stable species on the potential energy surface of CH_3O^{2+}· dications is not questioned by the result. It should also be mentioned that in line with the theoretical results, neither spontaneous nor collision-induced dissociation of CH_3O^{2+}· dications to either CH_2^+·/OH^+ and HC^+/H_2O^+· (eq 3 and 4, Scheme I) has been observed.

An MC–SCF Study of the Thermal Cycloaddition of Two Ethylenes

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Abstract: The transition structure region of the reaction of two ethylenes to form cyclobutane has been investigated in detail by ab initio molecular orbital methods. The calculations have been performed at the MC–SCF level with minimal (STO-3G) and extended (4-31G) basis sets. The various critical points have been fully optimized with MC–SCF gradients and characterized by computing the corresponding hessian matrices. On examination of the "forbidden" concerted supra–supra reaction path, it was found that no true transition structure exists: the critical points involved are, in fact, second-order saddle points. The concerted supra–antara approach was found to proceed via a very high energy transition state. The favored pathway is thus found to involve a stepwise approach proceeding via a gauche or trans tetramethylene diradical intermediate and involving corresponding fragmentation transition states.

I. Introduction

The thermal cycloaddition of two ethylenes is one of the "textbook" examples used in the illustration of the Woodward–Hoffmann rules[2] of orbital symmetry control in concerted reactions and is an example of a concerted thermally forbidden reaction. Thus the topology (i.e., the number and nature of the stationary points) of this surface is of considerable interest. Because orbital symmetry is not conserved for the $[2_s + 2_s]$ concerted reaction, one expects a sharply avoided crossing in the region of the transition state which cannot be described at the SCF level. For the nonconcerted process the transition states and intermediate minima will correspond to diradicaloid species which also require computational methods which transcend the SCF method.

The objective of the present work is to characterize the structure and nature of the critical points on the potential energy surfaces for the $[2_s + 2_s]$, the $[2_s + 2_a]$, and the nonconcerted approaches at the same level of computational accuracy. The use of MC–SCF gradient methods developed previously[3,4] should permit a reliable determination of the features of the full energy surface because diradicaloid structures and closed-shell species can be described with a similar degree of accuracy. On the other hand, this computational approach is not expected to provide an accurate treatment of the energetics of the reaction, which will probably

Scheme I
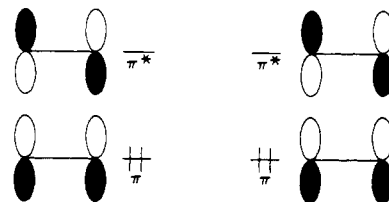
require dynamic correlation and large basis sets.

Previous calculations on the topology of this reaction have not been conclusive. Wright and Salem[5] have located a transition state for the $[2_s + 2_s]$ process using an STO-3G[6] basis with 2 × 2 CI (HOMO-LUMO); however, only partial geometry optimization was performed, and a detailed study of the nature of the Hessian matrix was not performed. Segal[7] has investigated the nonconcerted approaches using an SCF treatment at the STO-3G level followed by a 15-dimensional CI and has found that the tetramethylene diradical is a thermodinamicaly stable species existing in two stable conformations, a gauche and a trans.

Doubleday et al.[8] have questioned this finding on the basis of results obtained with a 2-configuration MC–SCF wave function at the extended 3-21G[9] level and have suggested that only the trans

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(9) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980,** *102,* 939–947.
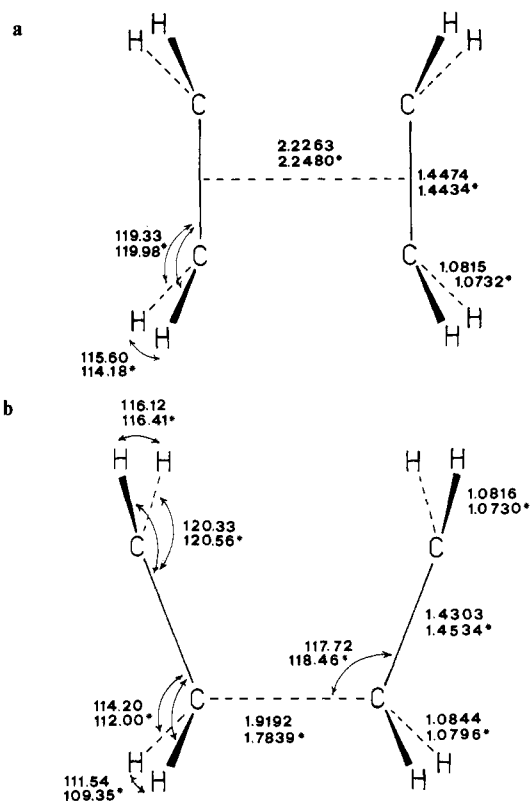
Figure 1. Optimized geometries computed at MC–SCF/STO-3G (no superscript) and MC–SCF/4-31G (asterisk) for (a) the reactangular (D_{2h}) and (b) the coplanar (C_{2v}) second-order saddle points.

