Table II. Ground-State Energies and Singlet-Triplet Splittings in Units of $J = \sqrt{(U/4)^2 + \beta^2} - U/4$

	spin		VB model		Hubbard model	
molecule	ground state	excited	ground state	splitting	ground state	splitting
1	1	0	−1.000	+2.000	−1.000	+2.000
2	0	1	−4.000	0.438	−3.725	0.204
3	1	0	−3.903	0.903	−3.800	0.769
4	0	1	−6.340	0.199	−6.012	0.067
5	1	0	−6.266	0.202	−6.030	0.077
8	0	1	−10.231	0.215	−10.085	0.090
9	1	0	−10.121	0.234	−10.031	0.040
10	0	1	−10.191	0.161	−10.061	0.055
11	1	0	−10.496	0.809	−10.439	1.035

as is reasonable.[30,31]

In Table II results are reported for those systems for which both VB and PPP-type computations were carried out. The VB calculations are reported with the constant of (3.1) chosen to be

$$\text{constant} = -J_{\pi\pi}N_\pi \qquad (7.2)$$

where N_π is the number of π-bonds, and the exchange parameter $J_{\pi\pi}$ is as given by (2.2) with $K_{ij} = 0$. Thence the VB- and Hubbard-model energies in units of $J_{\pi\pi}$ are more directly comparable, as verified in Table II. For systems with 4-membered rings, it has long been known that there is lack of agreement of energies (say as embodied in Hückel's $4n + 2$ rule) between the simple VB and Hückel MO models, and this persists on comparing VB and PPP models. Thus only systems without 4-cycles have been reported in Table II. The ground-state energies are similar and, though the differences in the ground-state energies via the two models are comparable to the singlet-triplet splittings, these splittings are of the same sign for the two models. There is some qualitative agreement in these splittings via the two models. There appears to be a tendency for the VB splitting to exceed that of the Hubbard model, with the ratio of VB splitting to Hubbard-model splitting increasing as the value of the splitting decreases. Moreover, the qualitative features here do not appear to depend strongly on the particular parameter values, of t/U or of $J_{\sigma\pi}/J_{\pi\pi}$. For instance, the choice of the ratio $J_{\sigma\pi}/J_{\pi\pi}$ of eq 3.2 as "small" as −0.10 has been tested, and like orderings of levels for the PPP-type and VB models was found.

VIII. Conclusion

The ground state spin predictions via the simple VB model for aromatic carbene species seems to be in remarkable agreement both with the results from brute-force computations on the PPP model and with the experimental evidence. Further examples in which the VB model predictions agree with experiment are found in ref 35. Moreover, the graph-theoretic construction for making this prediction for alternants is very simple. Some semiquantitative agreement is found between VB and PPP-type models.

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Ab Initio Calculations on the Ring Opening of Cyclopropane Radical Cation. Trimethylene Radical Cation Is Not a Stable Intermediate

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Abstract: Ab initio calculations with the 6-31G* basis set find no chemically significant stability for trimethylene radical cation (**2**). Although, with inclusion of electron correlation at the MP2 level of theory, there is apparently an energy minimum for a geometry of **2** with C_s symmetry, the barrier to hydrogen migration to form propene radical cation (**3**) is found to be less than 0.2 kcal/mol. At the MP2 level of theory the rearrangement of cyclopropane radical cation (**1**) to **3** involves conrotatory ring opening and passage over a transition state of C_2 symmetry. After correction for zero-point energy differences, the transformation of **1** to **3** is computed to be exothermic by 10.3 kcal/mol and to require an activation energy of 21.9 kcal/mol. The importance of electron correlation for correctly calculating the relative energies of species with localized and delocalized wave functions is demonstrated, and the finding that, with inclusion of sufficient correlation, the (0,0) geometry of **2** is stable to asymmetric distortion of the C–C bond lengths is discussed.

Observation of trimethylene radical cation (**2**), formed by ring opening of cyclopropane radical cation (**1**), has been claimed both in CF_2ClCCl_2F matrices[1] and in the gas phase.[2] Recently, however, we[3] and others[4] have reported the results of ab initio calculations that call into question whether the irreversible opening of **1** to **2** is possible energetically. In this paper we describe the results of additional calculations which indicate that **2** can re-

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arrange to propene radical cation (**3**) without any appreciable activation energy. In the region of the $C_3H_6^{\bullet+}$ energy surface that connects **1** with **3** our calculations find no intermediate of sufficient stability to be observable.

1

2

3

In our preliminary communication[3] we pointed out the role of electron correlation in preventing artifactual symmetry breaking at the (0,0) geometry of **2**. In this paper we discuss symmetry breaking in **2** more fully. We also describe results that illustrate the importance of including electron correlation in computing the relative energies of geometries with localized and delocalized wave functions, even in situations where the wave function for the delocalized species does not break symmetry.

Results

Symmetry Breaking at the (0,0) Geometry of 2. When unrestricted Hartree–Fock (UHF) calculations[5] were performed on **2**, with both the 3-21G[6] and 6-31G*[7] basis sets, a C_s geometry with unequal C–C bond lengths was found to be lower in energy than a C_{2v} geometry with equal C–C bond lengths.[3] However, when electron correlation was included at the second-order Møller–Plesset (MP2) level,[8] the relative energies of these two, UHF optimized, geometries were reversed.[3]

Although the exact wave function for a molecule in a nondegenerate state must possess the full molecular symmetry, it sometimes happens that approximate wave functions do not.[9] At levels of theory where spurious symmetry breaking occurs, the molecule in question will be found to prefer an asymmetric geometry that is appropriate for the broken-symmetry wave function. If the approximate wave function is constrained to have the same symmetry as the molecule, an infinitely small geometric distortion that causes the symmetry constraint to be lifted will necessarily produce a discontinuous drop in the energy.

In order to investigate computationally whether a molecule truly prefers a high- or low-symmetry geometry, spurious symmetry breaking in the wave function must be avoided. For a molecule like **2**, this requires that at a C_{2v} geometry a wave function with C_{2v} symmetry must be lower in energy than a wave function of C_s symmetry. Only when calculations are performed at a sufficiently high level that this is the case can the preferred geometry of a molecule like **2** be computed reliably.

In our previous work on **2**[3] we found that UHF wave functions exhibit spurious symmetry breaking. For example, when UHF calculations were performed at the 3-21G geometry that was optimized with C_{2v} symmetry constraints on the wave function, a UHF calculation with only C_s symmetry imposed on the wave function gave an energy 3.5 mhartrees lower than that obtained with the C_{2v} symmetry wave function. Not surprisingly, therefore, the optimized C_s geometry, with unequal C–C bond lengths, was found to be 4.9 mhartree lower in energy than the C_{2v} geometry.

