of the AMBER/OPLS results and the small errors for the charged residues are particularly reassuring.

Overall, these results provide important support for the quality of both force fields, though some increases in the root-mean-square deviations may be anticipated with more complete convergence. In fact, the minimization with AMBER/OPLS was extended to 1978 cycles at which point the gradient was 0.495 and the root-mean-square deviation for the protein atoms had only increased to 0.22 Å. Further testing of both force fields in molecular dynamics simulations for proteins in water is planned.

Conclusion

A wide range of computations on organic liquids, dilute aqueous solutions, hydrogen bonding, and ion–water complexes has provided a set of functions to describe the nonbonded interactions for proteins in crystals or aqueous solutions. In all, parameters have been reported for 25 amino acid residues and various terminal groups. The basis for the potential functions is comparatively sound and their form is attractively simple. Combination with bond stretch, angle bend, and torsional terms from the AMBER force field provides a complete model for proteins that is now available for application to innumerable problems addressing the structure, dynamics, and function of biomolecular systems. Initial tests on crystals of cyclic peptides and the protein crambin have demonstrated that the AMBER/OPLS force field yields root-mean-square errors of only 0.1–0.2 Å for the positions of nonhydrogen atoms.

Acknowledgment. Gratitude is expressed to the National Institutes of Health (GM32136) for support of this research, to Jiali Gao for computational assistance, and to Professor Martha M. Teeter for unpublished data and consultation.

A Theoretical Investigation of the Thermal Ring Opening of Bicyclobutane to Butadiene. Evidence for a Nonsynchronous Process[†]

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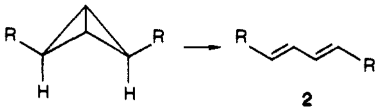
Abstract: An ab initio investigation of the ring opening of bicyclobutane (**1a**) to butadiene (**2a**) with geometries optimized at the HF/3-21G level predicts a two-step process with an intermediate 3-butenylidene (**5**). Since this prediction is in conflict with experimental results, the reaction surface was reinvestigated with geometries optimized at the MP2/3-21G level. This procedure leads to a transition state for the $\sigma 2_s + \sigma 2_a$ ring opening which lies 43.6 kcal/mol above bicyclobutane ([MP4SDTQ/6-31G*]//MP2/3-21G + ZPC//3-21G) in good agreement with the known barrier for the thermal ring opening of **1a** to **2a** of 40.6 kcal/mol. The geometry of the MP2/3-21G transition state, with one C–C bond lengthened by 0.783 Å and the other increasing by only 0.088 Å, indicates a nonsynchronous reaction. The disrotatory ring opening of **1a** (based on a C_2 transition state) has a predicted barrier of 97.0 kcal/mol at the [MP4SDQ/6-31G*] + ZPC//3-21G level of theory.

The bicyclo[1.1.0]butane ring system, with its strain energy of over 60 kcal/mol,[1] has been the subject of numerous theoretical and experimental investigations. Of particular interest have been studies of the ring opening to 1,3-butadienes. When the ring opening of bicyclo[1.1.0]butane (**1a**) to 1,3-butadiene (**2a**) is carried out thermally, the central bond remains intact while two opposite peripheral C–C bonds are broken in going to the product.[2-4] Studies of 1,3-dimethylbicyclobutanes have demonstrated that the reaction is highly stereoselective with exo substituents at C_2 and C_4 becoming cis,trans in the product butadiene in what has been characterized as a stereoselective $\sigma 2_s + \sigma 2_a$ reaction (eq 1).[3] Mechanistic interpretations of this ring opening have been somewhat problematic.[5-10] A disrotatory process is predicted to be forbidden from an analysis of a correlation diagram where orbitals can be assigned with respect to a C_2 axis that is maintained during the reaction. However, the conrotatory ring opening, which is often interpreted as the allowed [$\sigma 2_s + \sigma 2_a$] reaction, cannot be followed by any element of symmetry higher than C_1. Assuming that the reaction can be followed by an approximate correlation diagram may lead to erroneous conclusions.[6]



(1)

1a, R = H
b, R = CH_3
2

Dewar[8] has argued that most reactions involving the breaking or forming of two bonds are not synchronous and many are not concerted. MINDO/3 calculations[9] have found that the ring opening of bicyclobutane is a two-step reaction involving the intermediacy of the cyclopropylcarbinyl biradical, **3**. The stereochemistry of the reaction is maintained due to slow interconversion of the "biradicaloids" compared to further reaction to form

1a **3** **2a**

[†] Dedicated to Professor Michael J. S. Dewar on the occasion of his 70th birthday.