conformer of the tetramethylene diradical is a minimum. More recently, Doubleday et al.[10] have re-examined this problem using a 3-21G basis and a 20-configuration MC–SCF wave function and have concluded that there are no minima in the diradical region of singlet tetramethylene.

II. Methods

The calculations reported in this paper have been carried out at the MC–SCF level with minimal (STO-3G) and extended (4-31G[11]) basis sets. The various critical points have been fully optimized with MC–SCF gradients.[3] Integral and derivative calculations have been performed with the GAUSSIAN 80 series of programs.[12] The CI and MC–SCF codes are described in ref 13 and 14.

The CI wave function, ψ, used in the MC–SCF approach is a linear combination of configuration state functions, φ_K.

$$\psi = \sum c_K \varphi_K$$

The orbitals occurring in the φ_K are classified as (i) core orbitals which are doubly occupied in all configurations, (ii) valence orbitals, which have all possible occupancies in the φ_K; and (iii) virtual orbitals, which are unoccupied in all configurations. The set of configurations constitutes a full valence shell CI, and hence the energy is invariant to a transformation of the valence orbitals among themselves. The MC–SCF energy is optimized with respect to core–valence, core–virtual, and valence–virtual mixing as well as with respect to the CI coefficients.

For the addition of two ethylenes, the molecular orbitals can be constructed from the non-interacting ethylenes. In the present study we have selected the two π orbitals (π and π^*) of each ethylene for the valence space (see Scheme I).

This choice is appropriate for the motions investigated here since it allows proper dissociation of tetramethylene into two ethylenes and also permits the correct description of a diradicaloid intermediate or transition

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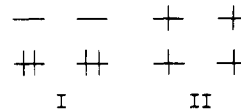
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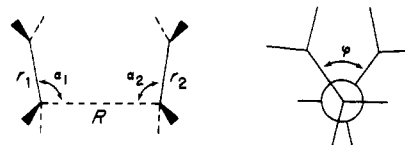
Scheme II

Scheme III

Table I. Total Energy Values (E, au) and Energy Differences (ΔE, kcal/mol) of the Critical Points in the Region of the Transition State for the Addition of Two Ethylenes

critical point[a]	STO-3G		4-31G	
	E	ΔE^b	E	ΔE^b
[2_s + 2_s] rectangular SOSP (D_{2h}) (Figure 1a)	−154.1273	30.58	−155.7830	25.99
[2_s + 2_s] coplanar SOSP (C_{2v}) (Figure 1b)	−154.1661	16.21	−155.8096	9.29
[2_s + 2_a] TS (C_2) (Figure 2)	−154.0929	61.75		
gauche fragmentation TS (Figure 3b)	−154.1730	11.88	−155.8203	2.57
trans fragmentation TS (Figure 4b)	−154.1751	10.58	−155.8238	0.38
Gauche M (Figure 3a)	−154.1895	1.55	−155.8213	1.95
trans M (Figure 4a)	−154.1914	0.0	−155.8244	0.0
gauche–trans TS (Figure 5a)	−154.1868	3.21		
gauche-cyclobutane TS (Figure 5b)	−154.1814	6.27		

[a] M denotes a minimum, TS a transition state, and SOSP a second-order saddle point. [b] Relative energies to the trans minimum in kcal/mol (for the STO-3G and 4-31G basis this point is 26.16 and 51.27 kcal/mol above two ethylenes).
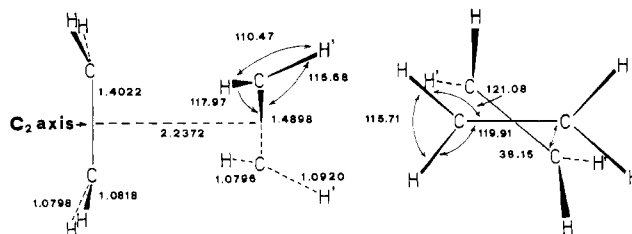

Figure 2. Optimized geometry computed at MC–SCF/STO-3G for the supra–antara first-order saddle point (C_2).

structure. In this valence space a complete CI for the singlet state has 20 configurations.