Spurious symmetry breaking is even stronger with an RHF wave function than with a UHF wave function. As shown in Table I, on reducing the symmetry imposed on the wave function from C_{2v} to C_s at the optimized C_{2v} geometry, the RHF energy is lowered by 10.5 mhartree. This is not surprising, since at the (0,0) geometry **2** may be regarded as having an allylic π system in which the antisymmetric combination of C–H bonds at the central carbon atom gives an orbital of π symmetry and contributes two π electrons. Even for the parent allyl radical, an RHF wave function exhibits spurious symmetry breaking.[10] In contrast, because a UHF wave function provides some correlation for electrons of opposite spin, a UHF wave function does not break symmetry for allyl.[11]

Table I. Energies of Various 3-21G Wave Functions at UHF Optimized (0,0) Geomertries of **2**

geometry	wavefunction	symmetry[a]	energy (hartrees)
C_{2v}	UHF	C_{2v}	−116.05563
C_{2v}	UHF	C_s	−116.05915
C_s	UHF	C_s	−116.06407
C_{2v}	RHF	C_{2v}	−116.04475
C_{2v}	RHF	C_s	−116.05524
C_s	RHF	C_s	−116.06052
C_{2v}	MCSCF[b]	C_{2v}	−116.06391
C_{2v}	MCSCF	C_s	−116.06419
C_s	MCSCF	C_s	−116.06829
C_{2v} ± 0.02 Å[c]	MCSCF	C_s	−116.06529
C_{2v}	CI[d] (RHF MOs)	C_{2v}	−116.15962
C_{2v}	CI (RHF MOs)	C_s	−116.15929
C_s	CI (RHF MOs)	C_s	−116.15488
C_{2v}	CI (MCSCF MOs)	C_{2v}	−116.16001
C_{2v}	CI (MCSCF MOs)	C_s	−116.15996
C_s	CI (MCSCF MOs)	C_s	−116.15305
C_{2v} ± 0.02 Å	CI (MCSCF MOs)	C_s	−116.15984

[a] Symmetry imposed on wavefunction. [b] 3 electron/3 orbital MCSCF in π space. [c] C–C bond lengths asymmetrically distorted by ±0.02 Å from UHF optimized C_{2v} geometry. [d] σ–π CI (see text). Type of orbitals used is given in parentheses.

In order to provide explicit correlation for the π electrons in **2**, multiconfiguration self-consistent-field (MCSCF) calculations were performed with GAMESS.[12] The MCSCF wave functions included all the configurations (4 in C_{2v} symmetry and 8 in C_s symmetry) that arise from all possible assignments of the three π electrons to the lowest three π MOs. Similar π MCSCF calculations predict a symmetrical molecular geometry for allyl.[13] Nevertheless, the π MCSCF wave function for **2** was found to exhibit spurious symmetry breaking. Although the preference for a C_s wave function at the optimized C_{2v} geometry is reduced to only 0.3 mhartree with π MCSCF, this preference is still sufficient to guarantee that a C_s geometry is lower in energy.

Spurious symmetry breaking occurs in the π MCSCF wave function because, although this wave function does correlate the π electrons, it provides no correlation between the π and the σ electrons. In the absence of such correlation, the σ electrons tend to favor localized π wave functions in charged radicals and diradicals.[9,14] Previous experience has shown that in such molecules inclusion of all single σ excitations from each of the important π configurations provides sufficient electron correlation to eliminate spurious symmetry breaking.[9,14]

Configuration interaction (CI) calculations were carried out at the UHF optimized (0,0) geometries of **2**, using the MELD package of programs.[15] Single excitations from each of the σ valence orbitals were allowed for all of the configurations that arise from occupancy of the lowest three π orbitals by three electrons. Modification of these π orbitals was permitted by simultaneously including all single excitations from them into the five remaining π orbitals. The resulting CI wave functions consisted of 8989 spin-adapted configurations in C_{2v} symmetry and 17987 in C_s symmetry. CI calculations were performed with both RHF and MCSCF orbitals.

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(5) These calculations were performed with Gaussian 82: Binkley, J. S.; Frisch, M. J.; Raghavachari, M.; Fluder, E.; Seeger, R.; Pople, J. A., Carnegie-Mellon University.

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Table II. UHF/6-31G* Optimized Geometries[a]

	1 (90,90)[c]	**2** (C_{2v}) (0,0)	**2**(C_s) (0,0)	**2**(^{2}A′) (0,90)	**2**(^{2}A″) (0,90)	**2**($C_{s'}$) (7,−7)	C_2 TS (33,33)	C_2 TS[b] (40,40)	C_1 TS (40,−87)
				Bond Lengths (Å)					
R_1	1.477	1.433	1.436	1.445	1.571	1.430	1.456	1.458	1.450
R_2	1.477	1.433	1.490	1.496	1.423	1.430	1.456	1.458	1.511
r_1	1.078	1.116	1.105	1.102	1.081	1.173	1.102	1.110	1.082
r_2	1.078	1.116	1.105	1.102	1.081	1.079	1.102	1.110	1.107
r_3	1.074	1.073	1.078	1.079	1.075	1.073	1.074	1.086	1.080
r_4	1.074	1.075	1.079	1.079	1.074	1.075	1.075	1.087	1.079
r_5	1.074	1.073	1.071	1.072	1.078	1.073	1.074	1.086	1.072
r_6	1.074	1.075	1.073	1.072	1.078	1.075	1.075	1.087	1.072
				Bond Angles (deg)					
R_1R_2	78.8	125.9	119.3	118.0	92.7	124.8	116.8	113.5	112.0
r_1R_1	114.4	108.3	104.2	104.3	109.2	88.4	109.6	111.1	111.8
$r_1\mathrm{R}_2$	114.4	108.3	113.8	113.8	115.2	88.4	109.3	108.9	114.0
r_1r_2	116.4	92.4	106.8	107.4	113.2	107.1	107.4	107.7	110.9
r_2R_2	114.4	108.3	113.8	113.8	115.2	116.8	109.6	111.1	109.8
r_3R_1	121.0	119.0	119.9	120.1	113.5	119.5	121.3	121.8	122.8
r_4R_1	121.0	122.9	123.2	122.8	126.5	121.2	120.7	120.2	120.2
r_5R_2	121.0	119.0	118.8	120.0	121.1	119.5	121.3	121.8	118.9
r_6R_2	121.0	122.9	121.5	120.0	121.1	121.2	120.7	120.2	120.6
				Dihedral Angles (deg)					
$r_3R_1R_2$	90.6	180.0	180.0	180.0	180.0	−177.4	144.1	137.7	140.7
$r_4R_1R_2$	−90.6	0.0	0.0	0.0	0.0	11.0	−30.1	−37.7	−40.7
$r_5R_2R_1$	−90.6	180.0	180.0	−92.9	−86.0	177.4	144.1	137.7	−92.6
$r_6R_2R_1$	90.6	0.0	0.0	92.9	86.0	−11.0	−30.1	−37.7	86.1

