Isomerization of Bicyclo[1.1.0]butane to Butadiene

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Abstract: Multiconfigurational wave functions were used to study the (1) concerted conrotatory, (2) concerted disrotatory, and (3) nonconcerted isomerization processes of bicyclo[1.1.0]butane (C_4H_6) to 1,3-butadiene. The barriers for (1), (2), and (3) are about 42, 56, and 116 kcal/mol, respectively, as calculated with the second-order multireference perturbation theory (PT2). The barriers obtained from the multireference CI (MRCI) are within 1 kcal/mol of the those predicted by PT2. The predicted conrotatory barrier is within 1 kcal/mol of the experimentally measured barrier. The predicted stereochemistry is in agreement with the experimental observations.

I. Introduction

Bicyclobutane (**1**) has received extensive study both experimentally[1–6] and theoretically.[7–10] In a recent paper[10c] we have examined the inversion process of bicyclo[1.1.0]butane using the internally contracted multireference configuration interaction (MRCI) method[11] and second-order perturbation theory with a complete active space self-consistent field (CASSCF)[12] reference function (PT2).[13] In this paper, we consider the isomerization reaction of bicyclo[1.1.0]butane to 1,3-butadiene (**2**).

1 (C₂ᵥ)   **2 (C₂ₕ)**
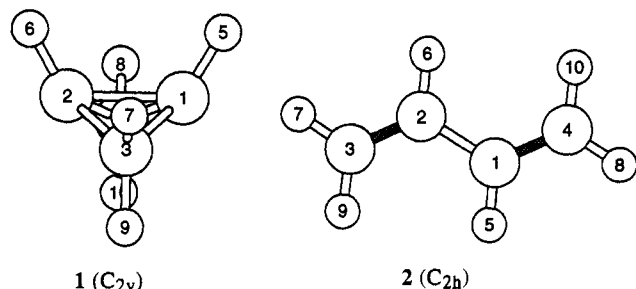
Numerous theoretical and experimental studies have been carried out to help unravel the energetics and pathways of this reaction. Experimentally, a thermolysis study of bicyclo[1.1.0]-butane has suggested that isomerization of **1** to **2** occurs with the central bond remaining intact, while two opposite peripheral C—C bonds are broken.[3] An activation energy of 40.6 kcal/mol[4] is needed to drive this reaction. Studies of bicyclo[1.1.0]-butane derivatives[5] have found that the isomerization follows a highly stereoselective concerted process. A labeling study[6] of a deuterated bicyclo[1.1.0]butane (one of the *exo*-hydrogens H_7 or H_8 is deuterium labeled) has inferred that thermal rearrange-

Table 1. 6-31G(d) Total (au) and Relative (kcal/mol) Energies of Bicyclobutane (**1**), *trans*-Butadiene (**2**), Bicyclobutane Bond Stretch Isomer (**4**), *cis*-Butadiene (**5**), *gauche*-Butadiene (**6**), Conrotatory Transition State (**7**), Disrotatory Transition State (**8**), Second-Order Stationary Point (**9**), and Nonconcerted Transition State (**10**)

struc- ture	wave function	total energy	relative energy E	relative energy H_0[b]
1	MCSCF(10,10)//MCSCF(10,10)	−154.98904(57.0)	0.0	0.0
	MRCI(10,10)//MCSCF(10,10)	−155.11561	0.0	0.0
	PT2F//MCSCF(10,10)	−155.41188	0.0	0.0
2	MCSCF(10,10)//MCSCF(10,10)	−155.05286(55.7)	−40.0	−41.3
	MRCI(10,10)//MCSCF(10,10)	−155.16525	−31.0	−32.4
	PT2F//MCSCF(10,10)	−155.45117	−24.7	−26.0[c]
4	MCSCF(10,10)//MCSCF(10,10)	−154.90976(54.6)	49.7	47.3
	MRCI(10,10)//MCSCF(10,10)	−155.02934	54.1	51.6
	PT2F//MCSCF(10,10)	−155.32864	52.2	49.8
5	MCSCF(10,10)//MCSCF(10,10)	−155.04803(55.7)	−37.0	−38.3
	MRCI(10,10)//MCSCF(10,10)	−155.16525	−27.8	−29.1
	PT2F//MCSCF(10,10)	−155.45117	−21.1	−22.4
6	MCSCF(10,10)//MCSCF(10,10)	−155.04846(55.5)	−37.3	−38.8
	MRCI(10,10)//MCSCF(10,10)	−155.16067	−28.3	−29.8
	PT2F//MCSCF(10,10)	−155.44642	−21.7	−23.2
7	MCSCF(10,10)//MCSCF(10,10)	−154.92153(54.3)	42.4	39.7
	MRCI(10,10)//MCSCF(10,10)	−155.04519	44.2	41.5
	PT2F//MCSCF(10,10)	−155.34147	44.2	41.5
8	MCSCF(10,10)//MCSCF(10,10)	−154.89930(53.0)	56.3	52.4
	MRCI(10,10)//MCSCF(10,10)	−155.01880	60.7	56.7
	PT2F//MCSCF(10,10)	−155.31575	60.3	56.3
9	MCSCF(10,10)//MCSCF(10,10)	−154.84849(50.9)	82.1	88.2
	MRCI(10,10)//MCSCF(10,10)	−154.96976	91.5	85.4
	PT2F//MCSCF(10,10)	−155.26560	91.8	85.7
10	MCSCF(10,10)//MCSCF(10,10)	−154.81374(50.8)	110.0	107.8
	MRCI(10,10)//MCSCF(10,10)	−154.92515	119.5	117.3
	PT2F//MCSCF(10,10)	−155.22285	118.8	116.4

