensional space spanned respectively by the CC terminal bond distance R (see Figure 1), the CH_2 rotation angle θ (planar CH_2 groups, $\theta = 0°$; perpendicular, $\theta = 90°$), the CH_2 flapping angle α, and a fourth parameter γ ascribing a fixed relationship between the two distinct internal CC bond distances (double and single bonds in the end products).

Perhaps the most tenuous of the aforementioned assumptions is that at no point in the electrocyclic reaction between cyclobutene and *cis*-butadiene does out-of-plane deformation of the carbon ring, as described by an angle φ (planar ring, $\varphi = 0°$), occur. The semiempirical valence bond calculations of van der Lugt and Oosterhoff[3] for the same systems, for example, have predicted that torsion of the ring does play an important role and *optimal* values of φ as high as 40° are calculated for small values of R (close to the cyclobutene structure). More recently *ab initio* calculations of Radom and Pople[4] and of Dumbacher[5] have indicated that *cis*-butadiene itself may favor as much as 20° torsion relative to the planar conformation. Furthermore, the results of van der Lugt and Oosterhoff indicate that torsion can have a major effect on the transformation mechanism itself. It therefore seems necessary to investigate the effects of out-of-plane ring deformation in the framework of *ab initio* SCF and CI calculations similar to those described in I to determine whether the proposed mechanism is affected by such considerations. In addition, explicit attention will be given to the HCC angle β since exploratory calculations have indicated that this parameter

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[1] (a) University of Nebraska; (b) Johannes Gutenberg Universität.

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

[3] W. Th. A. M. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969); also *Chem. Commun.*, 1235 (1968).

[4] L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

[5] B. Dumbacher, Ph.D. Thesis, Mainz, June 1970; also see *Theor. Chim. Acta*, **23**, 346 (1972).

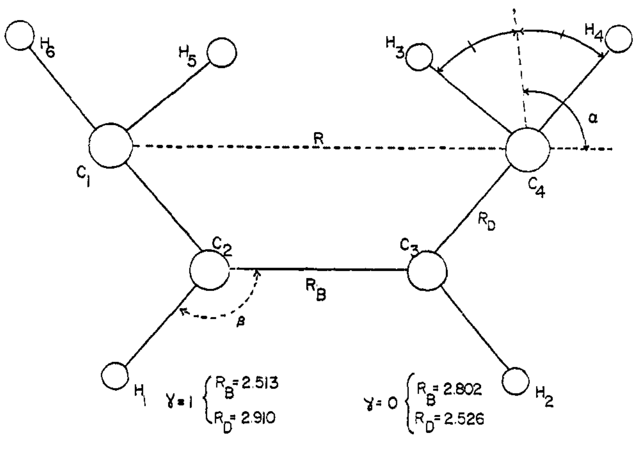

Figure 1. Definition of the reaction parameters for the cyclobutene–butadiene transformation. Not shown are the CH_2 rotation angle θ and torsion angle φ, which are defined in the text.

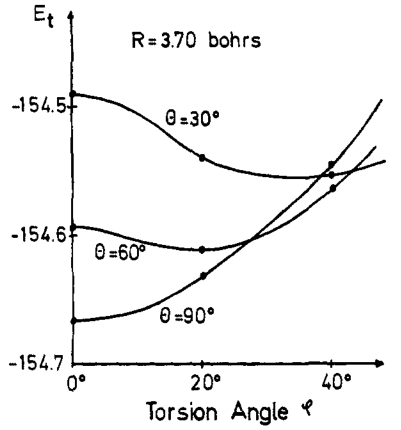

Figure 2. Total SCF energy E_t (hartree) for C_4H_6 as a function of the torsion angle φ for several values of the CH_2 rotation angle θ at R = 3.70 bohrs.

(also contrary to the assumptions made in I) may vary significantly throughout the course of the electrocyclic reaction.