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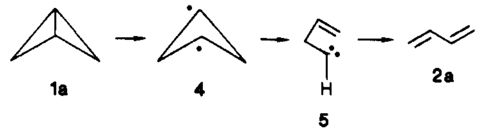
Table I. Total Energies (hartrees) and Zero Point Energies (kcal/mol) for Various Species Optimized at the 3-21G Level on the C_4H_6 Potential Energy Surface

	molecule	mol sym	3-21G	6-31G*	MP2/6-31G[a]	MP2/6-31G*[a]	MP4SDQ/6-31G[a]	ZPE[b]
1	bicyclobutane	C_{2v}	−153.98664	−154.86959	−155.14618	−155.38711	−155.18177	58.44 (0)
2	butadiene	C_{2h}	−154.05946	−154.91961	−155.21243	−155.42069	−155.25233	57.77 (0)
3	TS1	C_1	−153.90494	−154.78160	−155.07276	−155.30436	−155.10882	55.65 (1)
4	3-butenylidene	C_1	−153.93570	−154.80037	−155.06581	−155.27835	−155.11141	54.65 (0)
5	3-butenylidene	C_1	−153.93586	−154.80083	−155.06584	−155.27858	−155.11139	54.60 (0)
6	TS2	C_1	−153.91163	−154.78294	−155.07492	−155.29693	−155.11103	55.50 (1)
7	av TS1,TS2	C_1	−153.90633	−154.77873	−155.07220	−155.29721	−155.10875	
8	constrained TS	C_1	−153.87722	−154.74705	−155.05636	−155.28233	−155.09105	
9	disrotatory TS	C_2	−153.83954	−154.70669	−155.00601	−155.22539	−155.04216	54.32 (2)
10	C_2H_3	C_s	−76.96279	−77.39027	−77.50609	−77.60172	−77.53128	24.29 (0)

[a] Frozen core approximation. [b] Zero point energy (kcal/mol) and number of imaginary frequencies in parentheses.

butadiene. In this sense the biradicaloid retains a "memory" of the original stereochemistry.

In the photolysis of bicyclobutane, a cyclobutane-1,3-diyl intermediate, **4**, is often suggested.[11-13] This may then rearrange to 3-butenylidene (**5**) and thence to **2a** as shown in eq 2. Becknell, Berson, and Srinivasan[13] have shown in labeling studies that the photolysis of bicyclobutane to form butadiene follows the two competing mechanisms depicted in eq 1 and 2.



(2)

The electronic structure and properties of **1a** have been extensively studied.[14-22] As part of a comprehensive study of energetic species on the C_4H_6 potential energy surface,[23] we report here an ab initio investigation of the potential energy surface separating **1a** and **2a**. These calculations, at the highest level, predict an interesting least-motion approach to a nonsynchronous transition state for this reaction.

Results

All calculations were carried out with the GAUSSIAN 82[24] and GAUSSIAN 86[25] program packages. Full geometry optimizations[26] were carried out with the 3-21G basis set[27] or at the MP2/3-21G level except where noted. Single point calculations at the MP4SDQ/6-31G and MP2/6-31G* levels were combined to