[a] See Figure 1 for the definitions of the geometry parameters. [b] MP2/6-31G* optimized geometry. [c] Dihedral angles between the planes of each of the terminal methylene groups and that of the three carbon atoms

Table III. UHF/6-31G* and MP2/6-31G* Energies (kcal/mol) Relative to Propene Radical Cation (**3**)

molecule	UHF/6-31G*	MP2/6-31G*
3	0[a]	0[b]
1(90,90)[c]	15.3	9.8
2(C_{2v}) (0,0)	42.1	31.5
2(C_s) (0,0)	35.6	37.6
2(^{2}A′) (0,90)	35.5	39.1
2(2A″) (0,90)	37.3	38.4
2(C_s') (7,−7)	37.3	29.6
C_2 TS (33,33)	44.8	34.5[d]
C_1 TS (40,−87)	36.1	39.5

[a] E = −116.7734 hartrees. [b] E = −117.1122 hartrees. [c] Dihedral angles between the planes of each of the terminal methylene groups and that of the three carbon atoms. [d] The MP2/6-31G* optimized geometry for the C_2 transition state has the same energy.

As shown in Table I, starting from either set of orbitals, the CI calculations do not exhibit symmetry breaking. With both sets of orbitals the C_{2v} constrained CI wave function is slightly below the C_s wave function in energy at the UHF optimized C_{2v} geometry. The energy differences between all four of the CI wave functions at this geometry are small.[16]

Because the CI wave functions do not exhibit symmetry breaking at C_{2v} geometries, they can be used to determine whether **2** actually prefers a C_{2v} or C_s geometry. As shown in Table I, at the UHF optimized C_{2v} geometry the CI wave functions, derived from both RHF and MCSCF MOs, give lower energies than at the UHF optimized C_s geometry. These CI results are consistent with the result found previously when electron correlation was included via MP2 perturbation theory.[3]

The CI calculations show that, with inclusion of electron correlation sufficient to prevent symmetry breaking at the UHF optimized C_{2v} geometry, this geometry is preferred to the UHF optimized C_s geometry. Nevertheless, the calculations do not rule out the possibility that an asymmetric distortion of the C–C bond lengths from C_{2v} symmetry to some other C_s geometry is favorable in **2**. However, as shown in the last line of Table I, asymmetrically changing the C_{2v} C–C bond lengths by ±0.02 Å also increases the CI energy, which was computed starting with MCSCF MOs.[17] This finding indicates that the force constant for asymmetric distortion of the C–C bond lengths in **2** from C_{2v} symmetry is positive.

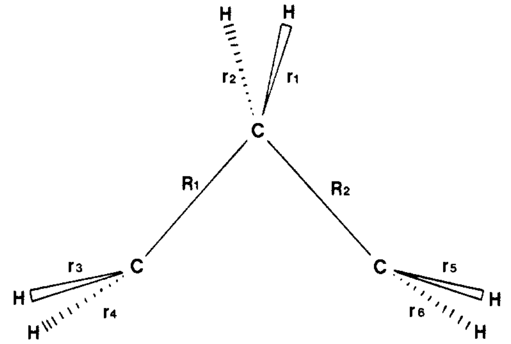

Figure 1. Bonds used to define optimized geometries of **2** in Table II.

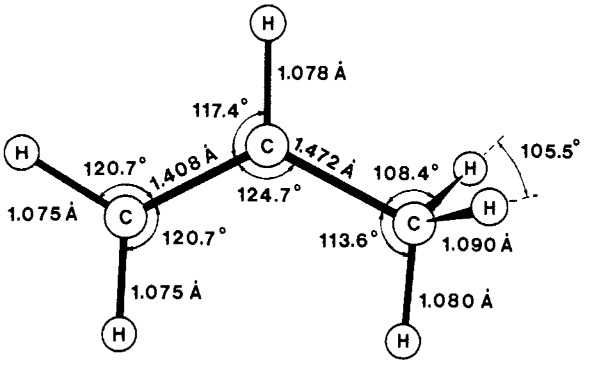

Figure 2. UHF optimized C_s geometry of **3**.

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[16] If full CI were performed, exactly the same energy would be obtained, starting with any set of orbitals. With the partial CI used, both sets of MCSCF MOs give slightly lower energies at the C_{2v} geometry than either set of RHF MOs.

[17] The CI energy, computed with RHF MOs, was also found to increase on asymmetric distortion of the CI optimized C–C bond lengths in the C_{2v} structure. At the C_{2v} geometry the CI optimized C–C bond length is 1.438 Å, which is 0.005 Å longer than the UHF value. On asymmetric distortion of the CI optimized C–C bond lengths by ±0.01 Å, the C_{2v} RHF energy of −116.04474 hartrees decreased by 11.62 mhartree; but the C_{2v} CI energy of −116.15969 hartrees increased by 0.52 mhartrees.

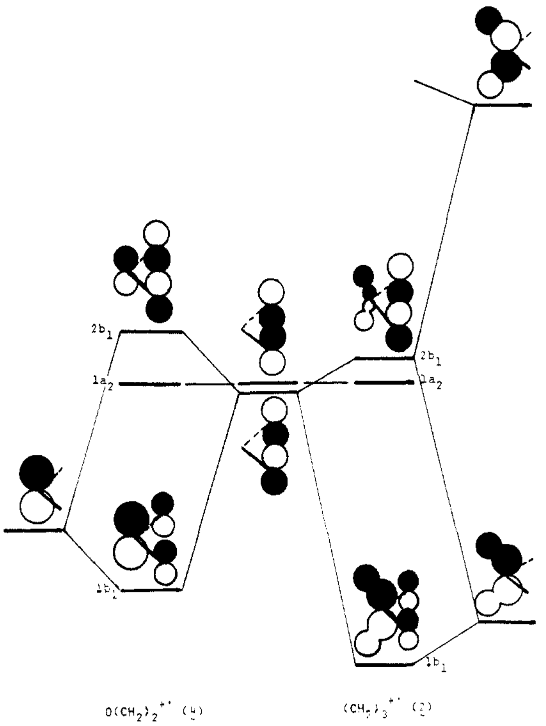

Figure 3. Schematic orbital interaction diagrams showing the origin of the π orbitals at the (0,0) geometries of **4** and **2**.