Effect of Ring Torsion at Different Values of *R*

Since the influence of ring torsion upon the mechanism for the electrocyclic reaction can be expected to be of greatest importance when the two terminal carbon atoms are in close proximity to one another, the first series of calculations investigating torsion effects are carried out at a value of R = 3.7 bohrs, roughly 25% greater than the equilibrium distance in the cyclobutene ground state. The torsion angle φ and the CH_2 rotation angle θ are varied independently at the selected value of R because the work of van der Lugt and Oosterhoff[3] has suggested a strong interdependence between them. It is assumed in the present calculations that the internal CC bond distances and the flapping angle α vary linearly with θ between their respective values in cyclobutene (θ = 90°) and *cis*-butadiene (θ = 0°); details concerning the choice of geometrical parameters and the basis set employed in the calculations can be found in I.

The resulting set of potential curves (for conrotation only) is shown in Figure 2. The first and most important conclusion to be drawn from these curves is that at this R value the *absolute* energy minimum occurs, as has been stated in I, for the perpendicular (θ = 90°) arrangement of CH_2 groups and for the planar ring of carbons (φ = 0°). At the same time these results differ considerably from those of the aforementioned semiempirical calculations[3] which indicate instead that a θ value of 20° should be optimal at this distance with approximately 40° torsion.

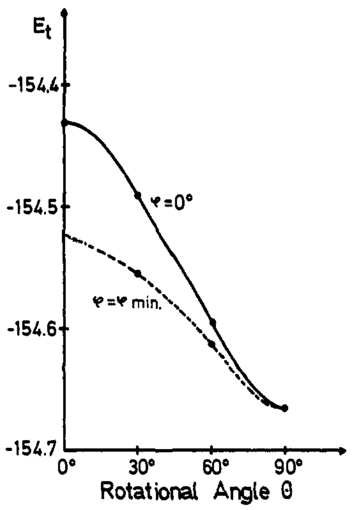

Figure 3. Total SCF energy E_t (hartree) for C_4H_6 as a function of the rotational angle θ for zero torsion (φ = 0) and the optimal torsion angle ($\varphi = \varphi_{min}$) at R = 3.70 bohrs.

On the other hand, the present calculations find that the carbon ring does become nonplanar for rotation angles less than 90°, with the optimal value of the torsion angle φ reaching approximately 20° for θ = 60°, and nearly 40° for θ = 30°. The obvious consequence is that out-of-plane ring distortion favors smaller values of the rotational angle, thereby somewhat reducing the energy barrier to rotation out of the perpendicular CH_2 conformation, at least for R = 3.7 bohrs (Figure 3). Although this effect does not alter the conclusion that at this distance the perpendicular conformation of CH_2 groups is still preferred, it does suggest that the rotational phase of the electrocyclic transformation may be initiated at a smaller separation of the terminal carbons than indicated by previous calculations in which ring torsion was not given explicit consideration.

Calculation of Optimal Potential Curves for θ = 0° and θ = 90° Conformations

In order to further investigate this possibility additional calculations have been carried out at R = 4.2 and 4.7 bohrs, respectively. For conformations with θ = 0° the effect of torsion is more important for the smaller of these two R values, as one might have expected, with the optimal value of φ changing from 52° at R = 4.2 bohrs to 40° at R = 4.7 bohrs. More significantly, the energy *lowering* obtained by allowing for ring torsion (measured relative to the corresponding φ = 0° conformation) decreases from 0.0423 hartree at 4.2 bohrs to only 0.0109 hartree at 4.7 bohrs. These results are quite consistent with those of the butadiene calculations[4,5] which indicate that at R = 5.5 bohrs and θ = 0° the energy changes brought about by ring torsion relative to the *cis*-butadiene conformation are very small.