With the valence space defined above, we have investigated the following reaction paths which are expected to be relevant on the basis of either the Woodward–Hoffmann rules or previously ab initio computations: (i) [2_s + 2_s] supra–supra approach; (ii) [2_s + 2_a] supra–antara approach; and (iii) nonconcerted approaches (i.e., gauche and trans approaches).

In some cases we have also performed an analysis of the surface in terms of diabatic components.[15,16] For this purpose we have carried out a CI analysis of the various approaches, using the orbitals obtained in the MC–SCF calculations at 20 Å. The adiabatic surface corresponding to the full CI expansion has been decomposed into two diabatic surfaces, one associated with configuration I (see Scheme II) plus all related one-electron charge-transfer configuratons (packet A) and the other associated with configuration II plus related one-electron charge transfers (packet B).

Configuration I is the reactant configuration and involves the singlet state of the two interacting ethylenes, while configuration II, the product configuration, correlates at infinite separation with the triplet states of the two ethylenes with the overall spin coupled to a singlet. With four unpaired electrons there is the possibility of coupling two pairs in two

(15) Bernardi, F.; Robb, M. A. *Mol. Phys.* **1983**, *48*, 1345–1355.
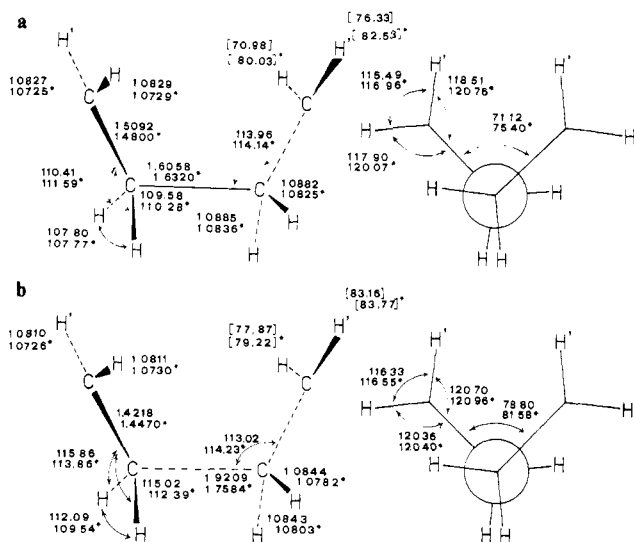(16) Bernardi, F.; Robb, M. A. *J. Am. Chem. Soc.* **1984**, *106*, 54–58.

Figure 3. Optimized geometries computed at MC–SCF/STO-3G (no superscript) and MC–SCF/4-31G (asterisk) for the tetramethylene gauche minimum (a) and fragmentation transition state (b); the values in brackets are the dihedral angles HCCC and H'CCC.

singlets and then coupling the result to an overall singlet or coupling first to two triplets then to a singlet. The packet II contains both possibilities but is dominated by the triplet–triplet coupling.

III. Results and Discussion

The critical points located in the transition-state region of the surface for the addition of two ethylene molecules to form cyclobutane are summarized in Table I (energetics) and Figures 1–5 (geometries). In Table I the energies of the critical points are also given relative to the energy of the trans tetramethylene diradical minimum. At the STO-3G and 4-31G levels this minimum lies 26.16 and 51.27 kcal/mol respectively above the value for two ethylenes; therefore, such energy differences are strongly basis set dependent. The notation used for the internal coordinates is given in scheme III.