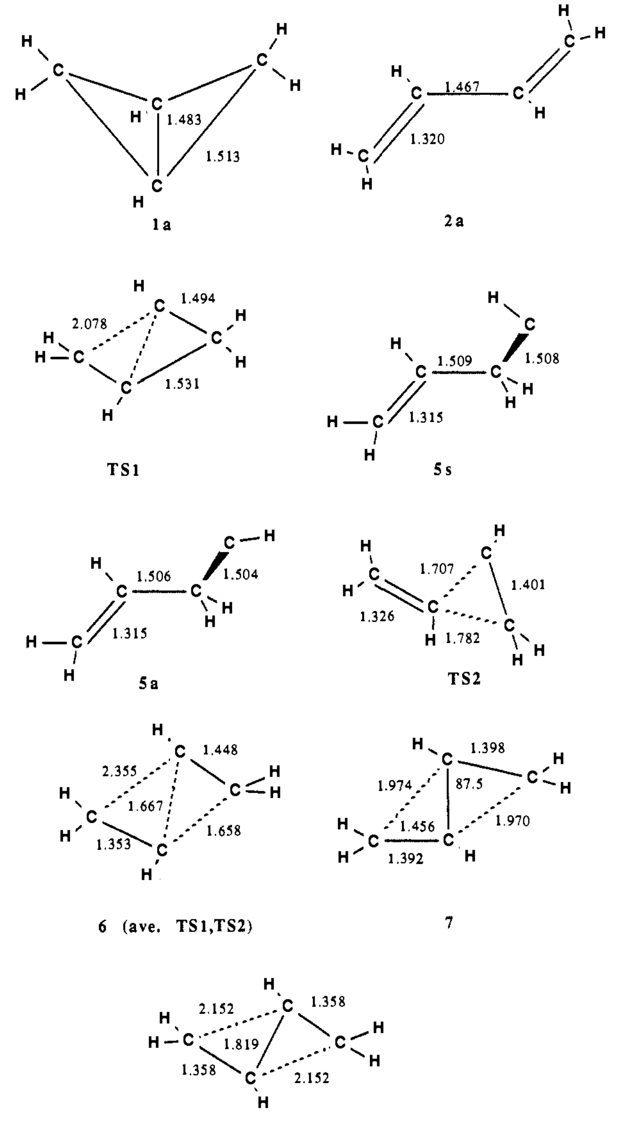


Figure 1. Relevant geometric parameters for species on the C_4H_6 potential energy surface optimized at the 3-21G level.

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Table II. Relative Energy (kcal/mol) of Various Species on the C_4H_6 Potential Energy Surface at 3-21G Optimized Geometries

	molecule	3-21G	6-31G*	MP2/6-31G	MP2/6-31G*	MP4SDQ/6-31G	[MP4SDQ/6-31G*][a] (+ZPC)
1	bicyclobutane	0.0	0.0	0.0	0.0	0.0	0.0 (0.0)
2	butadiene	−45.7	−31.4	−41.6	−21.1	−44.3	−23.8 (−24.5)
3	TS1	51.3	55.2	46.1	51.9	45.8	51.6 (48.8)
4	3-butenylidene	32.0	43.4	50.4	68.3	44.2	62.1 (58.3)
5	3-butenylidene	31.9	43.2	50.4	68.1	44.2	61.9 (58.1)
6	TS2	47.1	54.4	44.7	56.6	44.4	56.3 (53.4)
7	av TS1,TS2	50.4	57.0	46.4	56.4	45.8	55.8
8	constrained TS	68.7	76.9	56.4	65.8	56.9	66.3
9	disrotatory TS	92.3	102.2	88.0	101.5	87.6	101.1 (97.0)
10	C_2H_3	38.3	55.9	84.1	115.3	74.8	106.0 (96.1)

[a] At the additivity level with eq 1. The value in parentheses has been corrected for differences in zero point energy.

Table III. Total Energies (hartrees) for Various Species Optimized at the MP2/3-21G Level on the C_4H_6 Potential Energy Surface

	molecule	mol sym	MP2/3-21G	6-31G*	MP2/6-31G[a]	MP2/6-31G*[a]	MP4SDQ/[a] 6-31G	MP4SDTQ/[a] 6-31G
1a	bicyclobutane	C_{2v}	−154.351 16	−154.865 90	−155.148 92	−155.386 28	−155.184 64	−155.195 64
	TS1/CI	C_1	−154.278 52	−154.788 80	−155.073 41	−155.293 81	−155.113 13	−155.125 97
5s′	3-butenylidene	C_1	−154.273 14	−154.798 77	−155.068 72	−155.279 75	−155.114 70	
5a′	3-butenylidene	C_1	−154.273 03	−154.799 21	−155.068 66	−155.280 05	−155.114 55	
	TS2/CI	C_1	−154.282 38	−154.770 47	−155.081 08	−155.307 11	−155.115 98	−155.132 88
9		C_1	−154.278 80	−154.793 94	−155.072 82	−155.290 17	−155.114 60	
	TS1/CI open shell	C_1		−154.796 21	−155.057 15[b]	−155.276 10	−155.101 45	

[a] Frozen core approximation. [b] Spin projected energy (PMP2/6-31G) is −155.088 06 hartrees or 9.2 kcal/mol *lower* than TS1/CI, the closed shell solution, at the same level.

approximate[28] relative energies at the MP4SDQ/6-31G* level according to eq 3. Analytical second derivatives of stationary

$$\Delta E[\text{MP4SDQ/6-31G*}] = \Delta E(\text{MP4SDQ/6-31G}) + \Delta E(\text{MP2/6-31G*}) - \Delta E(\text{MP2/6-31G}) \quad (3)$$

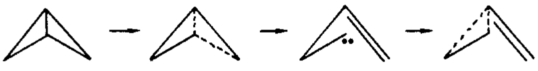
points at the 3-21G level were calculated with the CPHF method. In the interest of clarity, the results have been broken into two parts. The potential energy surface determined by geometry optimization at the HF/3-21G level (the 3-21G surface) will be discussed first. This will be followed by an analysis of the potential energy surface obtained by optimization at the MP2/3-21G level. Unless otherwise stated, all energies will be at the [MP4SDQ/6-31G*] (relative energies determined with eq 3) level with zero point corrections estimated at the 3-21G level.

