We wish to start the trajectories with the reagents at the transition-state value of the reaction coordinate and to sample all other degrees of freedom from a canonical ensemble. For the 64 water molecule case, this was done by placing the $Cl^- + CH_3Cl$ system in the center of the box and surrounding it with the water molecules added one by one. The positions and orientations of the water molecules were chosen randomly, rejecting any attempted placement that significantly overlapped with any of the molecules already placed in the box. The size of the box was chosen to obtain the desired density (in this case 1.0 g cm^{-3}). The asymmetric stretch of the $Cl^- + CH_3Cl$ system was then constrained to be zero (corresponding to the transition state of the system), and the potential energy of the entire system was minimized with respect to all other degrees of freedom. The system was then equilibrated to the appropriate temperature (298 K) over a period of 5 ps by using an algorithm which randomizes the velocities (sampling from the Maxwell–Boltzmann distribution) every 0.25 ps. During this equilibration, the value of the reaction coordinate (eq 5) of the reagents and the velocity of this degree of freedom were constrained to be zero. Ten independently created and equilibrated "seeds" were thereby produced by Gertner et al.[12] and were used to generate a total of 400 sets of initial configurations through a continuation of the dynamics and equilibration process.

We use 10 of these 64 water molecule initial condition files (one from each of the original independently created seeds) to generate the 256 water molecule initial condition files. In order to keep the same density of 1.0 g cm^{-3}, the unit cell for the 256 water molecule system must be a factor of $4^{1/3}$ larger than that for the 64 molecule system. For each of the 64 water initial condition files, we calculate the 14 closest periodic images (one for each face of the truncated octahedron) and retain only those molecules that lie within the appropriate unit cell for the 256 water system, randomly removing excess water molecules if the total is larger than 256. (This new system includes all the molecules in the original system.) By virtue of how it is constructed, this larger system has no unfavorable molecule–molecule interactions within its boundaries as it would if molecules were placed in it randomly. However, the molecules on the surface of the original (64 water) unit cell may interact unfavorably with periodic images of other solvent molecules. In order to correct this, we first increase the size of the unit cell by ~1 Å, in effect placing some vacuum around the system. Five hundred fs of constant temperature dynamics using the Nosê algorithm[89] is then run during which time the system expands into the larger volume. In the process, the unfavorable interactions with the periodic images are eliminated. Since this system is now at the wrong density, the linear dimensions of the unit cell are compressed by 2%, all solvent atom positions are also scaled by that factor, and constant temperature dynamics are run on the compressed system for 500 fs to equilibrate the system at the new volume. This compression–equilibration process is repeated until the original desired density is regained. This equilibration should also be sufficient to remove any traces of the symmetry remaining in the original system bootstrapped from the mosaic of smaller systems.

Theoretical Studies on the Ring-Opening Reactions of Bicycloalkyl Radicals: Homolytic β-Scission in Bicyclo[1.1.0]but-2-yl Radical

Santiago Olivella*,† **and Albert Solé**

Contribution from the Departments de Química Orgànica and Química Física, Universitat de Barcelona, Martí i Franquès 1, 08028-Barcelona, Catalunya, Spain. *Received April 30, 1990*

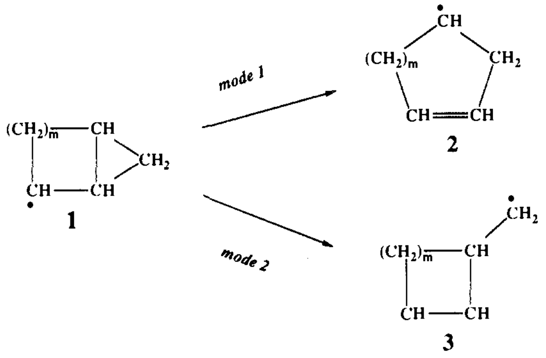
Abstract: Ab initio UHF and CASSCF calculations have been performed on the two modes of ring opening in bicyclo[1.1.0]but-2-yl radical (**8**), involving homolytic β scission of a C–C bond. Although the fusion bond cleavage in **8** to give cyclobutenyl radical (**9**) is formally an orbital-symmetry-forbidden electrocyclic process, the activation energy is calculated to be only ≈3 kcal/mol. This ring opening is predicted to take place via a highly nonsymmetric transition structure, which allows the mixing of the SOMO (a′ symmetry) and LUMO (a″ symmetry) of **8**, and the coupling between the crossing states (2A′ and 2A″), resulting in an adiabatic reaction on the ground-state potential surface. The alternative β-scission mode in **8**, involving cleavage of an outer cyclopropane bond to afford cyclopropenylmethyl radical (**10**), is predicted to have an activation energy of ≈26 kcal/mol. Although the partial breaking of such a peripheral bond in the transition state involves a great relief of the strain energy of the cyclopropane moiety in **8**, this is nearly compensated by the increase of strain energy that takes place simultaneously in the cyclopropyl ring of **8** because the partial making of an inner double bond.

I. Introduction

Radical species containing small strained bicycloalkyl structures are interesting because the rigid framework of carbon atoms can lead to unusual and even unprecedented chemical behavior. The presence of a large amount of strain energy makes the ring opening by cleavage of a β, γ C–C bond with respect to the radical center (i.e., β scission) a common process. In the case of bicyclo[*n*.1.0]alk-2-yl radicals (**1**), there are two types of β,γ C–C bonds and, therefore, two different modes of β scission can be envisaged (Scheme I). Thus, β scission of the fusion bond (mode 1) gives cycloalkenyl radicals (**2**), while β scission of the outer cyclopropane bonds (mode 2) would yield cycloalkenylmethyl radicals (**3**).

It has been pointed out that ring opening by β scission readily occurs in cycloalkyl radicals if the semioccupied molecular orbital (SOMO) can assume an eclipsed conformation with respect to the β,γ bond; namely, there is strong overlap between the SOMO and the orbitals of the bond about to break.[1] This stereoelectronic

Scheme I



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†CSIC Research Professor.