1. [2$_s$ + 2$_s$] and [2$_s$ + 2$_a$] Approaches. Two different types of [2$_s$ + 2$_s$] approach have been investigated: (i) a rectangular coplanar approach in which the two forming C–C bond distances are constrained to be equal and (ii) a coplanar approach where the constraint of two equal C–C distances is relaxed. In the former approach i the D_{2h} symmetry is preserved and in the latter approach ii the symmetry is reduced to C_{2v}. In our search for transition structures, we have found a critical point for each approach. However, in each case one finds that the hessian has two negative eigenvalues (for a "true" transition state the hessian can have only one negative eigenvalue). We shall refer to such a critical point as a "second-order saddle point". The physical significance of a second-order saddle point is quite simple: the energy is a maximum in two coordinates (as opposed to one for a first-order saddle point corresponding to a transition state). Further, the direction that corresponds to one of the negative eigenvalues will preserve the symmetry of the geometrical structure corresponding to the critical point, whereas the second negative eigenvalue corresponds to a direction which will break the symmetry. Such second-order saddle points have no chemical significance; however, in the present case, there is some theoretical interest in these points since they lie on the forbidden concerted pathway. Both [2$_s$ + 2$_s$] second-order saddle points lie considerably higher in energy than the region of the tetramethylene diradical.

The geometrical parameters for the two second-order saddle points computed at the STO-3G and 4-31G levels are given in Figure 1. At the STO-3G level both these critical points have been characterized by computing the related hessian matrices for the full set of internal coordinates, excluding those associated with the stretching and bending of the C–H bonds. The lower negative eigenvalue of the hessian matrix in each second-order saddle point is clearly associated with a transition vector connecting two
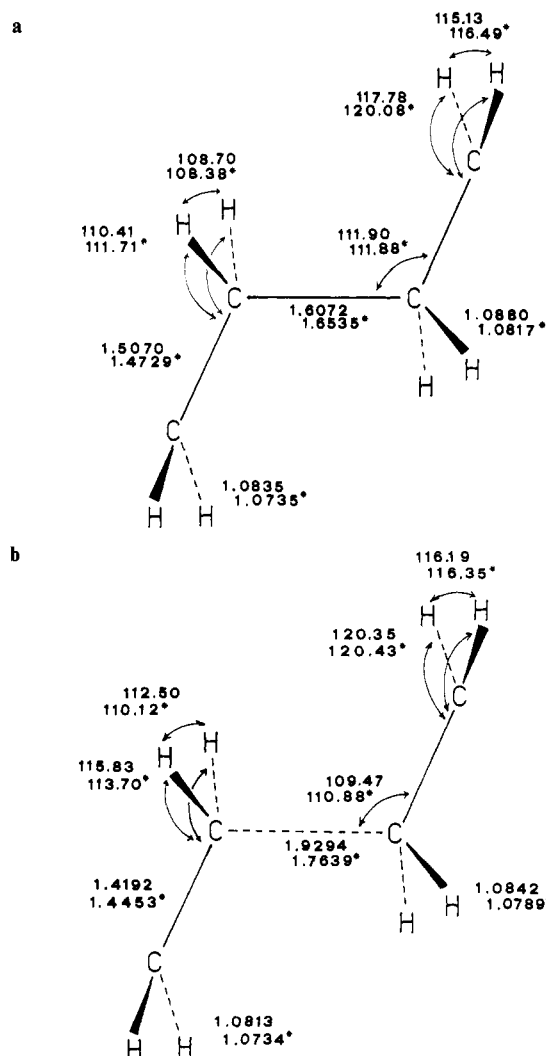

Figure 4. Optimized geometries computed at MC–SCF/STO-3G (no superscript) and MC–SCF/4-31G (asterisk) for the tetramethylene trans minimum (a) and fragmentation transition state (b).
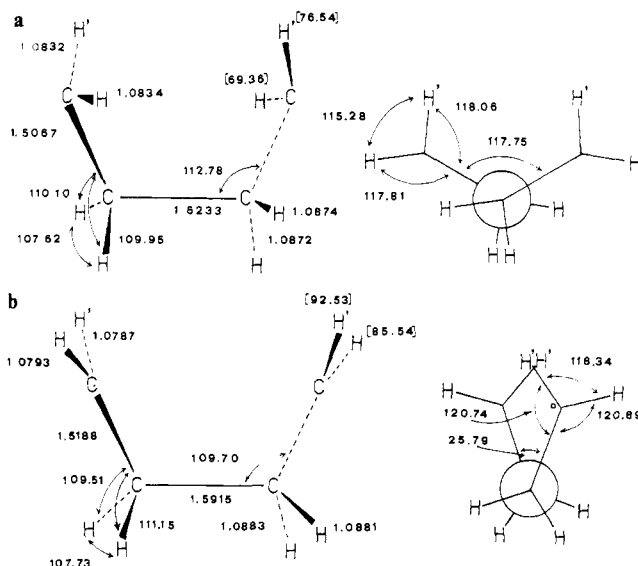