The 3-21G Potential Energy Surface. Total energies are given in Table I and relative energies are given in Table II for species optimized at the 3-21G level. Relevant geometric parameters are given in Figure 1 where the provided notation is also used in the text and tables. The first transition state located on this surface, TS1, was very asymmetric (Figure 1). Instead of breaking two opposite peripheral C–C bonds as might be expected from the experimental results, a peripheral C–C bond and the central C–C bond are broken forming 3-butenylidene (**5**). At the 3-21G level the barrier for formation of the carbene is 51.3 kcal/mol and it is reduced to 48.9 kcal/mol at the [MP4SDQ/6-31G*]+ZPC level.

Two conformations of carbene **5**, **5s** and **5a**, of C_1 symmetry were studied. These correspond roughly to a syn and anti orientation of the hydrogen on the carbene center with respect to the double bond. Table II demonstrates that there is very little difference in energy between these two carbene conformers. At the highest level, **5a** is more stable than **5b** by 0.2 kcal/mol and lies 58.1 kcal above **1a**. Since carbene **5** is destabilized by polarization functions and electron correlation while TS1 is stabilized relative to **1a**, these effects may have a qualitative influence on the reaction path.

The lowest energy barrier from the carbene to butadiene would undoubtedly be the 1,2-hydrogen migration to the carbene center which has been shown to occur with little or no barrier in ethylidiene.[29,30] This pathway was not calculated since labeling studies[4] have shown that thermal ring opening of **1** occurs without hydrogen migration. However, a second transition state on the 3-21G surface was located. This transition state, TS2, may be viewed as that corresponding to the formation of **2a** from **5** by a carbene insertion into a C–C bond. At the 3-21G level, TS2 is 47.1 kcal/mol above bicyclobutane while at the [MP4SDQ/6-31G*]+ZPC level this value is increased to 53.3 kcal/mol.

The activation barrier for the formation of **2a** from **5** via TS2 is 15.2 kcal/mol at the 3-21G level and becomes −4.7 kcal/mol at the higher level. Judging by the higher level calculations, it is possible that the carbene is not involved in the reaction at all and is simply an artifact of the method used to generate geometries. Since TS1 involves the breaking of the central bond and one peripheral bond while TS2 involves the reformation of the central bond and breaking the other peripheral bond as shown in eq 4, an interpolation between the two structures might provide an estimate of the true transition state. The geometries of TS1 and TS2 are similar so a simple average of the internal coordinates was made (**6**, Figure 1) and used for single point calculations. The predicted barrier at the higher level was 55.8 kcal/mol (no zero point correction) with respect to bicyclobutane, over 15 kcal/mol higher than the observed barrier of 40.6 kcal/mol.[31]


(4)

1a TS1 **5** TS2

It is possible that more accurate calculations including polarization and correlation would predict a synchronous reaction. To test this possibility, a transition state was located (**7**, Figure 1) while constraining the two inside angles of the breaking peripheral bonds to be equal. With use of this constraint, the two breaking C–C bonds are 1.974 and 1.970 Å in the transition state. The estimated barrier at the higher level was 66.3 kcal/mol (no zero point correction) and suggests that the reaction is not synchronous.

Disrotatory Ring Opening. Although the disrotatory ring opening of **1** is forbidden in a Woodward–Hoffmann sense,[5] a C_2 symmetry axis can be maintained throughout the transformation from **1a** to **2a**. The disrotatory transition state (**8**, Figure 1) is

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Table IV. Relative Energies (kcal/mol) of Various Species on the C_4H_6 Potential Energy Surface at MP2/3-21G Optimized Geometries

	molecule	MP2/3-21G	6-31G*	MP2/6-31G	MP2/6-31G*	MP4SDQ/ 6-31G	MP4SDTQ/ 6-31G	[MPSDQ/6-31G*][a] (+ZPC)
1a	bicyclobutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0 (0.0)
	TS1/CI	45.6	48.4	47.4	58.0	44.9	43.7	55.5 (52.7)[b]
5s′	3-butenylidene	49.0	42.1	50.3	66.9	43.9		60.5 (56.7)
5a′	3-butenylidene	49.0	41.8	50.4	66.7	44.0		60.3 (56.5)
	TS2/CI	43.2	59.9	42.6	49.7	43.1	39.4	50.2 (47.3)[c]
9	3-butenylidene	45.4	47.8	47.8	60.3	44.0		56.5
	TS1/CI open shell		43.7	57.6[d]	69.2	52.2		63.8

[a] At the additivity level with eq 3. The value in parentheses has been corrected for differences in zero point energy. [b] A consideration of triple substitution reduces the barier to 54.3 (51.5) kcal/mol. [c] A consideration of triple substitution reduces the barrier to 46.5 (43.6) kcal/mol. [d] If the largest spin contaminant is projected out,[35] this value becomes 38.2 kcal/mol.