With this evidence that, when sufficient electron correlation is included, the (0,0) conformation of **2** prefers C_{2v} symmetry, this geometry was reoptimized with the 6-31G* basis set. The UHF optimized C_{2v} geometry is given in Table II. As expected, its UHF energy (Table III) is higher than that of the UHF optimized C_s geometry, which has unequal C–C bond lengths (Table II) and a localized wave function. However, also as anticipated, when electron correlation is included at the MP2 level, the relative energies of the two geometries are reversed.

It is interesting to compare the optimized C_{2v} geometry for **2** with the optimized C_{2v} geometries of the singlet[18] and triplet[19] states of the neutral trimethylene diradical. Both states of the diradical have shorter C–H bond lengths (1.09 Å) and larger H–C–H bond angles (105°) at the central methylene group, longer C–C bond lengths (1.51 Å), and smaller C–C–C bond angles (114°) than the lowest ($^2A_2$) state of **2**. These differences in geometry can easily be understood, since both states of the diradical can be viewed as being formed by addition of one unit of electron density to the empty 2b$_1$ MO in the $^2A_2$ state of **2**.[20] This MO,[21] which is depicted schematically in Figure 3, is C–H bonding and H–H antibonding at the central methylene group, π antibonding between adjacent carbons, and π bonding between the terminal carbon atoms.

A 6-31G* UHF vibrational analysis was performed at the 6-31G* optimized C_{2v} geometry. As was the case with a 3-21G vibrational analysis, performed at the 3-21G optimized C_s geometry of **2**,[3] the 6-31G* vibrational analysis showed one imaginary frequency (432i cm^{-1}) and one low frequency (315 cm^{-1}). The imaginary frequency corresponded to disrotation of the two terminal methylene groups, accompanied by motions of the hydrogens at the central carbon that align one of them with the p orbitals on the terminal carbons. The low-frequency vibration corresponded to pure conrotation of the terminal methylene groups.

It is significant that the vibration of b$_2$ symmetry, involving asymmetric distortion of the C–C bond lengths, has a rather high frequency (999 cm^{-1}). This is due to the fact that the vibrational analysis was performed with force constants obtained from analytically evaluated second derivatives of the energy of the C_{2v} constrained wave function. Had the force constant for b$_2$ distortion of the C–C bond lengths been obtained by finite differences between the UHF energies at C_{2v} and C_s geometries, the spurious symmetry breaking that occurs at the UHF level of theory would have given an imaginary frequency for this vibration.

Cyclopropane (1) and Propene (3) Radical Cations. The vibration with the imaginary frequency that was found at the C_{2v} geometry of **2** appears to prepare **2** for migration of a hydrogen to form propene radical cation (**3**). The geometry of **3**, optimized by 6-31G* UHF calculations in C_s symmetry,[22] is shown in Figure 2; and its UHF and MP2 energies are listed in Table III.[23] As shown in Table III, **3** is the lowest energy point on the $C_3H_6^{\cdot+}$ potential surface that we have found, and the rearrangement of **2** to **3** is computed to be highly exothermic.

The low-frequency vibration of **2** corresponds to orbital symmetry allowed[24] conrotatory closure to one of the three equivalent geometries of lowest energy ($^2A_1$ wave function) on the potential surface for pseudorotation of cyclopropane radical cation (**1**).[25] This geometry, in which one C–C ring bond is much longer than the other two, has been previously optimized at the UHF 6-31G* level of theory by Radom and co-workers.[26] The UHF energy that we computed for **1** is given in Table III and is identical with that reported by them. Table III also contains the MP2 energy for **1** that we computed at this geometry. A UHF vibrational analysis for **1** at this geometry shows all positive frequencies, indicating that **1** is a true local minimum on the $C_3H_6^{\cdot+}$ potential surface.

(0,90) Geometries of 2. We also performed 6-31G* UHF optimizations of geometries of **2** with one methylene group twisted 90° from coplanarity with the three carbon atoms. There are two possible low-energy states that arise at such a C_s geometry, depending on whether the unpaired electron occupies the in-plane (a′) or out-of-plane (a″) p orbital. The optimized geometries of both the $^2A'$ and $^2A''$ states are given in Table II. As shown in Table III, at both the UHF and MP2 levels of theory the energies of these two states are very similar and close to that of the C_s structure that was optimized for the (0,0) conformation of **2**.

UHF vibrational analyses showed neither $^2A'$ nor $^2A''$ to be a stable intermediate, since the former was found to have one imaginary frequency and the latter two. In the $^2A'$ state the imaginary frequency of 258i cm^{-1} and the low frequency of 24 cm^{-1} both appear to prepare the radical cation for migration of a hydrogen from the central carbon to the carbocationic methylene group. The two modes differ chiefly in the amount and direction

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(18) Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 7506.

(19) Yamaguchi, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1984**, *106*, 5115.

(20) In the triplet the additional electron is placed in this MO. However, the lowest singlet state ($^1A_1$) requires a two-configuration wave function of the form $c_1|...1a_2^2\rangle - c_2|...2b_1^2\rangle$; so it is incorrect to say that the extra electron occupies 2b$_1$ in the lowest singlet state. Nevertheless, since c_2 is almost as large as c_1, the electron population in 2b$_1$ is nearly unity in this state too.

(21) See, for example: Jorgensen, W. L.; Salem, L. *The Organic Chemist's Book of Orbitals*; Academic Press: New York, 1973; p 162.

(22) A vibrational analysis established that this geometry has all real frequencies and, hence, is an energy minimum at this level of theory. 6-31G* UHF calculations have been reported also to give a planar geometry for the ethene radical cation, whereas semiempirical and large CI calculations find a slightly twisted geometry, in agreement with experiment [Belleville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 294]. Nevertheless, there is evidence that twisting in olefin radical cations decreases with alkyl substitution [Clark, T.; Nelsen, S. F. *Ibid.* **1988**, *110*, 868].

(23) The C_s geometry of **3** with a C–H bond of the methyl group cisoid to the vinyl group was found to be 1.46 kcal/mol lower in energy than the transoid conformation at the UHF level of theory. At the MP2 level the energy difference between the UHF optimized geometries was computed to be 1.09 kcal/mol. These conformational energy differences are respectively 0.61 and 0.87 kcal/mol smaller than those found in the neutral molecule at the same levels of theory [Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035]. The decrease in the computed conformational energy difference on removal of a π electron from propene is expected from the nodal pattern of the HOMO [Hehre, W. J.; Pople, J. A.; Devaquet, A. J. P. *J. Am. Chem. Soc.* **1976**, *98*, 664 and references therein].