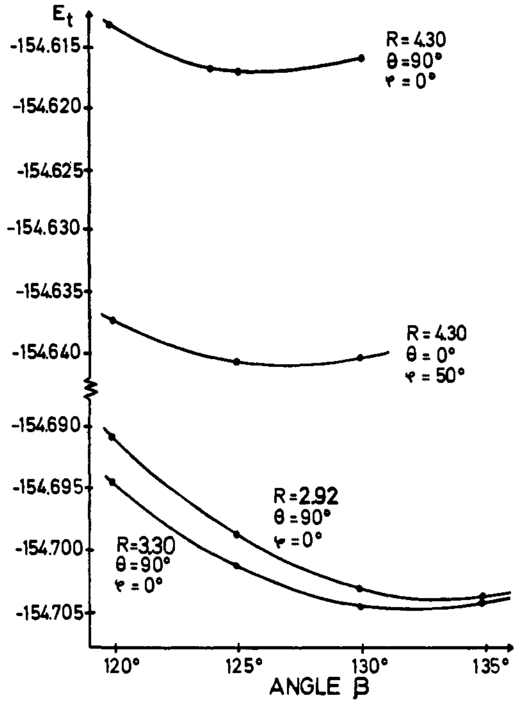

Figure 4. Total SCF energy E_t (hartree) for C_4H_6 as a function of the HCC angle β for different values of carbon termini separation R, CH_2 rotation angle θ, and torsion angle φ.

There is no indication, however, that ring torsion at larger values of R is favored for the perpendicular ($\theta = 90°$) arrangement of the CH_2 groups, In fact, at $R = 4.2$ bohrs a torsion of only 20° *increases* the SCF energy by 0.0323 hartree relative to that of the completely planar carbon ring, once again suggesting quite strongly that $\varphi = 0°$ is the optimal value as long as θ remains 90°.

Before the optimal R stretch potential curves for both $\theta = 90°$ and $\theta = 0°$ (including torsion effects) are constructed for comparison with those considered previously in I, it is important to also give explicit consideration to the change of the HCC angle β during the transformation process. This quantity has been optimized for four sets of R, θ, and φ values, namely for (2.92, 90°, 0°), (3.30, 90° 0°), (4.30, 90°, 0°), and (4.30, 0°, 50°), and the resulting SCF potential curves are given in Figure 4. It is clear from this figure that β optimization is quite important for small values of R; the optimal values of β and the energy lowerings produced by optimization relative to the value of $\beta = 120°$, which was used exclusively in I, are contained in Table I. In general it is found that the optimum value of β in a given conformation agrees quite well with that which occurs when the CH bond exactly bisects ∢CCC and, judging from the data obtained for the two conformations at $R = 4.30$ bohrs, this result appears to be independent of both θ and φ. It is therefore assumed in what follows that the optimum β depends only on R; for conformations close to the *cis*-butadiene equilibrium species ($R > 5.3$ bohrs) a fixed value of 120° is chosen for β.

Table I. Optimal Values of the HCC Angle β at Certain Values of the Torsion Angle φ, the CH_2 Rotation Angle θ, and the Distance R (in bohrs) between the Carbon Termini

R	θ	φ	β_{opt}	ΔE^a
2.92	90	0	133.4	0.0132
3.30	90	0	131.9	0.0103
4.30	90	0	127.1	0.0039
4.30	0	50	127.1	0.0037

[a] ΔE (in hartrees) is the energy lowering relative to a value of $\beta = 120°$ (SCF treatment). (All angles are given in degrees.)

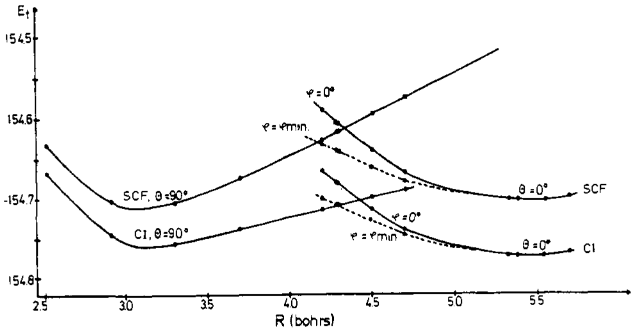

Figure 5. Potential curves (energy E_t in hartree) for planar ($\theta = 0°$) and antiplanar ($\theta = 90°$) C_4H_6 conformations for zero torsion ($\varphi = 0$) and the optimized angle of torsion ($\varphi = \varphi_{min}$) obtained from the SCF and the CI treatment; the CH_2 flapping angle α and the HCC angle β are also optimized.