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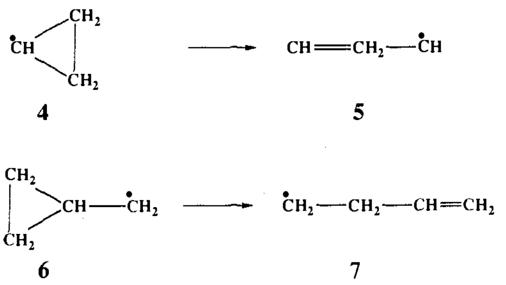
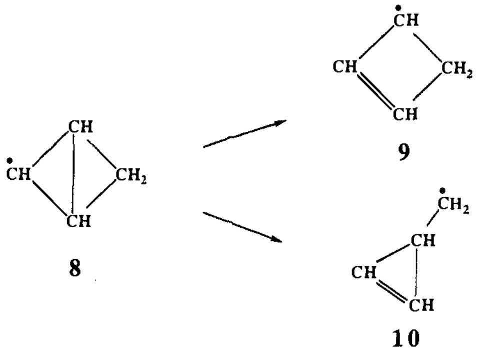
Scheme II



Scheme III



explanation accounts for the relatively reluctant ring opening of cyclopropyl radical (**4**) to give allyl radical (**5**)[2] and the rapid β scission of cyclopropylmethyl radical (**6**) to give homoallyl radical (**7**).[3]

As noted by Ingold and Walton,[4] the simplest radical of the 2-bicycloalkyl class **1**, namely, bicyclo[1.1.0]but-2-yl (**8**) (referred to hereafter as bicyclobutyl radical), is simultaneously both a cyclopropyl-type and cyclopropylmethyl-type radical. ESR studies have shown that in **8** the mode 1 β scission, namely, the rearrangement to cyclobutenyl radical (**9**), occurs exclusively.[5] While this ring opening is facile it is not instantaneous, so at temperatures below approximately −100 °C the ESR spectrum of **8** is observed. Since a simple drawing of **8** suggests that the fusion bond is orthogonal to the SOMO, the observed easy rearrangement of **8** to **9** has been considered as an example of contrastereoelectronic homolytic ring cleavage.[6] Mode 2 β scission would yield cyclopropenylmethyl radical (**10**), a highly strained product, and for this reason mode 1 ring opening is preferred because this leads to much greater relief of ring strain.[6]

Roberts and Walton[6] examined the β scission in **8** by self-consistent-field (SCF) molecular orbital (MO) calculations using the semiempirical methods MINDO/3[7] and MNDO.[8] These authors stated that neither of these methods was successful in calculating the transition structures for the **8** → **9** and **8** → **10** rearrangements. It appeared that such rearrangements involve crossing from one potential energy surface to another, and configuration interaction (CI) is required to handle this situation. However, in a subsequent theoretical study of the thermal conversion of **8** to **9**, using a spin-unrestricted version of MINDO/3 (UMINDO/3), Caballol and Canadell[9] found a true transition structure (only one negative eigenvalue of the force constant matrix) showing a nonsymmetrical geometry lying 1.5 kcal/mol above the exo conformation (**8a**) of radical **8**, which was calculated to be 5.4 kcal/mol more stable than the endo conformation (**8b**). The alternative (mode 2) rearrangement of **8** to **10** was not investigated in that UMINDO/3 study. Later ab initio spin-unrestricted Hartree–Fock (UHF)[10] calculations with the 4-31G basis set[11] on the equlibrium structure of **8** indicate that **8a** is 3.3 kcal/mol more stable than **8b** and that the barrier for the **8a** → **8b** inversion is only 3.6 kcal/mol.[12] As far as we know, no ab initio study has been devoted yet to the ring-opening reactions of **8**.

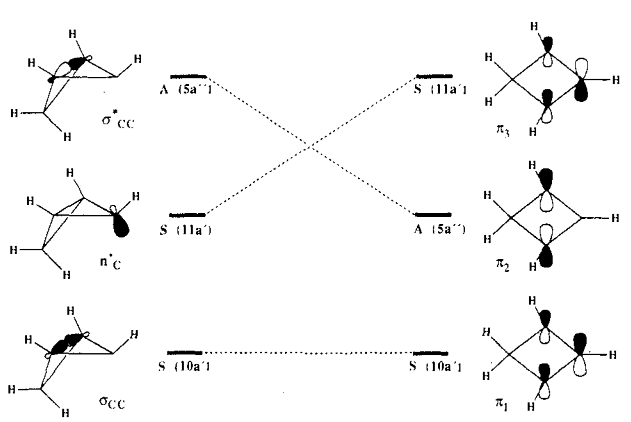
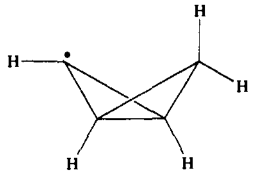
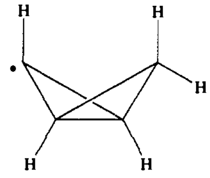


Figure 1. Molecular orbital correlation diagram for the disrotatory interconversion between *exo*-bicyclobutyl and cyclobutenyl radicals.



8a



8b

As a part of a comprehensive theoretical study of the thermal rearrangement reactions in bicycloalkyl radicals, here we report the first ab initio MO investigation of the $C_4H_5^\bullet$ potential energy surface associated with the two modes of ring opening in **8a** via β scission, using single-determinant and multiconfiguration wave functions, along with analytic energy gradient methods and force constant matrix analysis of the stationary points.

II. Elementary Theoretical Considerations

The first step in the present investigation was to determine the geometrical requirements of the transition structure for the ring opening of **8a** to give **9**, as well as the characteristics of the electronic wave function describing this electrocyclic process. For this purpose, we carried out a detailed analysis of the corresponding orbital and state correlation diagrams. In principle, during the ring opening of **8a**, the methine hydrogens adjacent to the fusion C–C bond might move in either a disrotatory or conrotatory fashion. However, owing to the severe geometrical constraint in **8a**, only the disrotatory motion can take place. Figure 1 shows the correlation diagram for the MOs most directly involved in the disrotatory conversion of **8a** into **9**. For **8a** these are the orbitals associated with the C–C bond that is broken (σ_{CC} and σ^*_{CC}) and the SOMO ($n^\bullet_c$), while for **9** these are the three π orbitals (π_1, π_2, and π_3). Each of these orbitals is classified by symmetry labels (S, symmetrical; A, antisymmetrical) relating to the symmetry plane that is maintained during the conventional

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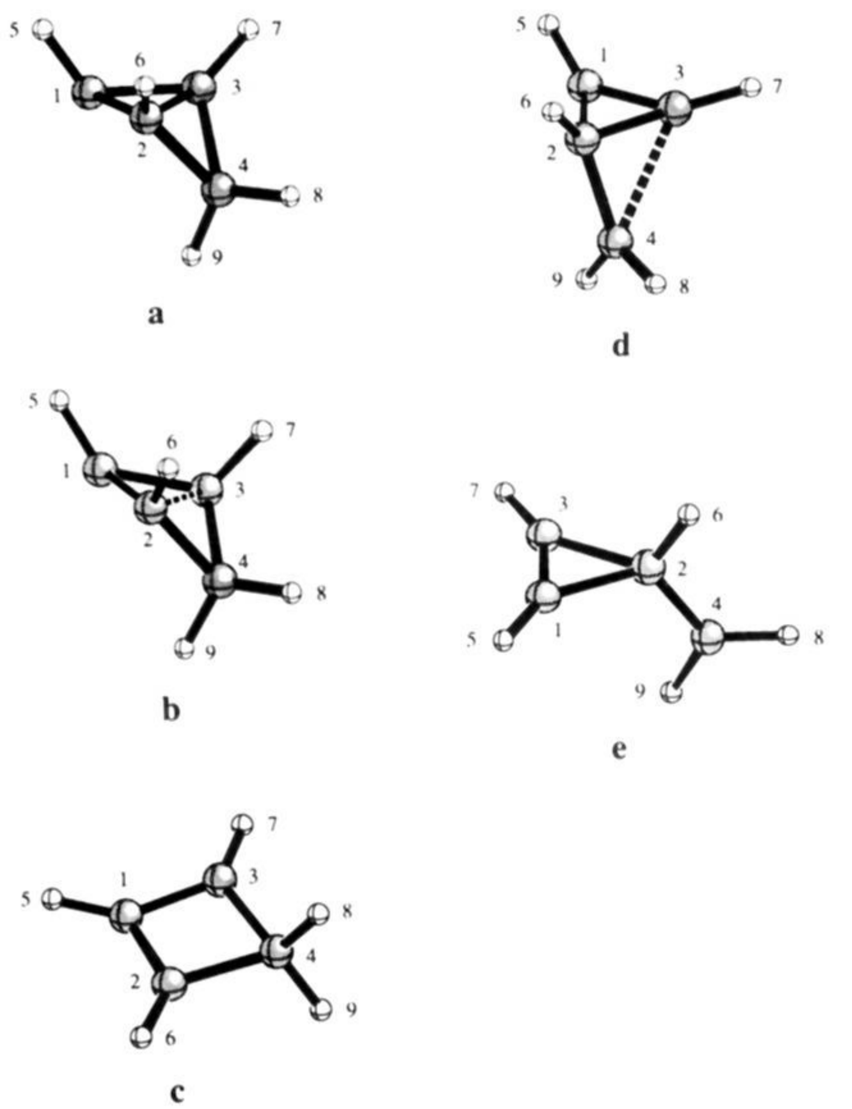