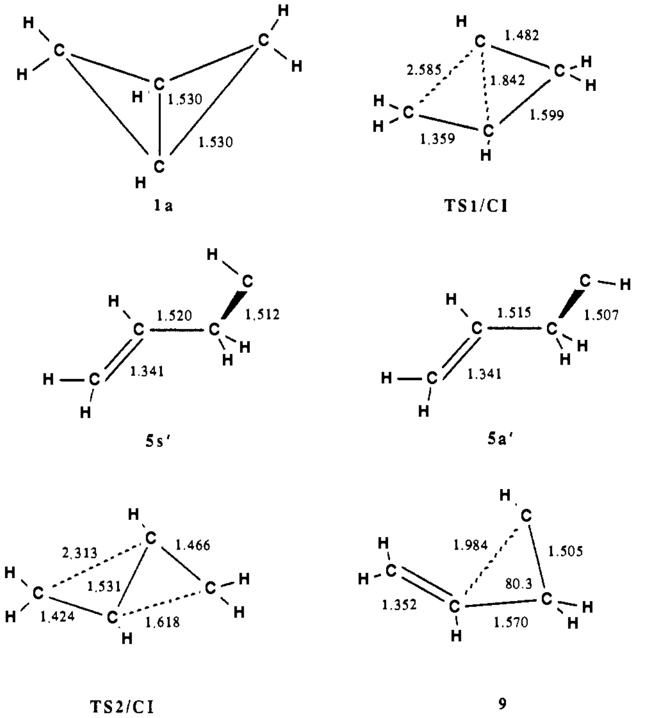

Figure 2. Relevant geometric parameters for species on the C_4H_6 potential energy surface optimized at the MP2/3-21G level.

97.0 kcal/mol higher than that for bicyclobutane and is characterized by two negative eigenvalues of the force constant matrix.[32] One imaginary frequency corresponds to the formation of radicals while the other corresponds to the formation of cyclopropylmethylene. It is interesting that neither mode corresponds to formation of **1a** or **2a**. It appears likely that the disrotatory ring opening of **1a** to **2a** is nonsynchronous (and also perhaps nonconcerted).

The MP2/3-21G Potential Energy Surface. The reaction surface was reinvestigated by optimizing geometries at the MP2/3-21G level (Figure 2, Tables III and IV). Including correlation increases both the peripheral and central bond lengths in **1a** to a common value of 1.530 Å. Experimentally the two types of bonds have the same length but are much shorter (1.498, 1.493 Å).[34] All energies in this section will refer to calculations at the MP2/3-21G geometry.

Starting with TS1 and searching for a transition state at the MP2/3-21G level, a structure was obtained (TS1/CI, figure 2) which was 45.6 kcal/mol higher in energy than bicyclobutane at the MP2/3-21G level. The structure appears to be similar to TS1 with a longer breaking central bond and one breaking peripheral bond that is substantially longer. At the [MP4SDQ/6-31G*]+ZPC level, TS1/CI is 52.7 kcal/mol higher in energy than bicyclobutane. The two carbene structures were determined at the MP2/3-21G level (**5s′**, **5a′**, Figure 2) and have geometries similar to **5s** and **5a** with the MP2/3-21G bond lengths all slightly longer than those at the 3-21G level. It appears that TS1/CI is the transition state relating **1a** to carbene **5**. However, at the MP2/3-21G level, the energy of TS1/CI is lower than carbene **5** (Table IV). In order to determine the structure on the product side of TS1/CI, a slight distortion of the transition state was made and the geometry optimized. The MP2/3-21G energy of the resultant carbene-like structure, **9**, which is characterized by an unusually small angle at a noncyclic saturated carbon (80.3°), is only 0.2 kcal/mol lower than that of TS1/CI. The stabilization of the structure is due to the conjugation of the π orbital with the empty orbital on the carbene center.

At the [MP4SDQ/6-31G*] level, **9** is 1.0 kcal/mol less stable than TS1/CI. Therefore it is likely that it will collapse without activation to bicyclobutane with a reverse barrier of 52.7 kcal/mol via TS1/CI. A consideration of triple substitutions at the 6-31G level (MP4SDTQ/6-31G) reduces the barrier to 51.6 kcal/mol (Table IV) at the additivity level.

Since TS1/CI and **9** can be written as distorted cyclopropylcarbinyl biradicals, they could have biradical character. For this reason, an open shell solution for TS1/CI was determined and used as a basis for the perturbative MP expansion. With use of this solution, the barrier at the [UMP4SDQ/6-31*]+ZPC level is 61.0 kcal/mol, only 8.3 kcal/mol higher than the barrier determined from the restricted solution at the same level. In fact if relative energies are compared at the MP2/6-31G level and the largest spin contaminant is projected out of the open shell solution,[35] the open shell solution is 9.3 kcal/mol more stable than the closed shell solution.