The final R stretch potential curves which are obtained by optimization of the angles α, β, and φ, with θ fixed respectively at 90 and 0°,[6] are contained in Figure 5. Comparison with the corresponding potential curves for zero torsion shows quite clearly that ring deformation does become an important factor for $\theta = 0°$ conformations as R approaches small values. In particular it is found that the R value for which the $\theta = 90°$ and $\theta = 0°$ curves cross is significantly smaller than that observed when no ring torsion is allowed.

A limited CI calculation has been carried out in order to get a more realistic description of the R stretch potential curves. The treatment is essentially the same as that used in I, with the exception that somewhat larger secular equations have been solved in the present work and that selection of the configurations is based on both off-diagonal and diagonal energies. The resulting CI potential curves are also contained in Figure 5, and it is seen that in this treatment the barrier to opening of the cyclobutene ring is greatly reduced compared to its SCF value.

The CI energy lowering relative to the SCF value (Figure 6) is seen to be very dependent on the nuclear geometry; the CI treatment becomes increasingly more important for the $\theta = 90°$ conformations as R increases from its equilibrium value in cyclobutene. This effect can be understood qualitatively in terms of the energetic behavior of the σ and σ^* MO's, the latter of which is formally not occupied in the ring isomer. As ring opening proceeds the importance of the configuration in which the σ^* MO is doubly occupied in preference to the σ counterpart is enhanced because the σ MO becomes less stable with increasing R while the σ^* gains stability (see Figure 3a of ref 7). In contrast, the CI lowering for the $\theta = 0°$ conformation is relatively independent of R.

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(6) As in I it is assumed that the internal CC bond distances do not change relative to their equilibrium values in the C_4H_6 isomer possessing the same value of the rotation angle θ; *i.e.*, the the hybridization depends solely on θ.

(7) R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *J. Amer. Chem. Soc.*, **93**, 5005 (1971).

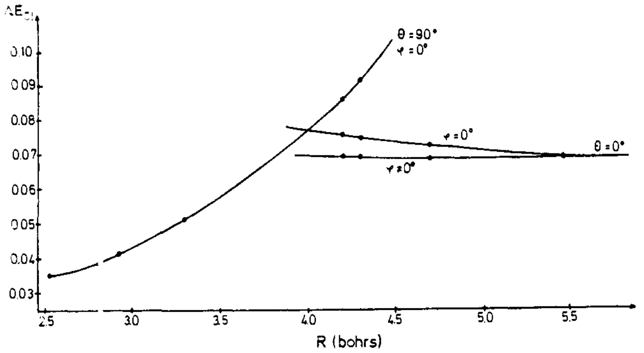

Figure 6. Energy lowering ΔE_{CI} (in hartree) due to CI relative to the corresponding SCF energy for the potential curves of Figure 5.

This effect in turn is clearly related to the fact that no bond is either broken or formed as R is decreased relative to the *cis*-butadiene equilibrium structure whereas a bond-breaking process occurs in opening the cyclobutene ring. Finally, the calculations indicate that the effect of CI is somewhat diminished upon optimization of the torsion angle φ for $\theta = 0°$ conformations.

Numerical details regarding the location of various energy minima and potential curve crossing points in Figure 5 are found in Table II. Even with optimization of β the calculations overestimate the equilibrium R value of cyclobutene. The SCF result agrees somewhat better with experiment but this would seem to result merely because of cancellation of errors; the CI method overestimates R_e by 0.08–0.10 Å and produces a slightly less sharply varying potential curve in the neighborhood of the minimum than does the SCF procedure. For *cis*-butadiene the agreement between calculated and experimental R_e values is much better, although there is of course some question about what is the experimental result in this case; the CI treatment has only a very minor effect on the shape of the R stretch potential curve in this region, as has already been discussed in connection with Figure 6.