Figure 5. Optimized geometries computed at MC–SCF/STO-3G for the gauche–trans transition state (a) and for the *gauche*-cyclobutane transition state (b); the values in brackets are the dihedral angles HCCC and H'CCC.

ethylenes with cyclobutane. In contrast, the second negative eigenvalue in the case of the rectangular second-order saddle point

(D_{2h} symmetry) is associated with the motion which distorts the
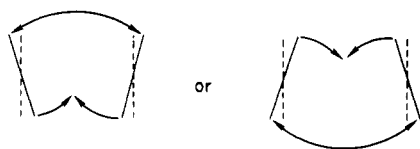
symmetry from D_{2h} and clearly leads to the coplanar C_{2v} second-order saddle point. For the latter the second negative eigenvalue of the hessian matrix corresponds to the $C_1C_2C_3C_4$ dihedral angle φ and motion along this coordinate leads to the gauche fragmentation transition state (which has C_2 symmetry).

These results indicate that a concerted supra–supra reaction path does not exist in the case of two ethylenes. This is in contrast with Wright and Salem[5] who have found a transition state along a rectangular coplanar approach; however, they considered only the CC bonds in ethylene and the separation between the ethylenes in the optimization.

A transition state has been found for the other possible concerted process $[2_s + 2_a]$. At the STO-3G level, this critical point is 62 kcal/mol above the tetramethylene trans minimum and clearly indicates that this approach is very unfavorable. Thus we have not extended the calculation to the 4-31G level. The optimized geometrical parameters are given in Figure 2. In this case the diagonalization of the hessian matrix, computed for the full set of internal coordinates, shows only one negative eigenvalue. The associated eigenvector is dominated by the interfragment distance between the two ethylenes.

2. Gauche and Trans Approaches. The region of the tetramethylene diradical is characterized by gauche and trans minima and by gauche and trans fragmentation transition states. These critical points have been optimized at both the STO-3G and 4-31G levels. The energy differences between these points are very small, particularly at the 4-31G level (see Table I). The geometrical parameters are given in Figures 3 and 4.

For both minima, at the STO-3G level, we have computed the second derivative matrix by finite difference in the subspace consisting of R, r_1, r_2, α_1, α_2, and φ (i.e., excluding the coordinates associated with the methylene groups). In both cases the diagonalization of this matrix showed all positive eigenvalues. These computed second-derivative matrices were updated numerically during the 4-31G geometry optimizations. Diagonalization of this updated second-derivative matrix showed again all positive eigenvalues for both conformers. As a final check, some second derivatives were recomputed numerically at the 4-31G level: in particular, in the case of the gauche conformer, the same subspace of internal coordinates was used. For the trans, only the second derivative for R was recomputed and found to have a positive sign.

A similar procedure has been used also for characterizing the two fragmentation transition states. In both cases the diagonalization of either the second-derivative matrices computed by finite difference at the STO-3G level or the updated second-derivative matrices at the 4-31G level showed only one negative eigenvalue.

Therefore the present results indicate that there are two local minima for the tetramethylene diradical corresponding to a gauche and a trans geometry, in agreement with the CI results of Segal.[7] On the other hand, Doubleday et al.[9] find no minima in the region of the tetramethylene diradical. However, because the computed barriers to fragmentation are very small, particularly at the 4-31G level (less than 1 kcal/mol), one must conclude, in agreement with Doubleday et al., that the high-temperature thermochemistry of such a reaction will not be influenced by such small dips in the potential surface.

A comparative analysis of the structures given in the Figures 1, 3, and 4 shows that, while most of the geometrical parameters do not change significantly in passing from the STO-3G to the 4-31G basis, the interfragment C–C distance (R) for the fragmentation transition states is very different in the two bases. The interfragment C–C distances at the STO-3G and 4-31G levels are respectively 1.92 and 1.78 Å for the coplanar $[2_s + 2_s]$ critical
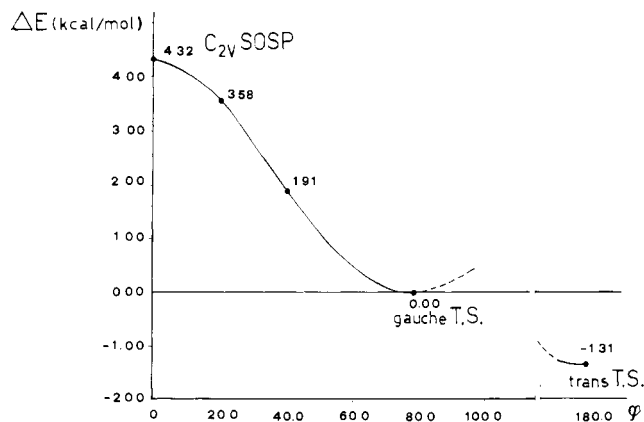