Figure 2. Computer plots of (a) the equilibrium structure of *exo*-bicyclobutyl radical, (b) the transition structure TS1, (c) the equilibrium structure of cyclobutenyl radical, (d) the transition structure TS2, and (e) the equilibrium structure of cyclopropenylmethyl radical.

disrotatory process, namely, the plane bisecting the central C–C bond in **8a**. Alternative symmetry labels appropriate to the irreducible representations (a' or a'') of the C_s point group are also included. Assuming that the equilibrium geometry of **8a** has C_s molecular symmetry,[12] its ground-state electron configuration can be written in short form as

$$...(9a')^2(3a'')^2(4a'')^2(10a')^2(11a')^1 \qquad (1)$$

As regards **9**, it is reasonable to assume that its equilibrium geometry has C_{2v} symmetry. Then the ground-state electron configuration is found to be

$$...(3b_2)^2(8a_1)^2(4b_2)^2(2b_1)^2(1a_2)^1 \qquad (2)$$

If C_{2v} molecular geometry is retained but the individual MOs are classified according to the lower symmetry point group C_s, then the ground-state electron configuration of **9** is written

$$...(3a'')^2(9a')^2(4a'')^2(10a')^2(5a'')^1 \qquad (3)$$

From configurations 1 and 3 if follows that the ground states of **8a** ($^2A'$) and **9** ($^2A''$) belong to different symmetry classes of the common point group C_s, and in order to conserve the ortibal symmetry, the disrotatory thermal reaction would thus always have to give an electronically excited state of the product. Therefore, if it is assumed that the rearrangement proceeds through a path conserving the symmetry plane bisecting the fusion C–C bond, it becomes apparent that the thermal interconversion between **8** and **9** is both orbital-symmetry forbidden and state-symmetry forbidden. It should be noted that, at variance with the symmetry-forbidden electrocyclic transformations of closed-shell systems, the electron interaction resulting from a CI treatment will not prevent the predicted crossing between the electron configurations 1 and 3 because these configurations belong to different symmetry classes and do not interact. Therefore, it appears that a CI treatment cannot force a correlation between the ground states of radicals **8a** and **9**. This suggests that the thermal electrocyclic conversion of **8** into **9** is a nonadiabatic reaction. However, this prediction seems to be in direct contradiction with the fact that the ESR spectrum of **8** cannot be observed at temperatures above −100 °C. For this reason, it seems unlikely that the reaction gives an electronically excited state of the product.

Perturbation by not fully concerted changes in the geometrical parameters during the reaction can lead to a complete annulment of the symmetry of **8a**, and consequently, this would allow an interaction between the aforementioned configurations of the unperturbed system, which should force the correlation between the ground states. On the basis of this hypothesis, it appears that in order to locate a true transition structure on the potential energy surface for the conversion of **8a** into **9**, it is necessary to destroy the initial molecular symmetry along the reaction path, by performing adequate distortions of the geometrical parameters in the sense of not allowing a synchronous change of their values from the reactant to the product.

Concerning the requirements that the wave function has to fulfill in order to describe adequately the essential electronic effects involved in the electrocyclic ring opening of **8a** to give **9**, we note that along the pathway the wave function should at least include the configuration interaction between the crossing pairs of configurations (i.e., 1 and 3) by destroying the symmetry element common to reactant and product. An obvious choice would be a multiconfiguration SCF (MCSCF) wave function of the "complete active space" (CAS) class.[13,14] However, the single-determinant UHF method may provide at much lower computational cost a description of the potential energy surface that would be qualitatively correct, in the sense that the stationary points located by using this simple wave function may be close in geometry to those calculated employing the CAS-MCSCF approach. As it will be shown later, this proves to be the case.

III. Unrestricted Hartree–Fock Calculations

The ab initio calculations reported in this section were performed within the framework of the UHF method with a locally modified version[15] of the GAUSSIAN 80 system of programs.[16] The equilibrium geometries of **8a**, **9**, and **10**, as well as the transition structures for the ring opening of **8a** to give **9** (designed TS1) and for the ring opening of **8a** to give **9** (designed TS2), were initially optimized by using the spin-unrestricted version of the AM1 (UAM1) semiempirical SCF MO method[17] with a locally modified version[18] of MOPAC program[19] and then further optimized with the 3-21G split-valence basis set[20] employing analytical gradient procedures.[21,22] The most relevant geometrical parameters of the optimized structures obtained for **8a**, TS1, **9** TS2, and **10** are given in Table I (Cartesian coordinates of all optimized structures of this investigation are available as supplementary material). Harmonic vibrational frequencies of the 3-21G-optimized structures were calculated both to characterize these staionary points as minima (representing equilibrium structures) or saddle points (representing transition structures) and to evaluate zero-point

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Table I. Selected Geometrical Parameters[a] of the UHF/3-21G-Optimized Equilibrium Structures of *exo*-Bicyclobutyl (**8a**), Cyclobutenyl (**9**), and Cyclopropenylmethyl (**10**) Radicals, and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)