Table II. Calculated Energy Data for Important Points of the Potential Curves in Figure 5. ΔE is Always Taken with Respect to the Cyclobutene Equilibrium Value

	R, bohrs	E, hartree[a]	ΔE, eV
	Crossing Point Data		
SCF ($\varphi = 0°$)	4.33	−0.6140	2.68
SCF ($\varphi = \varphi_{min}$)	4.18	−0.6300	2.24
CI ($\varphi = 0°$)	4.43	−0.7030	1.58
CI ($\varphi = \varphi_{min}$)	4.283	−0.7095	1.40
	Equilibrium Data		
	R_e, bohrs[b]		E, hartree[a]
Cyclobutene SCF	3.05		−0.7125
CI	3.12		−0.7610
cis-Butadiene SCF	5.48		−0.7045
CI	5.48		−0.7735

[a] Zero of energy is −154.00 hartrees. [b] Corresponding experimental values are 2.92 ["Tables of Interatomic Distances and Configurations in Molecules," *Chem. Soc., Spec. Publ.*, **No. 18** (1965)] or 2.956 bohrs [B. Bak, J. Led, L. Nygaard, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, **3**, 369 (1969)] and most likely 5.51 bohrs (ref 3).

The location of the crossing point of the R stretch potential curves for $\varphi = 0°$ varies somewhat from the value reported in I as a result of β optimization and the slight improvement in the CI procedure employed. Optimization of the torsion angle φ proves to be a substantially more important factor in locating the crossing point, causing a decrease in R of 0.15 bohrs in both the SCF and CI results. The addition of CI in the overall theoretical treatment is still seen to be the most important consideration, however, producing a lowering in the barrier to rotation of the CH_2 groups (measured from the cyclobutene equilibrium to the crossing point energy) of 1.10 eV in the $\varphi = 0°$ treatment and 0.84 eV in the calculation with optimized φ (Table II). When it is considered that the experimental activation energy for the thermal isomerization of cyclobutene[8] is only 1.4 eV, it is obvious that neither configuration interaction nor ring torsion should be ignored in the treatment of the reaction surface of an electrocyclic transformation; the present calculations indicate, however, that ring torsion plays a much more minor role in such a process than has been suggested by the aforementioned semiempirical calculations.[3]

Rotational Phase of the Electrocyclic Transformation

The calculations discussed in the preceding sections indicate that the main conclusion reached in I is still valid, namely that at a given value of R the most stable nuclear conformation possesses a θ value of *either* 90 or 0°. Even when ring torsion is taken into account in the calculation of the minimum energy path between the ground states of cyclobutene and *cis*-butadiene, it appears that only a very small change in R occurs simultaneously with the methylene rotation from 90 to 0°; the crossing point of the R stretch potential curves (Figure 5) is thus interpreted as the center of the narrow range of R values probable throughout the course of the *entire* CH_2 rotation.

A series of calculations has been carried out at 15° intervals of θ in order to obtain the potential curve for the rotational phase of the electrocyclic transformation. Since torsion is taken into account the crossing point R_T = 4.283 bohrs (Figure 5) is chosen as the fixed value of R while all other geometrical parameters are assumed to vary linearly with θ from their values at the θ = 90° and θ = 0° end points, respectively; details are given in Table III. The resulting CI potential curve for the methylene rotation is contained in Figure 7 for the conrotatory mode. The disrotatory mode has not been considered in this treatment;[9] instead rotational po-

Table III. Geometrical Parameters Corresponding to the Rotational Potential Curve in Figure 7[a]

θ	R	φ	α	β	C_1–C_2 (R_D)[b]	C_2–C_3 (R_B)[b]
0	4.283	50	57	127.2	2.526	2.802
15	4.283	42	55	127.2	2.590	2.754
30	4.283	33.5	53	127.2	2.654	2.706
45	4.283	25	51	127.2	2.718	2.657
60	4.283	17	49	127.2	2.782	2.609
75	4.283	8.5	47	127.2	2.846	2.561
90	4.283	0	44	127.2	2.910	2.513

[a] All angles are given in degrees, all distances in bohrs. [b] For notation see I.