(24) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

(25) Iwasaki, M.; Toriyama, K.; Nunome, K. *J. Chem. Soc., Chem. Commun.* **1983**, 202.

(26) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21. In agreement with experiment,[25] this is computed to be the geometry of lowest energy for **1**.

of the accompanying rotation at the methylene group bearing the unpaired electron.

By contrast, in the $^2A''$ state there is little motion of the hydrogens at the central carbon in either of the two modes with imaginary frequencies. The mode with calculated frequency 417i cm^{-1} corresponds to ring closure, chiefly by rotation of the methylene group bearing the unpaired electron. Pyramidalization of this center is associated with the imaginary frequency of 243i cm^{-1}.

Pathway Connecting 2 to 3. As noted above, the (0,0) geometry of **2** has an imaginary frequency for a disrotatory motion that positions a hydrogen on the central carbon for migration to one of the two equivalent terminal carbons. This vibrational coordinate reduces the molecular symmetry from C_{2v} to C_s, with the symmetry plane perpendicular to that of the three carbons. This vibrational coordinate was followed, and a C_s energy minimum was located. The geometry of this stationary point ($C_{s'}$) is given in Table II. Its energy, which is listed in Table III, is lower than that of the (0,0) geometry of **2**, not only at the UHF level but also when correlation is included at the MP2 level.

However, like the (0,0) structure, the $C_{s'}$ geometry too is not a UHF energy minimum but a saddle point, since a 6-31G* UHF vibrational analysis showed one mode with a large imaginary frequency (1894i cm^{-1}). The vibrational mode with this frequency corresponds to migration of the properly oriented hydrogen on the central carbon toward one of the terminal carbon atoms. When this vibrational mode was followed toward the geometry of **3**, the 6-31G* UHF energy decreased monotonically. These results indicate that, at the UHF level of theory, there is no energetic barrier to the conversion of **2** to **3**.

Nevertheless, it should be noted that the hydrogen migration results in a reduction of the molecular symmetry from C_s to C_1. Thus, the decrease in the UHF energy found on hydrogen migration could, in principle, be a consequence of the same type of spurious symmetry breaking that is observed at the (0,0) geometry when the same plane of symmetry is destroyed upon distortion of the C–C bond lengths from equality in the C_{2v} structure. However, since the vibrational analysis was performed with analytically evaluated second derivatives of the energy of the C_s wave function, the imaginary frequency found for hydrogen migration is not due to spurious symmetry breaking in the UHF wave function.

In order to test whether hydrogen migration might encounter an energy barrier when electron correlation was included, the vibration with the imaginary frequency at the UHF level of theory was followed; and the MP2 energy along this a$''$ coordinate was calculated. In contrast to the UHF energy, which went down, the MP2 energy went up. Thus, with inclusion of electron correlation at the MP2 level, the $C_{s'}$ geometry appears to be an intermediate, rather than a transition state.

This finding was not altered by going to higher levels in the perturbation theory expansion, for the MP3 energy along this vibrational coordinate also increased. Inclusion of polarization functions on hydrogen (6-31G** basis set)[7] also failed to alter the predicted increase in the MP2 energy along the a$''$ vibrational coordinate.

In order to assess the height of the barrier to hydrogen migration from the $C_{s'}$ geometry, the MP2 energies of several points along the least motion path connecting it to **3** were computed with the 6-31G* basis set, and the energy maximum along this pathway was located. As expected from the substantial exothermicity of this reaction, the maximum was found to be very close to the $C_{s'}$ geometry; and the MP2 energy at the maximum was computed to be only 0.3 kcal/mol higher than at the $C_{s'}$ geometry.

At the MP3 level this energy difference was reduced to 0.2 kcal/mol; and with the 6-31G** basis set, the MP2 energy difference was slightly less than 0.2 kcal/mol. Moreover, since we found the maximum along an arbitrary pathway from the $C_{s'}$ geometry toward **3**, rather than locating the actual transition state, 0.2 kcal/mol is an upper limit to the true barrier height to hydrogen migration. Consequently, although the $C_{s'}$ geometry of **2** does appear to be an energy minimum, the barrier to its rearrangement to **3** is so small that the existence of this minimum on the $C_3H_6{}^{\bullet+}$ potential surface has no chemical significance.

Pathway Connecting 1 to 2. As noted above, the conrotatory opening of **1** to **2** is allowed by orbital symmetry. Nevertheless, a barrier apparently occurs along this pathway, since the vibrational analysis at the (0,0) geometry of **2** shows conrotation of the two methylene groups to have a real, albeit small, frequency. Thus we performed 6-31G* UHF calculations to locate the conrotatory transition state that connects **1** and **2**.

The C_2 geometry found is given in Table II and its energy in Table III. As one might have expected from the fact that **1** is substantially lower in energy than **2**, the maximum energy along the conrotatory pathway connecting **1** and **2** occurs at a geometry that is closer to that of **2**. At the energy maximum the methylene groups have rotated 57° of the 90° necessary to transform **1** into the (0,0) geometry of **2**. As shown in Table III, the energy at this point is about 3 kcal/mol above that of the (0,0) geometry of **2** at both the UHF and MP2 levels of theory.

However, a UHF vibrational analysis found that the C_2 geometry has two imaginary frequencies and, thus, is not a true transition state, at least at the UHF level of theory. Both vibrations with imaginary frequencies involve methylene group rotation. The one with a calculated frequency of 385i cm^{-1} corresponds to conrotation, and the one with a computed frequency of 243i cm^{-1} involves disrotation, accompanied by motions of the hydrogens at the central carbon. The latter mode destroys the C_2 axis, thus taking the molecule to a C_1 geometry, which has no element of symmetry.

Pathway Connecting 1 to 3. The isomerization of **1** to **3** could, in principle, proceed by conrotatory opening of **1** to **2**, followed by hydrogen migration. However, at least at the UHF level of theory, the energy maximum along the C_2 pathway for conrotatory ring opening has two imaginary vibrational frequencies and, thus, is not a transition state on the global potential surface. Consequently, there must exist a lower energy pathway, where hydrogen migration accompanies ring opening, and which passes through a transition state of C_1 symmetry.

This transition state was also located with UHF calculations. A vibrational analysis established that it had only one imaginary frequency. This vibration (384i cm^{-1}) was followed and was found to lead to **1** in one direction and to **3** in the other.

The geometry of the transition state is given in Table II. It can be viewed as being close to the midway point for monorotatory ring opening to the A$'$ state of the (0,90) geometry, where the orbital containing the unpaired electron remains in the plane of the three carbon atoms. One hydrogen on the central carbon is well positioned for migration to the partially rotated carbocationic methylene group; and the imaginary frequency corresponds, in fact, to a vibration in which there is a large-amplitude motion of this hydrogen but scarcely any motion of the hydrogen geminal to it.