	8a	TS1	**9**	TS2	**10**
molecular symmetry	C_s	C_1	C_{2v}	C_1	C_s
Bond Lengths, Å					
C_1C_2	1.483	1.427	1.411	1.520	1.536
C_1C_3	1.483	1.534	1.411	1.394	1.281
C_2C_3	1.530	1.733	2.065	1.497	1.536
C_2C_4	1.514	1.507	1.557	1.479	1.469
C_3C_4	1.514	1.538	1.557	1.955	2.602
Bond Angles, deg					
$C_2C_1C_3$	62.1	71.6	94.0	61.7	65.3
$H_5C_1C_2$	125.1	125.7	133.0	139.0	144.6
$H_6C_2C_4$	130.0	126.1	133.5	128.7	116.0
$H_7C_3C_4$	130.0	123.0	133.5	125.3	128.5
$H_8C_4H_9$	115.2	113.9	110.8	119.4	119.0
Bond–Plane Angles, deg					
$(H_5C_1)(C_1C_2C_3)$	132.3	137.2	180.0	151.8	178.3
$(H_6C_2)(C_1C_2C_3)$	141.1	137.7	180.0	134.4	120.6
$(H_7C_3)(C_1C_2C_3)$	141.1	125.6	180.0	161.1	178.3
Plane–Plane Angles, deg					
$(C_4C_2C_3)(C_1C_2C_3)$	121.4	133.1	180.0	113.5	105.4
$(H_6C_2C_4)(C_1C_2C_3)$	130.2	133.8	180.0	111.9	90.0
$(H_7C_3C_4)(C_1C_2C_3)$	130.2	123.6	180.0	136.1	141.2
$(H_8C_4H_9)(C_1C_2C_3)$	90.0	89.0	90.0	86.1	90.0

[a] Atom numbering as in Figure 2.

vibrational energy corrections (ZPC) to the relative energies, by diagonalizing the mass-weighted Cartesian force constant matrix computed numerically by finite differences of analytical gradients.[23]

The optimized equilibrium structure of **8a** is essentially identical with that reported by Pacansky and Yoshimine,[12] computed with the 4-31G basis set. Moreover, at the UHF/3-21G level, the optimized equilibrium structure of the endo conformation (**8b**) was calculated to be 3.4 kcal/mol higher in energy than the exo conformation (**8a**), in full agreement with the results of that UHF/4-31G study. As regards **9**, the present calculations predict a planar arrangement of the four carbon atoms with the hydrogen atoms of the three methine groups lying on this plane. Such a result can be ascribed to the energy stabilization arising from the allylic delocalization of the odd electron in this planar geometry. In fact, the C_1C_2 bond length (1.411 Å) is only slightly larger than the UHF/3-21G-calculated C–C bond distance in **5** (1.389 Å).[24] On the other hand, the optimized equilibrium structure of **10** has a bisected conformation. At the UHF/3-21G level, the eclipsed conformation was calculated to lie 3.9 kcal/mol above this bisected conformation. Therefore, radical **10** is predicted to show an exact parallel to radical **6**, which exhibits the same preferred conformation.[25] Futhermore, it is worth mentioning that ESR studies[26] have shown that cyclobutenylmethyl and cyclopentenylmethyl radicals also prefer the bisected conformation.

The most salient geometrical features of TS1 are the unequal C_1C_2 and C_1C_3 bond lengths and the fact that the C_3H_7 methine group has rotated 15.5° (relative to its position in **8a**) while the C_2H_6 methine group has rotated only 3.4°. These geometrical characteristics are similar to those observed in the transition structure calculated at the UHF/3-21G level for the ring opening of **4** to give **5**.[24] Both cases indicate that *the minimum reaction path does not involve synchronous rotation of the methine groups; one methine group approaches its final position in the resulting radical more rapidly than the other.* Interestingly, in TS1, the length (1.733 Å) of the C–C bond undergoing cleavage is significantly shorter than in the transition structure (1.988 Å) calculated for the ring opening of **4** to give **5**.[24] This result suggests that the **8a** → **9** rearrangement has an earlier transition state than the **4** → **5**. Regarding the alternative transition structure TS2, it is interesting to compare its geometrical parameters with those calculated for the reactant **8a**. It can be seen that in going from **8a** to TS2 the angle between the two ring planes, $(C_4C_2C_3)(C_1C_2C_3)$, decreases 8° and the $H_8C_4H_9$ methylene group rotates 4°. These geometrical changes, tending to increase the overlap between the SOMO and the bond undergoing cleavage (C_3C_4), are consistent with the aforementioned stereoelectronic requirements of the ring opening in cycloalkylmethyl radicals. In TS2 the latter bond has stretched to 1.955 Å, which is a bond length slightly larger than the value (1.841 Å) found in the transition structure calculated for the ring opening of **6** to give **7**.[27] Another point of particular interest is that in going from **8a** to TS2 the length of the C_1C_3 bond changes from 1.483 to 1.394 Å. This result indicates that *the CC double bond of **10** becomes notably formed at the transition structure TS2.*

Finally, in order to obtain reliable relative energies, additional single-point calculations were performed with the split-valence plus d-polarization 6-31G* basis set,[28] and with incorporation of all-electrons correlation using Moller-Plesset (MP) perturbation theory terminated at second order (UMP2).[29] It is known that the MP perturbation treatment may be slow to converge for large spin contamination.[30] Recent work has shown that projecting out the largest spin contaminants (spin annihilation) after perturbation corrections are made for electron correlation improves agreement with experiment.[31,32] For that reason, our best energies, denoted PUMP2/6-31G*, were calculated by annihilation of the first two spin contaminants (i.e., quadruplet and sextet states) from the UMP2/6-31G* wave function, employing the fomalism developed by Knowles and Handy,[32] as implemented in CADPAC systems of programs.[33] The total energies obtained at the various levels of theory, along with the expectation values of the spin-squared operator S^2, ($\langle S^2 \rangle$), and the zero-point vibrational energies (ZPE) of **8a**, TS1, **9**, TS2, and **10** are summarized in Table II. The relative energies are given in Table III.

At the present highest level of theory, namely, from the PUMP2/6-31G*-calculated energies, the potential energy barrier for the formation of **9** via TS1 is 4.6 kcal/mol. Inclusion of the ZPC leads to an energy of activation at 0 K of 2.9 kcal/mol. This value is consistent with early UMINDO/3 calculations by Caballol and Canadell predicting an activation energy of 1.5 kcal/mol.[9] It is worth mentioning that our initial UAM1 calculations predicted an activation energy of 3.0 kcal/mol for the **8** → **9** ring opening. While no experimental value is available, the ESR spectrum of **8** cannot be observed at temperatures above −100 °C, implying that the rate of rearrangement is then greater than the rate of removal of radicals by combination or disproportionation. Furthermore, we note that for the related ring opening of **4** to give **5** the energy of activation of 0 K calculated at the same level of theory (24.0 kcal/mol)[34] is in satisfactory agreement with the experimental activation energy of 22 ± 2 kcal/mol.[35] As regards

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Table II. Calculated Total Energies (Hartrees) and Zero-Point Vibrational Energies (kcal/mol) of *exo*-Bicyclobutyl (**8a**), Cyclobutenyl (**9**), and Cyclopropenylmethyl (**10**) Radicals, and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)[a,b]

species	state	UHF/3-21G	UHF/6-31G*	UMP2/6-31G*	PUMP2/6-31G*	ZPE
8a	$^2A'$	−153.34801 (0.757)	−154.23396 (0.757)	−154.74765 (0.751)	−154.74872 (0.750)	49.3
TS1	A	−153.33878 (0.925)	−154.22275 (0.887)	−154.73222 (0.846)	−154.74141 (0.750)	47.6
9	$^2A_2$	−153.42101 (1.009)	−154.28827 (0.998)	−154.77296 (0.927)	−154.79017 (0.750)	48.2
TS2	^2A	−153.31059 (1.066)	−154.18484 (1.044)	−154.68441 (0.977)	−154.70164 (0.750)	45.8
10	$^2A''$	−153.35885 (0.772)	−154.23207 (0.771)	−154.73813 (0.758)	−154.74086 (0.750)	46.7

[a] All calculations at the UHF/3-21G-optimized geometries. [b] The expectation values of the spin-squared operator S^2 are indicated in parentheses. In the case of UMP2 and PUMP2 levels of theory, the expectation value of S^2 refers to the first-order corrected wave function.