Figure 6. Cross section of the energy hypersurface along the torsional angle φ.
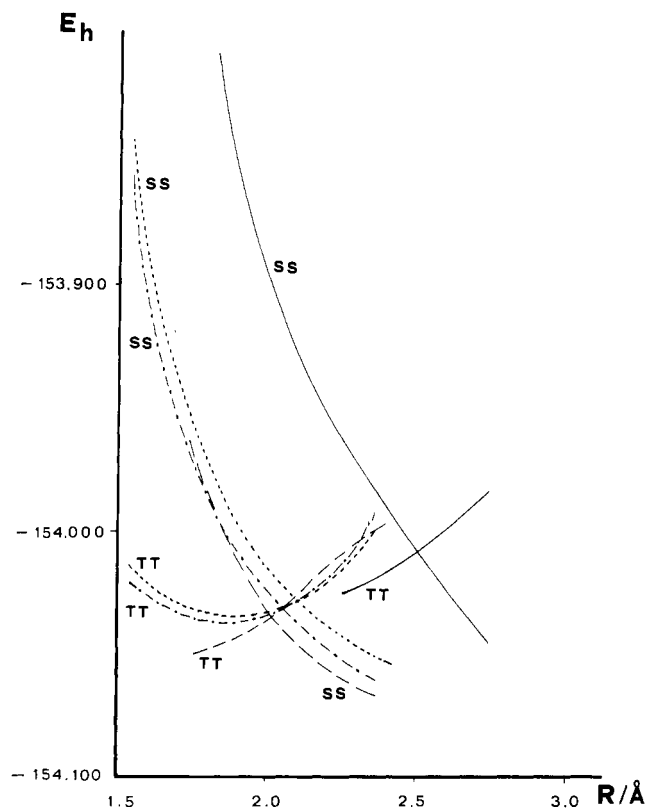

Figure 7. Cross section of the diabatic curves associated with packet A (singlet–singlet SS) and B (triplet–triplet TT) for (i) the D_{2h} rectangular $[2_s + 2_s]$ (—), (ii) the coplanar C_{2v} (···), (iii) the gauche (–·–) and (iv) the trans (- - -) approach.

point, 1.92 and 1.76 Å for the gauche transition state, and 1.92 and 1.76 Å for the trans transition state. In contrast, the corresponding C–C distances for the gauche minimum are 1.61 and 1.63 Å, respectively, and for the trans minimum 1.61 and 1.65 Å, respectively. Furthermore, the barriers to fragmentation are reduced from approximately 10 kcal/mol at the STO-3G level to less than 1 kcal/mol at the 4-31G level.

In the tetramethylene surface we have found two other transition states, one connecting the trans and gauche minima and the other along the path connecting the gauche minimum to cyclobutane. Both these transition states have been optimized only with the STO-3G basis set. On the basis of the previous results, the STO-3G level seems to provide reliable description of critical points with short interfragment C–C distances. The structure of the transition state connecting the gauche and trans minima given in Figure 5a is very similar to that of the minima (except for the value of the dihedral angle φ). The geometry of the *gauche*-cyclobutane transition state is given in Figure 5b. The main

geometrical change is again associated with the dihedral angle φ, which becomes quite small (40°). Another interesting feature is the planarization of the two methylene centers and the decrease of the CCC angles. Both the barrier between the trans and gauche minima and that between the gauche minimum and cyclobutane are very low (1.69 and 5.08 kcal/mol relative to the gauche minimum at the STO-3G level).

One of the most interesting observation is that the interfragment C–C distance (R) is almost the same for the $[2_s + 2_s]$ coplanar (C_{2v}) second-order saddle point and the gauche and trans fragmentation transition structures. Thus these three structures lie on a "ridge" that separates reactants and products. Figure 6 illustrates the energy profile of this ridge along φ. The curve shows two minima corresponding to the gauche and trans fragmentation transition structures. Thus the main feature for the addition of two ethylene is that the surface is divided into two parts by a ridge occurring at an almost constant value of R (1.92 and 1.76 Å at the STO-3G and 4-31G levels, respectively) for all values of φ.