As shown in Table III, at the UHF level of theory the C_1 transition state lies 8.7 kcal/mol below the maximum along the C_2 conrotatory path for ring opening. However, with the inclusion of electron correlation at the MP2 level, the energies are reversed, with the C_2 geometry now 5.0 kcal/mol below the C_1 transition state.

The reason for this reversal is the selective stabilization of delocalized wave functions by the inclusion of electron correlation.[9] Since the C_1 transition state has a wave function with the carbocationic center largely localized on one methylene group and the odd electron on the other, it benefits much less from including electron correlation than does the C_2 geometry, where the positive charge and odd electron are delocalized over two centers.

The stabilization of the C_2 geometry, relative to the C_1, by the inclusion of electron correlation suggests that at the MP2 level the maximum along the conrotatory pathway might be a true transition state and might lie along the lowest energy pathway connecting **1** to **3**. In fact, an MP2 vibrational analysis at the MP2 optimized, C_2 energy maximum found this geometry to have only one imaginary frequency (361i cm^{-1}), which is associated with a conrotatory motion of the terminal methylene groups. Thus, this geometry is a true transition state at the MP2 level of theory. The vibration with the lowest real frequency (233 cm^{-1}) at the MP2 level corresponds to the other vibration that has an imaginary frequency (243i cm^{-1}) at the UHF level of theory.

The fact that the conrotatory transition state is an energy maximum in a symmetry breaking vibration at the UHF, but not the MP2, level of theory opens the possibility that at this geometry, as at the (0,0) conformation, there is spurious symmetry breaking in the UHF wave function. The observation that a vibrational analysis, based on analytical second derivatives of the C_2 constrained UHF wave function, exhibits an imaginary frequency for this vibration shows that spurious symmetry breaking in the UHF wave function is not required in order to obtain this result; but neither is spurious symmetry breaking in the UHF wave function ruled out.

In order to test for spurious symmetry breaking in the UHF wave function at the C_2 transition state, its energy was recomputed with a UHF wave function on which no symmetry was imposed. The energy was within 0.01 mhartree of that obtained with the imposition of C_2 symmetry. This result indicates that there is no significant symmetry breaking in the UHF wave function at the C_2 transition state.

Unlike the case at the (0,0) geometry, where interaction between the terminal methylene groups is very small, at the conrotatory transition state bonding between the methylene groups is sufficiently strong that spurious symmetry breaking in the UHF wave function appears not to occur. Nevertheless, at the UHF level of theory the electronic localization which accompanies hydrogen migration toward one methylene group is sufficiently favorable that an imaginary frequency is found for the vibrational mode that promotes this reaction.

This is the case at both the C_2 and $C_{s'}$ geometries. At both geometries the force constant for hydrogen migration changes from negative to positive on going from a UHF to an MP2 wave function. This change makes the $C_{s'}$ geometry a minimum (albeit a very shallow one) and the C_2 geometry a true transition state on the MP2 energy surface.

Since at the MP2 level the energy of the C_1 transition state lies above that of the C_2 transition state, we investigated whether the MP2 energy of the former would decrease monotonically toward that of the latter. In fact, we found it possible to transform the C_1 structure into the C_2 transition state by a least-motion pathway that involved an MP2 barrier of only 0.2 kcal/mol. Since an arbitrary pathway was chosen, it is not unlikely that a slightly different pathway could be found which involves no energy barrier at the MP2 level. Thus, the existence of a C_1 transition state at the UHF level appears to be an artifact of insufficient inclusion of electron correlation at this level of theory. With inclusion of electron correlation at the MP2 level of theory, the lowest energy pathway that connects **1** to **3** involves conrotatory ring opening of **1** and passage across a C_2 transition state, followed by hydrogen migration to form **3**.

Discussion

The finding that, with inclusion of σ–π electron correlation, the (0,0) geometry of trimethylene radical cation (**2**) prefers a geometry with equal C–C bond lengths and a delocalized wave function is interesting, particularly as it contrasts with the previous result that, at a comparable level of theory, the isoelectronic $O(CH_2)_2^{\cdot +}$ radical cation (**4**) prefers a geometry with unequal C–O bond lengths and a localized wave function.[27] On the basis of the expectation that the antisymmetric combination of C–H orbitals in **2** should be less available for delocalization than the oxygen π lone pair in **4**, one might have made the opposite prediction.

The same type of second-order Jahn–Teller effect argument that we used previously to rationalize the ease of an asymmetric molecular distortion in **4**[27] also would lead one to predict that **2** should distort from C_{2v} to C_s symmetry even more easily. In both radical cations this b_2 distortion is facilitated by mixing of the $^2A_2$ ground state with a $^2B_1$ excited state in which the unpaired electron is promoted from the $1a_2$ nonbonding π MO to the antibonding $2b_1$ π MO. According to the theory of the second-order Jahn–Teller effect, the energy lowering provided by this mixing is inversely proportional to the energy difference between $^2A_2$ and $^2B_1$. Thus, the smaller the energy difference between $1a_2$ and $2b_1$ MOs, the larger the energy lowering on mixing should be.[27]

One would expect a smaller $1a_2 \rightarrow 2b_1$ excitation energy in **2** than in **4**. This is illustrated schematically in Figure 3. Because the π C–H bonding orbital at the central carbon in **2** is lower in energy than the oxygen nonbonding p orbital in **4**, the π C–H orbital in **2** is expected to interact less strongly with the b_1 combination of π orbitals on the terminal methylene groups. This should result in a lower energy for $2b_1$ in **2** than in **4**. Morevoer, in **2** there is additional mixing of the b_1 combination of terminal methylene π orbitals with the C–H antibonding MO of the same symmetry. This mixing serves to stabilize the $2b_1$ MO in **2**, further lowering its energy in **2** compared to **4**.

Since the $1a_2$ MO has a node at the central atom, its energy is much less affected than that of $2b_1$ by the replacement of CH_2 in **2** by O in **4**. Consequently, the relative sizes of the $1a_2 \rightarrow 2b_1$ excitation energies in **2** and **4** depend principally on the relative energies of the $2b_1$ MOs. Because the $2b_1$ MO in **2** is expected to have a lower energy than that in **4**, a smaller $1a_2 \rightarrow 2b_1$ excitation energy is predicted in **2**.

The qualitative expectations from Figure 3, regarding the relative sizes of the $1a_2 \rightarrow 2b_1$ excitation energies in **2** and **4**, are confirmed by the results of ab initio calculations. At the optimized C_{2v} geometry of **2** the UHF energy difference between $^2A_2$ and $^2B_1$ amounts to 34.6 kcal/mol, whereas in **4** this energy difference is 85.3 kcal/mol. On the basis of the smaller energy difference between these states in **2** than in **4**, one would predict that **2** should distort from C_{2v} symmetry more easily than **4**.