Table III. Calculated Relative Energies (kcal/mol) of *exo*-Bicyclobutyl (**8a**), Cyclobutenyl (**9**), and Cyclopropenylmethyl (**10**) Radicals, and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)[a]

species	state	UHF/3-21G	UHF/6-31G*	UMP2/6-31G*	PUMP2/6-31G*	PUMP2/6-31G*+ZPC
8a	$^2A'$	0	0	0	0	0
TS1	^2A	5.8	7.0	9.7	4.6	2.9
9	$^2A_2$	-45.8	-34.1	−15.9	−26.0	-27.1
TS2	^2A	23.5	30.8	39.7	29.5	26.0
10	$^2A''$	-6.8	1.2	6.0	4.9	2.3

[a] All calculations at the UHF/3-21G-optimized geometries.

Table IV. Occupation Numbers of the Relevant Natural Orbitals of the UHF/3-21G Wave Function of *exo*-Bicyclobutyl (**8a**), Cyclobutenyl (**9**), and Cyclopropenylmethyl (**10**) Radicals, and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)[a]

species	state	natural orbitals occupation numbers[b]		
8a	$^2A''$	1.9988 (10a′)	1.0000 (11a′)	0.0011 (5a″)
TS1	^2A	1.9128 (14a)	1.0000 (15a)	0.0872 (16a)
9	$^2A_2$	1.8764 ($2b_1$)	1.0000 ($1a_2$)	0.1235 ($3b_1$)
TS2	^2A	1.8385 (14a)	1.0000 (15a)	0.1615 (16a)
10	$^2A''$	2.0000 (11a′)	1.0000 (4a″)	0.0000 (5a″)

[a] All calculations at the UHF/3-21G-optimized geometries. [b] The number and symmetry of the natural orbits are indicated in parentheses.

the energy of reaction for the **8a** → **9** ring opening, at the PUMP2/6-31G*+ZPC level this is predicted to be −27.1 kcal/mol. While no experimental thermochemical data are available for this reaction, we mention that for the **4** → **5** rearrangement the calculated energy of reaction at the same level of theory is −30.3 kcal/mol.[34] The latter result, though too negative, compares acceptably with the approximate enthalpy of reaction, −22.8 ± 4.9 kcal/mol, estimated from the experimental[36] heats of formation of **4** and **5**. Therefore, the calculated energy of reaction for the ring opening of **8a** to afford **9** is probably too negative by 7 kcal/mol.

For the alternative ring opening of **8a** to give **10**, an energy of activation at 0 K of 26.0 kcal/mol is predicted from the PUMP2/6-31G*+ZPC-calculated energies. While no experimental value is available, the present result is in keeping with the experimental fact that the β scission of **8** leads exclusively to **9**, implying that the activation energy for the **8** → **10** rearrangement is much higher than for **8** → **9**. Furthermore, the reliability of our theoretical procedure in computing the barrier height for the **8a** → **10** rearrangement can be assessed from the activation energy predicted in the case of the related ring opening of **6** to give **7**. In fact, at the PUMP2/6-31G*+ZPC level this activation energy is computed to be 7.8 kcal/mol,[27] in excellent agreement with the recommended experimental value of 7.26 kcal/mol.[37] Finally, we note that the energy of reaction for the isomerization of **8a** to **10** is predicted to be 2.3 kcal/mol at the PUMP2/6-31G*+ZPC level. While no experimental thermochemical data are available for this reaction, it is worth mentioning that for the **6** → **7** rearrangement the energy of reaction calculated at the same level of theory is 0.3 kcal/mol,[27] which is in reasonable agreement with the value of −3.15 kcal/mol estimated from thermochemical data.[38] The predicted energy of reaction for the ring opening of **8a** to afford **10** is then probably too positive by 3 kcal/mol.

IV. Multiconfiguration SCF Calculations

An examination of the $\langle S^2 \rangle$ values listed in Table II reveals considerable spin contamination in the UHF wave function of structures TS1, **9** and TS2. Since their optimum molecular geometry have been determined by using the UHF/3-21G wave function, which shows the heaviest spin contamination, one wonders about the reliability of the geometrical results obtained in the previous section. Therefore, we performed additional calculations employing the CAS-MCSCF approach, hereafter designated CASSCF, to assess the reliability of the UHF/3-21G-optimized structures for TS1, **9**, and TS2.

The CAS was selected following the procedure recently suggested by Pulay and Hamilton,[39] based on the fractional occupation of the natural orbitals of the UHF wave function (designated UNOs). Table IV lists the occupation numbers of the relevant UNOs of **8a**, TS1, **9**, TS2, and **10**, computed from the UHF/3-21G wave function. In the case of TS1, **9**, and TS2, the fractional occupancies of the UNOs indicate that there are three "active" orbitals, hereafter denoted ϕ_i, ϕ_m, and ϕ_k, where ϕ_m is the MO describing the unpaired electron. As expected, for TS1 and TS2 ϕ_i and ϕ_k are the bonding and antibonding MOs of the C–C bond being broken. Regarding **9**, ϕ_i and ϕ_k are the highest doubly occupied and the lowest unoccupied π MOs, respectively. Distribution of the three reacting electrons within the three "active" orbitals with all possible couplings leads to a MCSCF wave function for TS1, **9**, and TS2 formed as a linear combination of eight doublet spin-adapted configuration state functions (CSFs). In the case of **8a** and **10** there is not any significant fractional occupancy of the UNOs. This indicates that in the region of the potential surface around the equilibrium geometries of **8a** and **10** the electron correlation is dynamical,[40] and consequently, there are no "active" orbitals. This feature is in keeping with the fact

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Table V. Selected Geometrical Parameters[a] of the ROHF/3-21G-Optimized Equilibrium Structures of *exo*-Bicyclobutyl (**8a**) and Cyclopropenylmethyl (**10**) Radicals, and of the CASSCF/3-21G-Optimized Equilibrium Structure of Cyclobutenyl Radical (**9**) and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)