Starting with TS2, a new transition state, TS2/CI, was eventually determined at the MP2/3-21G level. TS2/CI is 43.2 kcal/mol higher in energy than bicyclobutane but lower in energy than any of the carbene structures. This transition state, which interconverts **1a** and **2a** contains a bridgehead bond that has not lengthened, while the two opposite breaking peripheral bonds have lengthened by 0.783 and 0.088 Å. At the [MP4SDQ/6-31G*] level the **1a** → **2a** barrier is 50.2 kcal/mol. If the zero point correction is estimated as 2.9 kcal/mol, which is the value for TS2 at the 3-21G level, the barrier is 47.3 kcal/mol. Finally, including triple substitutions at the 6-31G level (MP4SDTQ/6-31G) reduces the barrier a further 3.7 kcal/mol and leads to a barrier of 43.6 kcal/mol, in reasonable agreement with the experimental value[31] of 40.6 kcal/mol.

In order to confirm that TS2/CI was the transition state which interconverts **1a** and **2a**, the vibrational frequencies were calculated[36] at the MP2/3-21G level. The single imaginary frequency (339i cm^{-1}) corresponds primarily to conrotatory motion of the

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[32] Budzelaar et al.[33] have also calculated the disrotatory ring opening transition state of bicyclobutane at the 3-21G level and single point calculations at higher levels. The total energy they report for this transition state is 6.7 kcal/mol higher in energy at the 3-21G level than the value reported here.

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[36] In order to determine vibrational frequencies, finite differences were taken of analytical first derivatives of the correlated wave function. The calculations, which required 4 CPU hours on a Cray X-MP/416, were carried out by C. M. Rohlfing.

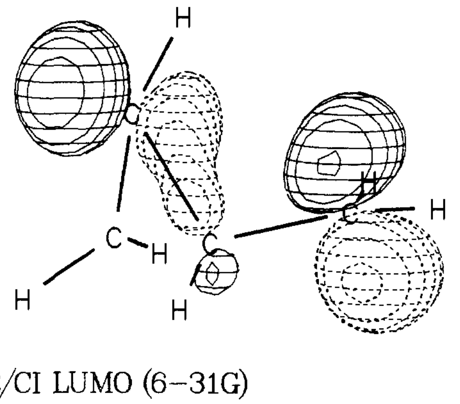

Figure 3. A Salem–Jorgensen plot of the LUMO of TS2/CI. The bridgehead carbon–carbon bond will be stabilized by a treatment which includes electron correlation since the LUMO will be partially occupied.

two methylene groups. However, there is significant motion indicated for all atoms in the transition vector. The zero point energy is calculated to be 52.41 kcal/mol which is 3.1 kcal/mol less than the zero point energy of TS2 calculated at the 3-21G level. However, the majority of this difference can be accounted for by the known tendency of correlated wave functions to yield lower zero point energies.[37]

Discussion

Geometry optimization at the 3-21G level leads to the conclusion that the thermal ring opening of **1a** to **2a** proceeds via a mechanism similar to that in eq 2 involving TS1 and the intermediacy of carbene **5**. The calculated activation energy along this pathway of 48.8 kcal/mol is 8.2 kcal higher than that which has been reported. The predicted intermediacy of **5** is contrary to the experimental observation that a hydroen does not migrate during the thermolysis of **1** to **2**.[4] Since eq 2 has been shown to be operative in the photolytic ring opening of **1**, TS1 may be a transition state along this potential energy surface. When carbene **5** is generated by the photolysis of the corresponding diazo compound at −78 °C, the products are **1a** and **2a** in a 1:5 ratio.[38] The pathway to **1a** in this system may be via TS1 in competition with hydrogen migration.

Simple thermochemical considerations indicate that carbene **5** cannot be involved in the thermolysis of **1a**. If the energy difference between 1-butene and **5** is similar to the ΔH in going from CH_4 to CH_2 of 120 kcal/mol,[39] the ΔH_f of **5** may be estimated at 120 kcal/mol. This is probably an upper limit since it does not take into account the fact that **5** is an alkyl-substituted carbene which may have some homoconjugative interaction with the double bond. These estimates place **5** some 58–68 kcal above **1a** while the experimentally determined transition state is only 40.6 kcal above that of **1a**.[31] It is interesting that our ab initio calculations predict carbene **5** to lie 58.1 kcal/mol above **1a** (Table II).