Since this is not found to be the case, it is clear that the relative propensities of **2** and **4** to distort from C_{2v} symmetry are not predicted correctly by the relative sizes of the energy gaps between the two states that are mixed by the distortion. Instead, the explanation for why **2** distorts less readily than **4** must be sought in the relative sizes of the matrix elements that represent the mixing of $1a_2$ with $2b_1$ on molecular distortion from C_{2v} symmetry.

The size of this matrix element depends upon the coefficients of the terminal π AOs in $1a_2$ and the π AO on the central atom in $2b_1$. The former coefficients are determined by symmetry in both **2** and **4**, but the latter coefficient is not. There is good reason to expect that the coefficient of the π AO on the central atom in $2b_1$ should be smaller in **2** than in **4**.

As shown in Figure 3, in **2** the $2b_1$ MO can be regarded as being formed by mixing both the bonding and antibonding C–H orbitals of b_1 symmetry on the central carbon with the b_1 combination of π AOs on the terminal methylenes. Perturbation theory shows that the bonding C–H orbitals are mixed into $2b_1$ in an antibonding fashion and that the antibonding C–H orbitals are mixed into $2b_1$ in a bonding way. The orbital phases with which the bonding and antibonding C–H MOs are mixed into $2b_1$ are shown in Figure 3.

Because of the phases with which the bonding and antibonding C–H orbitals enter $2b_1$, the contribution of the p orbital at the central carbon tends to cancel and that of the hydrogens is reinforced. Consequently, a great deal of the probability density at the central atom in $2b_1$ is not in the carbon p orbital, which interacts strongly with the $1a_2$ MO on asymmetric distortion, but on the hydrogen atoms, which do not.

In contrast, since there is just one b_1 orbital at the central atom in **4**, the oxygen π lone pair orbital, there is a much stronger interaction between $1a_2$ and $2b_1$ on asymmetric distortion of the bond lengths in **4** than in **2**. It is to this difference that we attribute the greater stability of **2** toward asymmetric distortion.

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(27) Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513. At higher levels of theory a C_{2v} geometry for **4** is slightly favored over geometries with unequal C–O bond lengths, but the potential surface for asymmetric distortion of these bonds is so flat that an unequivocal prediction of the symmetry of the equilibrium geometry is difficult to make [Bouma, W. J.; Poppinger, D.; Saebo, S.; MacLeod, J. K.; Radom, L. *Chem. Phys. Lett.* **1984**, *104*, 198].

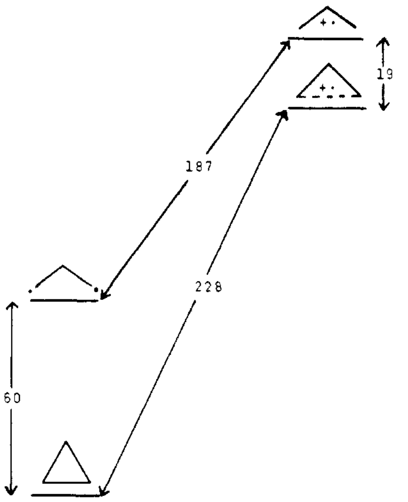

Figure 4. Thermocycle for estimating the energy difference between **1** and **2** from experimental data. All energies are given in kcal/mol.

Since the (0,0) geometry of **2** is predicted to be a transition state, rather than a stable intermediate, the stability toward asymmetric distortion of its C–C bond lengths is, perhaps, largely of theoretical interest. In contrast, the significantly higher energy (21.7 kcal/mol at the MP2 level) of this geometry of **2**, compared to the optimized geometry of **1**, is of practical importance, because it rules out the irreversible opening of **1** to **2**, which has been claimed to occur in $CF_2ClCFCl_2$ matrices.[1]

It is possible to construct a thermocycle, using reactions for whose energy there is experimental data, to show that the prediction of a substantial energy difference between **1** and **2** is at least qualitatively correct. The thermocycle is shown in Figure 4, and the estimated energies for each step are also given.

The energy necessary to form cyclopropane radical cation (**1**) adiabatically from cyclopropane has been measured by several different methods to be about 9.9 eV (228 kcal/mol).[28] The enthalpy difference between cyclopropane and trimethylene diradical can be equated[29] with the 60 kcal/mol activation enthalpy found for cis–trans isomerization of cyclopropane-d_2.[30] Since ab initio calculations on (0,0) trimethylene show only a small splitting between the singlet and triplet states of the diradical,[18,31] ionization of either state is expected to require about the same energy as that of the 1-propyl radical. The adiabatic ionization potential of 1-propyl has been measured as 8.1 eV (187 kcal/mol).[32]

The thermocycle shown in Figure 4 yields an estimated energy difference between **1** and **2** of 19 kcal/mol. Our MP2 value of 21.7 kcal/mol for the energy difference between **1** and the (0,0) geometry of **2** becomes 18.9 kcal/mol after correction for the computed difference in zero-point vibrational energies. The essentially exact agreement between the experimental and calculated estimates of the energy difference between **1** and **2** is undoubtedly fortuitous.

Since theory and experiment both agree that in the gas phase the opening of **1** to **2** is highly endothermic, the fact that irreversible ring opening apparently occurs in $CF_2ClCFCl_2$ matrices to afford a localized trimethylene radical cation indicates a very strong, stabilizing interaction between a nucleophile and the carbocationic methylene group. The nature of the nucleophilic group which coordinates to the carbocation has been the subject of considerable speculation.[1,3,4,33]

Our calculations find that not only is **2** much higher in energy than **1** but also that **2** is not a stable intermediate on the $C_3H_6{}^{\bullet+}$ potential surface. Although it is true that, at the MP2 level of theory, the $C_{s'}$ geometry of **2** does appear to be an energy minimum, the barrier to hydrogen migration to form **3** is computed to be so small (<0.2 kcal/mol) that **2** should not be observable. Depending on the geometry at which it were formed, **2** should either close to **1** or rearrange to **3**.

Although neither the UHF nor the MP2 calculations indicate the existence of a stable intermediate on the potential surface that connects **1** with **3**, the MP2 calculations do indicate that the transformation of **1** to **3** occurs in two distinct stages. First, **1** undergoes ring opening via a conrotatory transition state. Only after crossing the transition state is a bifurcation point reached, beyond which positioning one of the hydrogens of the central methylene group for migration becomes favorable.