	8a	TS1	**9**	TS2	**10**
molecular symmetry	C_s	C_1	C_{2v}	C_1	C_s
	Bond Lengths, Å				
C_1C_2	1.483	1.435	1.409	1.518	1.531
C_1C_3	1.483	1.538	1.409	1.384	1.281
C_2C_3	1.528	1.819	2.064	1.499	1.531
C_2C_4	1.514	1.514	1.557	1.478	1.474
C_3C_4	1.514	1.549	1.557	1.998	2.603
	Bond Angles, deg				
$C_2C_1C_3$	62.0	75.4	94.2	62.0	65.3
$H_5C_1C_2$	124.7	126.9	132.9	138.8	144.7
$H_6C_2C_4$	130.0	125.4	133.5	128.2	115.5
$H_7C_3C_4$	130.0	118.4	133.5	125.6	128.6
$H_8C_4H_9$	115.3	113.3	110.9	119.4	119.2
	Bond–Plane Angles, deg				
$(H_5C_1)(C_1C_2C_3)$	131.6	140.3	180.0	151.9	178.6
$(H_6C_2)(C_1C_2C_3)$	141.1	134.2	180.0	134.3	121.0
$(H_7C_3)(C_1C_2C_3)$	141.1	119.7	180.0	163.2	178.6
	Plane–Plane Angles, deg				
$(C_4C_2C_3)(C_1C_2C_3)$	121.4	136.4	180.0	110.9	105.4
$(H_6C_2C_4)(C_1C_2C_3)$	130.2	132.4	180.0	108.9	90.0
$(H_7C_2C_4)(C_1C_2C_3)$	130.2	118.2	180.0	135.5	141.3
$(H_8C_4H_9)(C_1C_2C_3)$	90.0	89.2	90.0	84.7	90.0

[a] Atom numbering as in Figure 2.

that for these radicals the $\langle S^2 \rangle$ value of the UHF/3-21G wave function (see Table II) is close to the expected value (0.75) for a pure doublet state. Therefore, a single-determinant wave function will suffice for computing the equilibrium geometries of **8a** and **10**. For the sake of comparison, these geometries were reoptimized by employing a spin-restricted open-shell Hartree–Fock (ROHF)[41] wave function. All CASSCF and ROHF calculations were carried out by using the GAMESS system of programs.[42] Molecular geometries were optimized with the 3-21G basis set either by the Murtagh–Sargent[21] (equilibrium structures) or the Schlegel[22] (transition structures) muliparameter search routines, employing analytically calculated forces. The most relevant geometrical parameters of the optimized structures obtained for **8a**, TS1, **9**, TS2, and **10** are given in Table V. The harmonic vibrational frequencies of these structures were calculated with the 3-21G basis set by diagonalizing the mass-weighted Cartesian force constant matrix, computed numerically by finite difference of analytical gradients.

The difference in the geometries optimized with the UHF and ROHF methods for **8a** is virtually nil, rising to 0.002 Å for the C_2C_3 bond length, 0.4° for the $H_5C_1C_2$ bond angle, and 0.6° for the $(H_5C_1)(C_1C_2C_3)$ bond–plane angle. This result is consistent with the low spin contamination shown by the UHF/3-21G wave function of this radical. For radical **10**, whose UHF wave function shows a rather low spin contamination, both methods also give essentially identical optimized geometries, the largest differences rising to 0.005 Å in the C_1C_2 bond length, 0.5° in the $H_6C_2C_4$ bond angle, and 0.4° in the $(H_6C_2)(C_1C_2C_3)$ bond–plane angle. As regards radical **9**, though its UHF wave function is heavily spin contaminated, the difference in the geometries optimized with the UHF/3-21G and CASSCF/3-21G methods also is virtually nil, rising to 0.002 Å for the C_1C_2 bond length and 0.2° for the $C_2C_1C_3$ bond angle. The latter result parallels that obtained by Takada and Dupuis[43] for radical **5**. Finally, by comparison of Tables I and V, it is readily seen that the CASSCF and UHF methods give similar optimized geometries for the transition structures TS1 and TS2, though their UHF wave functions suffer from large spin contamination. Thus, for TS1 the main geometrical differences are the C_2C_3 bond length, the $H_7C_3C_4$ bond angle, the $(H_7C_3)(C_1C_2C_3)$ bond–plane angle, and the $(H_7C_3C_4)(C_1C_2C_3)$ plane–plane angle, which are predicted 0.086 Å longer, 4.6° smaller, 5.9° smaller, and 5.4° smaller, respectively, by the CASSCF calculations. In the case of TS2, the molecular geometries obtained from the two methods differ by up to 0.043 Å in the bond lengths (C_3C_4), 0.7° in the bond angles ($H_7C_3C_4$), 2.1° in the bond–plane angles ($(H_7C_3)(C_1C_2C_3)$), and 3.0° in the plane–plane angles ($(H_6C_2C_4)(C_1C_2C_3)$).

Table VI. List of Configurations Contributing 1% or More to the CASSCF/3-21G Wave Functions of *exo*-Bicyclobutyl (**8a**), Cyclobutenyl (**9**), and Cyclopropenylmethyl (**10**) Radicals, and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)

species	state	CI mixing coeff	electronic confign		
TS1	^2A		14a	15a	16a
		0.9503	2	1	0
		−0.2086	1	1	1
		−0.2049	0	1	2
9	$^2A_2$		$2b_1$	$1a_2$	$3b_1$
		0.9570	2	1	0
		−0.2449	1	1	1
		−0.1554	0	1	2
TS2	^2A		14a	15a	16a
		0.9464	2	1	0
		−0.2513	1	1	1
		−0.1958	0	1	2

To rationalize the remarkable similitude found above between the transition structures predicted by the crude UHF method and the more sophisticated CASSCF treatment, it is instructive to examine the CI coefficients of the MCSCF expansions of TS1 and TS2. These are listed in Table VI for the electron configurations contributing 1% or more to the CASSCF/3-21G wave function. For the sake of comparison, the configurations of radical **9** are also given in Table VI. First of all, we note that for TS1, **9**, and TS2, besides the ground-state electron configuration which always has the largest contribution, there are one singly and one doubly excited configurations contributing significantly to the MCSCF expansion. The doubly excited configuration is one in which two electrons are raised from ϕ_i to ϕ_k, namely $(\phi_i)^2 \rightarrow (\phi_k)^2$. In the ring-opening reaction of **8a** to give **9**, by mixing this configuration with the ground-state one, the MCSCF wave function correlates the two electrons forming the C_2C_3 bond in **8a** and TS1. Analogously, in the ring-opening reaction of **8a** to afford **10**, by mixing this doubly excited configuration with the ground-state one, the MCSCF wave function correlates the two electrons forming the C_3C_4 bond in **8a** and TS2. As regards the singly excited configuration, it is one of the two doublet spin-adapted CSFs associated with the excited configuration generated by promotion of one electron from ϕ_k to ϕ_k, namely, $(\phi_i)^1 \rightarrow (\phi_k)^1$. Specifically, its CSF can be written in short form as[44]

$$^2\Psi = (6)^{-1/2}\{2|\ldots\phi_i\phi_k\bar{\phi}_m| - |\ldots\phi_i\bar{\phi}_k\phi_m| - |\ldots\bar{\phi}_i\phi_k\phi_m|\} \quad (4)$$