When geometries are optimized at the MP2/3-21G level a transition state (TS2/CI) whose energy is in good agreement with experiment is obtained. TS2/CI has the attractive feature that the C_1–C_3 bond remains intact during the ring opening in accordance with experimental observations. The reason for the large effect of electron correlation on the transition state can be seen by examining the Salem–Jorgensen[40] plot of the LUMO (Figure 3). The interaction between C_1 and C_3 will be attractive in a correlation treatment which effectively allows partial occupation of the LUMO.

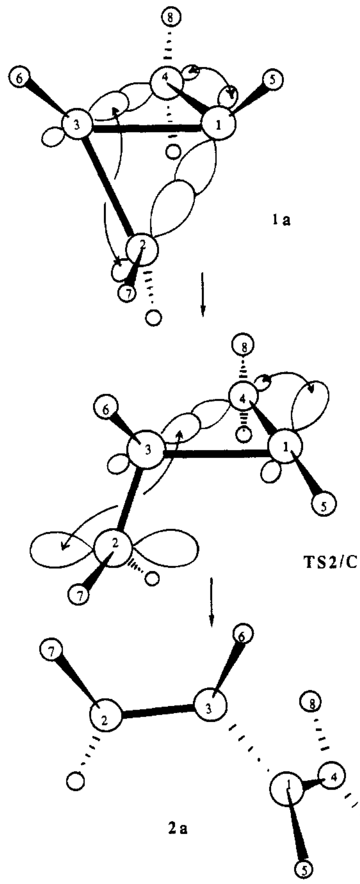

Figure 4. Structures of **1a**, TS2/CI, and **2a** demonstrating geometric changes and orbital overlaps which occur in going from reactant to transition state to product.

The geometry of TS2/CI is interesting in light of the complex motions necessary to carry **1a** to **2a**. Figure 4, which compares the geometries of **1a**, TS2/CI, and **2a**, illustrates that the only two important changes which occur in going from **1a** to TS2/CI are lengthening of the peripheral C–C bond by 0.783 Å and a dramatic inversion at the erstwhile bridgehead carbon at the terminus of this bond. A consideration of the geometry of TS2/CI leads to the prediction that an exo substitutent (H_7 in Figure 4) at C_2 of the bond most lengthened in going to TS2/CI will become trans in the substituted 1,3-butadiene product. This is a consequence of the fact that the H_6–C_3–C_2–H_7 dihedral angle in TS2/CI of 28° forces these hydrogens to become cis in the final product. At the same time, the exo substitutent in the other ring (H_8 in Figure 4) is forced to become cis in the product butadiene as a consequence of the inversion at C_1 which results in a H_8–C_4–C_1–H_5 dihedral angle of 150°. Thus, in the allowed $\sigma 2_s + \sigma 2_a$ mode, the bond that is most broken in the transition state (C_1–C_2 in Figure 4) is the bond that is being added to suprafacially. The C_2–C_3 bond in TS2/CI has a rotational barrier of 42.2 kcal/mol (MP2/6-31G),[41] indicating significant π-bond character. Thus the stereochemistry is "locked in" since as one peripheral bond breaks, rotation is inhibited by a developing π bond in the adjacent peripheral bond.

Perhaps the most interesting facet of TS2/CI is the inversion at C_1 that occurs upon going to the transition state. When one considers that orbital symmetry considerations predict that the isomerization of **1** to **2** will proceed via a $\sigma 2_s + \sigma 2_a$ pericyclic reaction, the inversion in going to TS2/CI is simply the "growing in" of the back lobe at C_1 that allows the overlap which will eventually result in the π bond between C_1 and C_4. It is interesting that while much of the discussion of the ring opening of **1** has been

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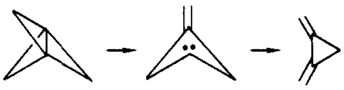
[41] The geometry of the transition state (TS2/CI) was frozen except for the methylene group which was made planar and then rotated by 90.0°. Single point calculations were made at the MP2/6-31G level.

concerned with evaluations of the conrotatory and/or disrotatory nature of the openings of both rings, these calculations predict that very little of these rotations occur in going to the transition state. In fact, an examination of the events that must occur after the transition state is reached in proceeding from TS2/CI to **2a** reveals that rehybridizations at C_1, C_2, and C_4 lead directly to a 1,3-butadiene in which the C_2–C_3–C_1–C_4 dihedral angle between the two fully formed double bonds is 90° and thus lacks only the delocalization energy of **2a**. Although it is possible that TS2/CI could lead to an *s-cis*-butadiene, steric constraints probably dictate that the 90° rotation about the central bond will occur in such a way that *s-trans*-butadiene will be generated.