The existence of a bifurcation point follows from the fact that at the (0,0) geometry of **2** the vibrational mode that positions one of the hydrogens on the central methylene group for migration to a terminal carbon has a negative force constant. However, at the transition state for ring opening the only negative force constant is for methylene group conrotation. Somewhere between these two points on the potential surface there must be a bifurcation point at which the force constant for the former motion changes sign.

It is to be emphasized that neither the transition state at the (0,0) geometry nor the pair of transition states near the $C_{s'}$ geometry of **2** is the transition state that connects **1** and **3**. The latter two transition states allow the interchange of the two equivalent forms of **3** by a succession of two 1,2-hydrogen shifts. The $C_{s'}$ geometry serves as an intermediate, but one which is less than 0.2 kcal/mol below the pair of mirror image transition states which connect it to the two equivalent forms of **3**.[34]

From Table II the MP2 energy difference between **3** and the $C_{s'}$ geometry is 29.6 kcal/mol, which is reduced to 26.4 kcal/mol after correction for the zero-point vibrational energy difference between the $C_{s'}$ geometry and **3**. The MP2 energy of the C_{2v} (0,0) geometry is computed to be 2.0 kcal/mol higher in energy than that of the $C_{s'}$ geometry (2.8 kcal/mol after correction for the difference in zero-point energies). The (0,0) geometry is the C_{2v} transition state that allows exchange of the hydrogen at the central carbon in **3** with a methyl hydrogen via successive 1,2 shifts.

The MP2 energy of the transition state for conrotatory ring opening of **1** is 3.0 kcal/mol above that of the (0,0) geometry, both before and after zero-point energy corrections. The C_2 transition state is the highest point on the pathway that connects **1** and **3**, and at the MP2 level it is calculated to be 24.7 kcal/mol above **1** in energy. Correcting for the 2.8 kcal/mol greater zero-point energy of **1**, compared to the transition state, gives an MP2 activation energy of 21.9 kcal/mol for rearrangement of **1** to **3**.

On the basis of studies involving charge-transfer ionization of cyclopropane in the gas phase, Lias and Buckley suggested an energy barrier of about 30–37 kcal/mol for ring opening of **1** to **3**.[28] Gas-phase experiments by Ausloos and co-workers[35] and by Van Velzen and Van der Hart[36] have also provided evidence that generation of **1** with sufficient excess energy leads to formation of **3**. However, McLafferty and co-workers failed to find evidence for formation of **3** from **1** at high ionization energies, and they suggested that the barrier to rearrangement must be >37 kcal/mol.[37]

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(34) After our manuscript was submitted, calculations on the transition state for a 1,3-hydrogen shift in propene radical cation were published [Clark, T. *J. Am. Chem. Soc.* **1987**, *109*, 6838]. The 6-31G* UHF geometry and UHF and MP2 energies of the UHF transition state were identical with those obtained by us for the $C_{s'}$ geometry.

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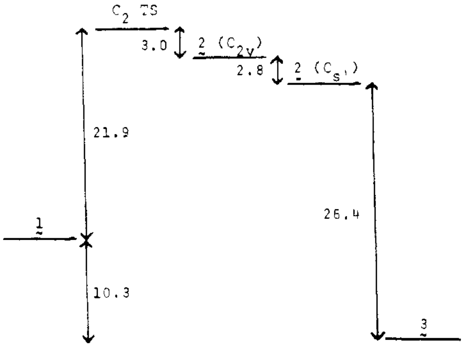

Figure 5. Relative MP2 energies (kcal/mol) of important stationary points on the $C_3H_6^{\cdot +}$ potential surface, after correction for zero-point energy differences. C_2 TS is the transition state for ring opening of **1**, **2** (C_{2v}) is the transition state for exchange of a methyl hydrogen with the hydrogen on the central carbon in **3**, and **2** ($C_{s'}$) is an intermediate, resulting from a 1,2-hydrogen shift in **3**, but separated from **3** by a barrier of <0.2 kcal/mol.

Most recently, Gross and co-workers have studied the gas-phase chemistry of **1**.[2] On the basis of this chemistry, they were able to verify the existence of a structural change in activated **1**; but they showed that the behavior of the species formed was different from that observed from **3**. Consequently, they suggested that activated **1** undergoes ring opening to form trimethylene radical cation (**2**). They were careful to note, however, that the radical cation formed from activated **1** might not be "a unique chemical species existing on a separate minimum on a potential surface" but rather might be a vibrationally excited form of **1** "with an enlarged C–C–C bond angle".[2]

As discussed above, our calculations find no evidence for a chemically significant minimum that corresponds to **2** on the $C_3H_6^{\cdot +}$ potential surface. The only species we have located that are calculated to have sufficient stability to be observed are **1** and **3**.

We calculate that the rearrangement of **1** to **3** is exothermic by 9.8 kcal/mol at the MP2 level, which increases to 10.3 kcal/mol after correction for zero-point energy differences. This is in reasonable agreement with an experimental value of slightly less than 13 kcal/mol.[38]

Because of the exothermicity of the rearrangement of **1** to **3**, as shown in Figure 5, the C_2 transition state for this reaction is predicted to be fully 32.2 kcal/mol above **3** in energy after zero-point energy corrections. Thus, formation of **3** by rearrangement of **1** should lead to radical cations possessing this much excess internal energy. Unless this energy were efficiently quenched, the chemistry of these vibrationally excited ions might differ significantly from that observed from relatively unenergized molecules of **3**.

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Transition Structures of Pericyclic Reactions. Electron Correlation and Basis Set Effects on the Transition Structure and Activation Energy of the Electrocyclization of Cyclobutene to Butadiene

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Abstract: Cyclobutene (**1**), *s-trans*-butadiene (**2**), and the conrotatory transition structure **3** of the electrocyclic ring opening of **1** have been located at the ab initio RHF and MP2 levels of theory and with semiempirical techniques. Geometries of all three structures are reasonably insensitive to changes in basis set or inclusion of electron correlation. At the RHF level and with MNDO and MINDO/3, activation energies and heats of reaction are overestimated, while at the AM1, MP2/6-31G*, MP2/6-31G*//RHF/3-21G, and MP4SDTQ/6-31G*//MP2/6-31G* levels they are in good agreement with the experimental values.

The electrocyclic ring opening of cyclobutene (**1**) to form butadiene (**2**) is a pericyclic reaction that proceeds by a concerted, conrotatory pathway.[1] Many theoretical calculations of the transition-state geometry and energy of this system have been reported.[2-11] All calculated geometries of cyclobutene (**1**) and the transition state **3** are similar, regardless of the level of theory used. On the other hand, estimates of the activation energy differ rather widely. In order to carry out a general investigation of

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