All attempts to locate the transition structures for the **8a** → **9** and **8a** → **10** rearrangements employing a MCSCF wave function including only the doubly excited $(\phi_i)^2 \rightarrow (\phi_k)^2$ and ground-state configurations were unsuccessful. It turns out, therefore, that in order to describe adequately those transition structures, the MCSCF expansion must also include the singly excited configuration given in eq 4. Apparently, in addition to the doubly excited configuration $(\phi_i)^2 \rightarrow (\phi_k)^2$, which is required to correlate the electron pair of the bond undergoing cleavage, the spin coupling in the CSF of eq 4 is essential to describe the electronic changes taking place at the transition state. These consist in starting the formation of a CC π bond by coupling the formerly unpaired

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Table VII. CASSCF-Calculated Total Energies (Hartrees) of *exo*-Bicyclobutyl (**8a**), Cyclobutenyl (**9**), and Cyclopropenylmethyl (**10**) Radicals, and of the Transition Structures for the Ring Opening of **8a** To Give **9** (TS1) or **10** (TS2)[a,b]

species	state	CASSCF/3-21G	CASSCF/6-31G*
8a[c]	$^2A'$	−153.36391 (0.0)	−154.24755 (0.0)
TS1	^2A	−153.36138 (1.6)	−154.24007 (4.7)
9	$^2A_2$	−153.43695 (−45.8)	−154.30261 (−34.5)
8a[d]	^2A	−153.36268 (0.0)	−154.24769 (0.0)
TS2	^2A	−153.32986 (20.6)	−154.20154 (29.0)
10	$^2A''$	−153.38366 (−13.2)	−154.25385 (−3.9)

[a] At the ROHF/3-21G-optimized geometries of **8a** and **10**, and at the CASSCF/3-21G-optimized geometries of **9**, TS1, and TS2. [b] The quantities in parentheses are the relative energies (in kcal/mol). [c] Taking as active orbitals the bonding and antibonding MOs associated with the C_2C_3 bond, and the SOMO. [d] Taking as active orbitals the bonding and antibonding MOs associated with the C_3C_4 bond, and the SOMO.

electron in **8a** with one of the two electrons of the β C–C bond being broken while the other electron is localized on the new radical site (i.e., the γ-carbon).

At this point we note that the spatial function of eq 4 is closely related to that of the CSF representing the quartet state arising from the singly excited configuration $(\phi_i)^1 \rightarrow (\phi_k)^1$. In fact, the wave function of the $\langle S_z \rangle = +^1/_2$ component of this quartet can be written, in the single-configuration approach, as[44]

$$^4\Psi = (3)^{-1/2}\,\{2|...\phi_i\phi_k\bar{\phi}_m| + |...\phi_i\bar{\phi}_k\phi_m| + |...\bar{\phi}_i\phi_k\phi_m|\} \quad (5)$$

Annihilation of this quartet from the UHF/3-21G wave function of TS1, **9**, and TS2 leads to the calculated $\langle S^2 \rangle$ values of 0.753, 0.766, and 0.764, respectively. This means that the quartet state of eq 5 is the main spin contaminant in the UHF wave function of these species. The admixture of such a quartet state with the ground-state doublet occurring in the UHF wave function of TS1 and TS2 allows for some electron correlation effect between orbitals of different spin and provides the flexibility required to describe satisfactorily the geometry of these transition structures. Therefore, in some way the CSF of eq 5 plays in the UHF wave function of TS1 and TS2 the same role as that of the CSF of eq 4 in their CASSCF wave function, so it turns out that both theoretical procedures should predict essentially identical geometries for these transition structures.

Finally, in order to compare the enegies of structures **8a** and **10** with those of TS1, **9** and TS2, the MCSCF energy computations were extended to the ROHF/3-21G-optimized equilibrium geometries of **8a** and **10**. In such single-point calculations both the MCSCF expansion and nature of the orbitals were defined by analytical continuation from TS1 and TS2. Thus, for **8a** the bonding and antibonding MOs of the C–C bond undergoing cleavage in the corresponding ring-opening reaction were taken as the "active" orbitals ϕ_i and ϕ_k, respectively, in addition to the MO describing the unpaired electron (ϕ_m). As regards **10**, the bonding (11a′) and antibonding (5a″) MOs of the C_1C_3 π bond were taken as the "active" orbitals ϕ_i and ϕ_k, respectively, and the 4a″ MO as the "active" orbital ϕ_m. The total and relative energies calculated at the CASSCF level of theory with the 3-21G and 6-31G* basis sets are given in Table VII.

When the relative energies in Tables III and VII are compared, it is readily seen that the CASSCF/6-31G* and PUMP2/6-31G* calculations give essentially identical potential energy barriers for each mode of ring opening in **8a**. Thus, for the **8a** → **9** rearrangement the CASSCF/6-31G*-calculated barrier height is only 0.1 kcal/mol lower than that calculated from the PUMP2/6-31G* energies, and for the alternative ring-opening mode, **8a** → **10**, the barrier height predicted by both theoretical procedures differs in 0.5 kcal/mol. Such a remarkable agreement provides a strong support to the barrier heights determined from the single-point PUMP2/6-31G* energies computed at the UHF/3-21G-optimized geometries. Regarding the energies of reaction, the values computed with the CASSCF treatment are too negative, as compared with the values predicted by the PUMP2 method. Thus, for the **8a** → **9** rearrangement the difference between the energies of reaction calculated by the two methods with 6-31G* basis set is 8.5 kcal/mol, and for **8a** → **10** rearrangement the difference is 8.8 kcal/mol. In this regard, it is worth mentioning that for the related ring-opening reactions **4** → **5** and **6** → **7**, for which approximate experimental heats of reaction are available, the energies of reaction calculated at the CASSCF/6-31G* level are too negative by about 12 and 9 kcal/mol, respectively. These results suggest that although the CASSCF/6-31G* treatment describes satisfactorily the difference in electron correlation energy between the radical **8a** and the transition structures TS1 and TS2, this procedure is not adequate to account for the overall change in correlation energy that occurs in going from **8a** to either **9** or **10**. Better energies of reaction can only be obtained by including dynamical electron correlation effects in addition to the nondynamical ones accounted in the CASSCF treatment; for example, when CI including all singly and doubly excited configurations (CISD) relative to the zeroth-order CASSCF wave function is performed.[45] Such sophisticated multireference (MR) CISD computations require at least an order of magnitude more computer time than the simple PUMP2 calculations. Since the PUMP2/6-31G* computations give reasonable energies of reaction for the archetypal **4** → **5** and **6** → **7** rearrangements, we felt that such MR-CISD calculations were not justified in the present study.