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(8) W. P. Hauser and W. D. Walters, *J. Phys. Chem.*, **67**, 1328 (1963).

(9) Nuclear conformations associated with the disrotatory mode under conditions of ring torsion contain no nontrivial symmetry

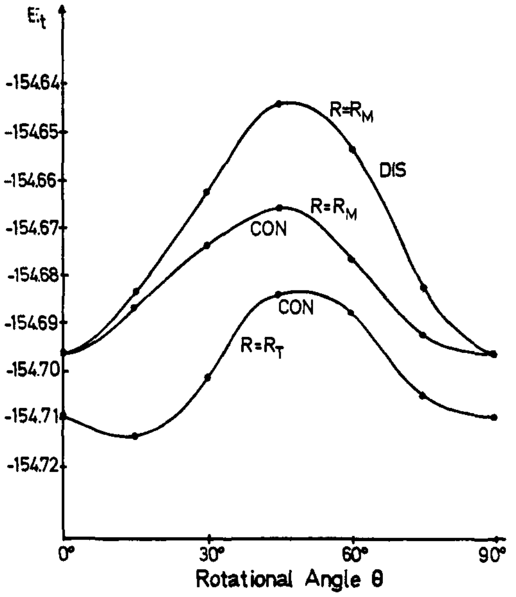

Figure 7. Total energy E_t (hartree) of C_4H_6 as a function of the CH_2 rotation angle θ obtained from the CI calculations. The lower curve is for the conrotatory mode at $R = R_T$ taking torsion into account (geometrical parameters are contained in Table III); the upper curves are for zero torsion at $R_M = 5.46$ bohrs and for both the dis- and conrotatory mode of rotation.

tential curves for both modes under the assumption of zero torsion (at $R_M = 4.47$ bohrs) are included in the figure for comparison.

The most interesting feature of the present conrotation curve is the fact that it possesses a minimum for θ away from 0° (at approximately $\theta = 14°$); no such complication is observed in the case of the conrotation curve without torsion.[10] This finding is of course an exception to the previous supposition that at a given R value either a $\theta = 90°$ or $\theta = 0°$ conformation is most stable. On the other hand, the minimum in this curve is still only 0.0043 hartree (less than 3 kcal/mol) below the two equal end points, and therefore such a result clearly requires only a minor change in the proposed reaction mechanism. Thus the present calculations suggest that (a) methylene rotation becomes favorable at a slightly smaller value of R than R_T (see Figure 5), (b) rotation does not proceed directly from $\theta = 90°$ to $\theta = 0°$ but rather to a value of about 15° at which point a torsion angle of approximately 45° is optimum, and finally (c) further R stretch occurs with *gradual* reduction of both the torsion and rotation angles. The mechanism still retains its basic stepwise character, with by far the greater part of the methylene rotation occurring with essentially no change in the distance between the carbon termini.

The finding that the conformations at small θ are subject to a significant amount of torsion coupled with the fact that the ultimate product in such thermal isomerizations is the trans isomer ($\varphi = 180°$) and not the cis conformation raises at least one more question as to whether the reaction does not proceed *directly* to *trans*-butadiene. In the region of R_T (at $R = 4.2$ bohrs to be exact), however, the calculations indicate that the cis isomer (or at least a slightly nonplanar conformation with this R value) is involved since the energy is observed to increase 11 kcal/mol when φ is varied from its optimum value of 52 to 90° (for the trans conformation, of course, $\varphi = 180°$). Thus the barrier to cis–trans isomerization is *at least* 11 kcal/mol at these relatively small R values, about three times larger than that for equilibrium butadiene.[4,5] Statistically, energy differences of this magnitude do not rule out the possibility that methylene rotation and complete torsion do not occur simultaneously, but it appears much more probable that the two processes occur at decidedly different values of R, that is, that cyclobutene is first converted to *cis*-butadiene by means of a stepwise mechanism and that this species then equilibrates by means of a torsional displacement with its trans isomer.