The origin of this ridge is associated with the intersection of the two diabatic surfaces corresponding to packets A and B. As previously defined, packet A involves configuration I (see Scheme II) plus all related one-electron charge-transfer configurations and packet B configuration II plus all related one-electron charge-transfer configurations. In Figure 7 the behavior of these diabatic curves is shown for the $[2_s + 2_s]$ coplanar, the gauche, and the trans approaches. The computations have been performed at the STO-3G level with the optimized geometries of the corresponding second-order saddle points and transition states. In all cases there is a crossing between the two diabatics, which are associated one with two closed-shell ethylenes and the other with two triplet ethylenes coupled to a singlet. In the same figure we have also shown the behavior of the two diabatic curves for the $[2_s + 2_s]$ rectangular approach, where the crossing occurs at a larger value of the interfragment distance, in agreement with the results of the geometry optimization.

The other critical points associated with the tetramethylene diradical region, i.e., the gauche and trans minima, the gauche-trans transition state, and the *gauche*-cyclobutane transition state, all lie on the side of the ridge dominated by the diabatic surface associated with packet B. Therefore, the gauche–trans and the *gauche*-cyclobutane transition states originate from conformational effects, while the gauche and trans fragmentation transition states originate from the crossing of the two diabatic surfaces.

IV. Conclusions

In this paper we have presented a detailed ab initio study at the MC–SCF level of the transition-structure region of the reaction of two ethylenes to form cyclobutane.

On examination of the concerted supra–supra approach it was found that no transition structure exists. Rather, one finds only second-order saddle points which have no chemical significance and thus the concept of a forbidden concerted pathway is without foundation. The other concerted pathway corresponding to a $[2_s + 2_a]$ approach is inaccessible energetically, since it involves a very high energy transition state. Thus the favored pathway involves a stepwise approach with a diradical intermediate. In this case both a gauche and a trans approach are possible. We have found gauche and trans intermediates and corresponding fragmentation transition structures with small barriers to fragmentation, particularly at the 4-31G level.

There is a ridge separating reactants and products, which is associated with the intersection of two diabatic surfaces, one corresponding to two closed-shell ethylenes and the other to two triplet ethylenes coupled to a singlet. The tetramethylene diradical fragmentation transtition structures and the coplanar C_{2v} second-order saddle point lie on this ridge, while the other critical points associated with the tetramethylene diradical lie all on the side of the ridge dominated by the diabatic surface associated with the two triplet ethylenes coupled to a singlet.


Transition-State Modeling in Acyclic Stereoselection. A Molecular Mechanics Model for the Kinetic Formation of Lithium Enolates

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Abstract: As the initial phase of a study of the aldol condensation, molecular mechanics was used to calculate the energies of model transition states for the formation of cis and trans enolates from a number of ketones and esters. Regression analysis was used to correlate these energies with the corresponding experimentally determined cis:trans enolate ratios reported in the literature for kinetic deprotonation with LDA in THF or in THF:HMPA mixtures at −70 °C. An analysis of the regression equations allowed some comparisons to be made between the geometries of the models and that of the actual transition state. This analysis strongly suggests that the transition state leading to the cis isomer is destabilized by a steric interaction with the base, thus supporting the concept of a cyclic transition state. That this interaction is greatly diminished in the presence of HMPA suggests that the transition state is much more loosely organized in this solvent. The correlation equations can be used to quantitatively predict the cis:trans enolate ratios which would be expected from the kinetic deprotonation of simple ketones and esters with LDA in THF or THF:HMPA mixtures at −70 °C.

Acyclic stereoselection has become an extremely active field of research in recent years and is an increasingly useful synthetic technique.[1] Of the numerous reactions studied in this area, the aldol condensation and its variations have perhaps been the most heavily utilized.[2,3] Since the stereoselectivity of a reaction often
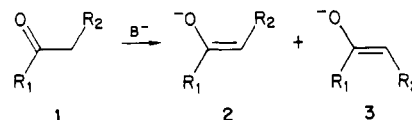
results from a subtle balance of many factors, an understanding of the factors governing a given reaction is essential for its full

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