In light of the geometry of TS2/CI, it is instructive to consider a molecule such as [1.1.1]propellane (**10**), a bicyclobutane in which inversion at C_1 is precluded. Thermolysis of **10** in a flow system at 430 °C leads to dimethylenecyclopropane (**12**).[42] In this case, it is possible that the reaction proceeds through the intermediacy of 3-methylenecyclobutylidene (**11**), which then undergoes the known cyclobutanylidene to methylenecyclopropane rearrangement to give **12**. In this case, thermochemical calculations predict that the barrier for opening of **10** to **11** is 46.3 kcal/mol.[44] It may be that the transition state for this process is analogous to that of TS1 calculated in this work for carbene formation from **1a**.

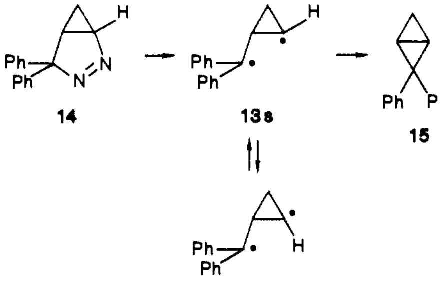


10 **11** **12**

The fact that one peripheral C–C bond is lengthened by 0.783 Å while the other only increases by 0.088 Å in going from **1a** to TS2/CI indicates that the reaction is strongly nonsynchronous and that the transition state resembles the cyclopropylcarbinyl biradical (**3**) as originally proposed by Dewar and Kirschner.[9] However, a consideration of the experimental thermochemistry of the conversion of **1a** to **2a** appears to rule out the intermediacy of a true biradical. Wiberg and Lavanish[4] have estimated that biradical **3** will lie some 49 kcal above **1a** while the activation energy for the conversion of **1a** to **2a** is only 40.6 kcal. An estimate of the ΔH_f of **3** with updated BDE's[45] and allowing for a 3-kcal/mol stabilization of the cyclopropylcarbinyl radical[46] leads to essentially the same conclusion with **3** predicted to lie 49.3 kcal above **1a**. Hence, there exists in TS2/CI an additional stabilization over that found in biradical **3**. An examination of the molecular orbitals of TS2/CI reveals that some of this stabilization results from an interaction of what was originally the MO of the central bond in **1** with its predominate p character and the p orbital on C_2 of TS2/CI. This can be demonstrated by examining Salem–Jorgensen[40] representations of the bonding (HOMO-2) and antibonding combinations (LUMO) of the orbitals involved. The HOMO of TS2/CI involves an interaction of the back lobe of the inverted carbon p orbital at C_1 with the p orbital on C_2.

While the thermochemical considerations discussed above appear to preclude the intermediacy of a true biradical in the thermolysis of **1a**, the introduction of suitable substitutents on **1** could render **3** energetically accessable. In fact, the pyrolysis of hexa- and pentamethylbicyclo[1.1.0]butane[47,48] leads to some products that are best explained through the intermediacy of a biradical such as **3**. The thermolysis of **1b** to *cis,trans*-2,4-hexadiene in eq 1 is attended by the formation of small amounts of *trans,trans*-2,4-hexadiene and 1-methyl-2-vinylcyclopropane,[3] both of which are products that could result from the biradical.

Biradical **3** has been postulated as an intermediate in the photochemical cyclization of **1a** to **2a**.[49] The diphenyl-substituted biradical, **13**, has been generated in the pyrolysis and photolysis of 4,4-diphenyl-2,3-diazabicyclo[3.1.0]hex-2-ene (**14**).[50] Although the chemistry of this and related diazabicyclo[3.1.0]hex-2-enes is complicated by a competing cycloreversion to a diazo compound,[50,51] biradical **13** is thought to close to 2,2-diphenylbicyclo[1.1.0]butane (**15**) rather than rearrange to the corresponding butadiene. It is interesting that **13s** as it is initially generated will not have the inverted geometry at C_1 that we calculate for TS2/CI and it may be that inversion at C_1 would lead to **13a** which would be a precursor to the butadiene. Since the inversion of cyclopropyl radicals has a calculated barrier of 5.5 kcal/mol,[52] it is possible that this inversion cannot compete with closure to **15**.



14 **13s** **15** **13a**

Conclusion

In order to obtain a transition state for the ring opening of **1a** whose energy is consistent with experimental observations, electron correlation must be included in the geometry optimizations. When this is done and the geometry of the transition state computed at the MP2/3-21G level, the calculations indicate that the ring opening of **1a** proceeds via a strongly nonsynchronous reaction path. The route to the transition state requires a minimum of atomic motion with only the lengthening of one bond and inversion of the bridgehead carbon at the terminus of this bond. The requirement that the transition state be reached with economy of atomic motion appears to outweigh the need for more complex motions in which both bonds are cleaved in concert. Thus, the ring opening of **1a** may be thought of as following a least motion pathway to the transition state.[10]

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Registry No. 1a, 157-33-5; **2a**, 106-99-0.

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