Finally, it should be pointed out that even though the present calculations have not attempted to obtain a comparison of the barriers to con- and disrotation, respectively, the results of I, which neglect torsion effects, should represent a fairly accurate estimate of the energy difference between the two barrier heights. Experimentally[11] this quantity has been estimated to lie between 10 and 15 kcal/mol, in very good agreement with the CI result of 0.59 eV or 14 kcal/mol. The SCF method, on the other hand, gives a much worse result (50 kcal/mol) because of its poor representation of the disrotatory ground state.[12] It is important to note that this deficiency is shared by various semiempirical methods (at least those which employ a single configuration wave function) and this fact probably explains to a large extent why such techniques have led to large overestimations of the relative stability of one rotational mode over the other in thermal transformations. The valence bond calculations of van der Lugt and Oosterhoff,[3] for example, find the disrotatory barrier height to be about 100 kcal/mol above that of conrotation; the CNDO calculations of Archard[14] find a similar value (90 kcal/mol). The deficiency in single configuration treatments is of course not restricted to the present situation; the ethylene rotational barrier, for example, is also greatly overestimated unless CI is introduced[4,15] and the calculation of the binding energies of most diatomic molecules is well known to be unsatisfactory in any single configuration treatment.

Summary and Conclusion

Energy relationships found in the present CI treatment among the equilibrium forms of cyclobutene, *cis*- and *trans*-butadiene, and various activated complexes are given in Table IV. The top of the barrier to the electrocyclic transformation corresponds to a rotation angle of $\theta = 48.5°$; values for the other corresponding geometrical parameters can be estimated by linear interpolation from Table III. The total barrier height is 0.7 eV

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elements. Among other things this fact implies that orbital symmetry is *formally* conserved in such a process, but of course it still seems extremely probable that the conrotatory mode is calculated to have the lower barrier height even when the limit of zero torsion is not maintained.

(10) It should be noted that once the carbon ring undergoes torsion there is no longer a plane of symmetry at $\theta = 0°$ for the rotational potential curve and thus no requirement of an extremum at this value of the rotational angle.

(11) O. L. Chapman, private communication.

(12) The wave function for the disrotated species at the top of the barrier is inherently a two-configuration species, as has been pointed out earlier by Longuet-Higgins and Abrahamson,[13] and can therefore not be described well in the SCF (single configuration) approach.

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

(14) F. Archard, Thèse, L'Université de Bordeaux, 1971.

(15) R. J. Buenker, S. D. Peyerimhoff, and H. L. Hsu, *Chem. Phys. Lett.*, **11**, 65 (1971).

Table IV. Tabulation of Pertinent Energy Values Obtained from the CI Calculations and Comparison with Corresponding Experimental Values[a]

	E_t, hartrees	ΔE, eV	Exptl, eV
Conrotatory maximum ($\theta = 48.5°$)	−154.6833	2.114	1.4[b]
Crossing point R_T ($\theta = 0°$ and $\theta = 90°$)	−154.7095	1.401	
Cyclobutene (calculated equilibrium)	−154.7610	0.0	0.0
cis-Butadiene (calculated equilibrium)	−154.7735	−0.34	−0.40[c]
trans-Butadiene (calculated equilibrium)	−154.7798	−0.51	−0.50[d]

[a] ΔE is always with respect to the calculated cyclobutene ground-state energy. [b] Reference 8. [c] G. Feler, *Theor. Chim. Acta*, **12,** 412 (1968). A value of approximately 20 kcal (0.86 eV) is quoted by W. G. Dauben, 13th Chemistry Conference of the Solvay Institute, Interscience, New York, N. Y., 1967, p 171; a value of about 15 kcal (0.65 eV) is estimated by R. Srinivasan, *J. Amer. Chem. Soc.*, **84,** 4141 (1962), for the corresponding energy difference of dimethylcyclobutene and dimethylbutadiene. [d] The difference between the energies of *trans*- and *cis*-butadiene is 2.3 kcal/mol according to J. G. Aston, G. Ssasz, H. W. Wooley, and F. G. Brickwedde, *J. Chem. Phys.*, **14,** 67 (1946), and 1.7 ± 0.5 kcal/mol according to E. B. Reznikova, V. I. Tulin, and V. M. Tatevskii, *Opt. Spektrosk.*, **13,** 200 (1962).

greater than the activation energy of this reaction,[8] roughly a 50% overestimation of this quantity.