V. Interpretative Discussion on the Predicted Activation Energies for the Two Modes of Ring Opening in Bicyclobutyl Radical

On the basis of the results reported in sections III and IV, the activation energy at 0 K for the ring-opening reaction of **8a** to give **9** is predicted to be 3 kcal/mol, while for the ring opening of **4** to afford **5** this is computed to be 24 kcal/mol. On the other hand, the geometrical parameters of the cyclopropyl moiety in TS1 (i.e., $C_1C_2C_3$) are quite similar to those determined for the transition structure of the ring opening of **4**. Moreover, according to the energies of reaction calculated at the PUMP2/6-31G*+ZPC level, the **4** → **5** rearrangement is about 3 kcal/mol more exothermic than the **8a** → **9** and, therefore, a somewhat lower activation energy would be expected for the former rearrangement as compared with the latter (Hammond's postulate). It is of interest to inquire as to the source of the large difference in the calculated activation energies of these apparently analogous ring-opening reactions. In this regard, we note that the activation energy for the β scission of a C–C bond in an aliphatic acyclic radical where an olefinic bond is simultaneously formed has been shown to be in the range 33 ± 2 kcal/mol.[46] In the ring-opening reactions of cyclic radicals via β scission, there can be ring strain energy, which is relieved in the transition state if the ring is considerably less strained than in the radical. If this is the case, the change in ring strain should lower the energy of activation. Thus, from the experimental activation energy for the **4** → **5** rearrangement (22 ± 2 kcal/mol), it is inferred that the transition state of this ring-opening reaction contains 11 kcal/mol less ring strain energy than radical **4**. Regarding the rearrangement of **8a** to **9**, the calculated activation energy of 3 kcal/mol suggests that the transition state TS1 contains 30 kcal/mol less ring strain energy than radical **8**. This much greater relief of strain energy, as compared with that estimated above for the formation of the transition state in the related ring-opening reaction of radical **4**, can be attributed primarily to the larger amount of ring strain in the former radical. In fact, it is worth noting that the conventional ring strain energy of bicyclobutane (67.0 kcal/mol) is more than twice that of cyclopropane (27.6 kcal/mol).[47] Thus, though the **8a** → **9** rearrangement involves the formation of a strained four-membered carbocyclic radical,[48] the ring strain energy relieved in going from the reactant to the transition state

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(45) For a review, see: Shavitt, I. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Vol. 3.

(46) Benson, S. W.; O'Neal, H. E. *Kinetic Data on Gas Phase Unimolecular Reactions*; NSRDS, NBS-21; U.S. Government Printing Office: Washington, DC, 1970.

(47) Benson, S. W. *Thermochemical Kinetics*; John Wiley: New York, 1976; p 273.

(48) The conventional ring strain energy of cyclobutene is 29.8 kcal/mol.[47]

is greater than in the case of the **4** → **5** rearrangement. Consequently, it can be concluded that the much lower activation energy predicted for the ring-opening reaction of **8a** to give **9**, as compared with that for the ring opening of **4** arises mainly from the larger ring strain energy in the former radical.

As regards the alternative mode of ring opening in **8a** to afford **10**, it is remarkable that the predicted activation energy at 0 K (26.0 kcal/mol) is about 19 kcal/mol higher than the experimental activation energy (7.26 kcal/mol) for the apparently analogous **6** → **7** rearrangement. However, on the basis of the expected difference in the ring strain energy relieved in going from each radical to the corresponding transition state, it is not difficult to understand such a large difference in the energy of activation. First we note that the ring opening of **8a** by β scission of the peripheral bonds involves the incorporation of a CC double bond into the cyclopropyl moiety of this radical, while the ring opening of **6** leads to the formation of an acyclic olefinic bond. We have noted previously (see section III) that in TS2 the nascent CC π bond is at an advanced stage of making, so there can be a considerable increase of strain energy in the cyclopropyl ring of this transition state. Therefore, in going from **8a** to TS2 there is a great relief of ring strain energy in the cyclopropane moiety (i.e., $C_2C_3C_4$) that is nearly outweighed by the increase of strain energy that takes place in the cyclopropyl ring, due to the simultaneous partial making of an inner double bond. To give support to this assertion, we note that the conventional ring strain energies of cyclopropane and cyclopropene are 27.6 and 53.7 kcal/mol,[47] respectively, so the integration of a double bond into a three-membered carbocycle provokes an increase in the ring strain energy of ca. 26.1 kcal/mol.

VI. Conclusions

The following conclusions can be drawn from the ab initio UHF and CASSCF calculations reported here:

(1) The formally orbital-symmetry-forbidden ring opening of **8a** to give **9** takes place via a highly nonsymmetric transition structure, namely, with unequal C_1C_2 and C_1C_3 bond lengths, one methine group having rotated 21° (relative to its position in **8a**) whereas the other has rotated only 7°. This nonsymmetric geometry allows the mixing of the SOMO (a′ symmetry) and LUMO (a″ symmetry) of **8a** and the coupling between the crossing states ($^2A'$ and $^2A''$), resulting in an adiabatic reaction on the ground-state potential energy surface.

(2) Within the framework of the MCSCF approach, the transition structures for the two modes of ring opening in **8a** can be located successfully only if the CI expansion includes an excited doublet state arising from single excitation of one electron from the highest doubly occupied MO to the LUMO. This singly excited configuration appears to be essential in describing the electronic changes that take place in such transition structures. These consist in starting the formation of a CC π bond by coupling the formerly unpaired electron in **8a** with one of the two electrons of the β C–C bond being broken while the other electron is localized on the new radical site.

(3) Due to the substantial mixing of the $\langle S_z \rangle = +^1/_2$ component of the first quartet state into the UHF/3-21G doublet wave function, this method enables the calculation of the transition structures for the two modes of ring opening in **8a**, giving optimized geometries that are essentially identical with those located by using the computationally more expensive CASSCF/3-21G approach. Futhermore, the barrier heights calculated at the PUMP2/6-31G*//UHF/3-21G level differ in 0.5 kcal/mol or less from those determined from the CASSCF/6-31G*//CASSCF/3-21G-calculated energies. Therefore, the present results show that the PUMP2/6-31G*//UHF/3-21G approach is a good theoretical procedure for predicting the activation energies of the ring-opening reactions in bicycloalkyl radicals, especially in the case of large molecular systems, where the computation of the energy and its gradient based on CASSCF wave functions can be extremely costly.

(4) The low energy of activation (≈3 kcal/mol) predicted for the β scission of the fusion bond in **8a** to afford **9** is attributed to the great relief of ring strain in going from **8a** to the transition state. In sharp contrast, the β scission of the peripheral bonds is predicted to require a much larger activation energy (≈26 kcal/mol). This is due to the fact that the ring strain relief that accompanies the formation of the transition state, because of the partial ring opening of the cyclopropane ring in **8a**, is nearly compensated by the increase of ring strain that occurs in the cyclopropyl moiety of this transition state, arising from the partial making of an inner double bond.

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Supplementary Material Available: Cartesian coordinates (in angstroms) of the optimized equilibrium structures of **8a**, **9**, and **10**, and of the transition structures TS1 and TS2, calculated at various levels of theory (4 pages). Ordering information is given on any current masthead page.