Once it is realized that the CI calculations considering excitations from only the highest four orbitals (out of 15 altogether) to the lowest four MO's is still successful in lowering the R stretch part of the barrier by 0.84 eV relative to the SCF result, there seems a good possibility that a major portion of the 0.7-eV discrepancy could be eradicated by use of a larger CI to better balance the correlation energy difference between equilibrium cyclobutene and the perpendicular prerotation conformation. Part of this discrepancy is no doubt also caused by the use of a relatively limited AO basis in the present theoretical treatment. The purely rotational part of the barrier (at least in the conrotatory case) is much more adequately represented by the method used, but some reduction is clearly possible by explicitly optimizing such geometrical parameters as α, φ and γ (*i.e.*, internal CC distances) rather than simply assuming their linear variation with θ. It is also worth pointing out in this connection that the measured activation energy should be compared strictly to the energy difference between vibrational levels rather than to the separation between the absolute minimum and the maximum in the calculated potential curves; consideration of the zero-point vibrational energy in cyclobutene and the possibility of tunnelling in reaching the postrotation conformation near the top of the barrier would tend to lower the present calculated value for the activation energy. These considerations would seem to be of relatively minor importance, however, in comparison with the effects resulting from the use of only a limited CI and the foregoing of a complete optimization of geometrical parameters in the rotational phase of the reaction.

Another interesting aspect to Table IV is the good agreement found between calculated and experimentally determined relative stabilities of the equilibrium participants in this electrocyclic transformation. Once again it is found that the CI method is crucial in obtaining these results; the SCF method by itself, for example, actually predicts cyclobutene to be more stable than *cis*-butadiene by 5 kcal/mol (Table II).[16]

In conclusion, the present *ab initio* SCF and CI calculations find that even after optimization of the torsion angle φ and the HCC angle β is considered, the basic conclusion obtained in I concerning the mechanism for the concerted electrocyclic transformation of cyclobutene and *cis*-butadiene is left essentially unaltered. Torsion definitely helps to stabilize $\theta = 0°$ conformations at small values of R, thereby decreasing the amount of ring opening which must occur before the actual rotation is initiated. The fact that previous semiempirical valence bond calculations have predicted that the rotational phase of the reaction takes place for R values not greatly removed from the cyclobutene equilibrium separation (indeed they do not find cyclobutene to be bound with respect to R stretch) is quite possibly a consequence of assuming sp^2 hydridization at the termini for both butadiene *and* cyclobutene. More recent semiempirical calculations by Archard,[14] which do not employ this assumption, have also arrived at a stepwise mechanism for this reaction, although torsion has not been given explicit consideration in this study either.

The mechanism indicated by the present calculations does differ from that found in I in that it attributes a nonzero rotational angle ($\theta = 15°$) to the postrotation conformation, in addition to a ring torsion angle of 50°. The torsion barrier to the trans conformation, however, is *at least* 10 kcal/mol, *i.e.*, substantially higher than that observed (and calculated[4]) for the isomerization of *cis*- to *trans*-butadiene, and thus it seems most likely that the cis isomer *is* an intermediate in this reaction, although direct conversion at the rotation point is certainly a possibility. In stretching from the postrotation conformation the calculations indicate that the torsion angle φ (and probably also the CH_2 rotation angle θ) decreases fairly rapidly in the formation of the cis isomer.

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(16) The difference in the effectiveness of the CI on the two systems again can be understood qualitatively in terms of simple MO theory. Butadiene possesses *two* pairs of relatively unstable occupied and stable unoccupied species (χ_1 and χ_4, χ_2 and χ_3) whereas cyclobutene at equilibrium possesses only one (π and π^*) which makes CI less effective for this system than for butadiene.