[a] Zero-point vibrational energies are in parentheses; the molecule numbering system is given in Figure 1. *[b]* Including zero-point correction. *[c]* Experimental barrier = 40.6 kcal/mol (ref 4).

ment of **1** follows a concerted process with the two methylene groups moving in a conrotatory fashion, as predicted by Woodward—Hoffmann rules.[7]

Theoretically, Dewar and Kirschner[9a] have predicted that

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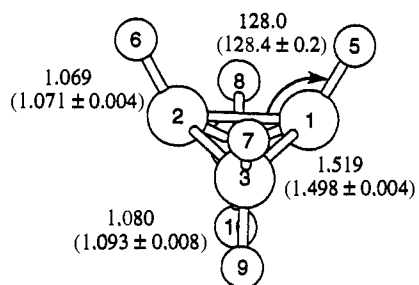(4) (a) Frey, H. M.; Stevens, I. D. R. *Trans. Faraday Soc.* **1965**, *61*, 90. (b) Srinivasan, R.; Levi, A.; Haller, I. *J. Phys. Chem.* **1965**, *58*, 1775. (c) Becknell, A. F.; Berson, J. A.; Srinivasan, R. *J. Am. Chem. Soc.* **1985**, *107*, 1076. (d) Adam, W.; Oppenlander, T.; Zang, G. *J. Am. Chem. Soc.* **1985**, *107*, 3921. (e) Adam, W.; Oppenlander, T. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 661 and references cited therein.

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1 (C$_{2v}$) Bicyclobutane

128.0
(128.4 ± 0.2)

1.069
(1.071 ± 0.004)

1.519
(1.498 ± 0.004)

1.080
(1.093 ± 0.008)
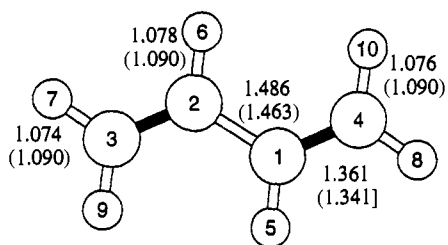
Distances (in Å)
r(7,3) = 1.078 (1.093 ± 0.008)
r(1,2) = 1.521 (1.497 ± 0.003)

Angles (in degrees)
α(7,3,9) = 114.5 (115.6)
β(3,1,2,4) = 122.1
β(7,3,2,1) = 106.8
β(9,3,2,1) = -108.9

2 (C$_{2h}$) *trans*-Butadiene
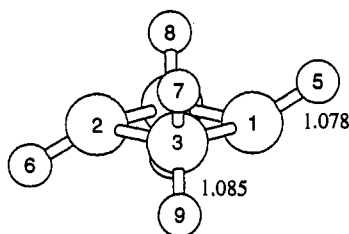
1.078
(1.090)

1.486
(1.463)

1.076
(1.090)

1.074
(1.090)

1.361
(1.341]

Angles (in degrees)
α(7,3,2) = 121.5 (121.8)
α(9,3,2) = 121.1 (121.8)
α(5,1,4) = 119.8 (121.8)
α(4,1,2) = 123.8 (123.3)

4 (C$_{2h}$) Bicyclobutane Bond Stretch Isomer
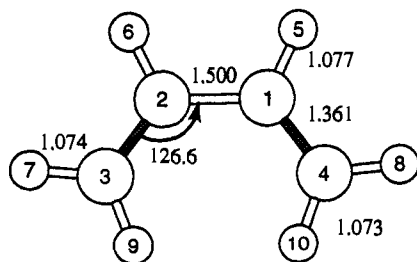
1.078

1.085

Distances (in Å)
r(1,3) = 1.555
r(1,2) = 2.168
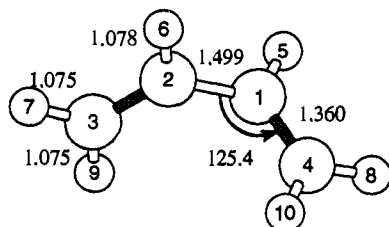
Angles (in degrees)
α(5,1,2) = 140.8
α(5,1,3) = 122.7
α(7,3,1) = 113.5

5 (C$_{2v}$) *cis*-Butadiene

1.500

1.077

1.074

126.6

1.361

1.073

Angles (in degrees)
α(7,3,2) = 120.7
α(9,3,2) = 122.6
α(5,1,4) = 118.0

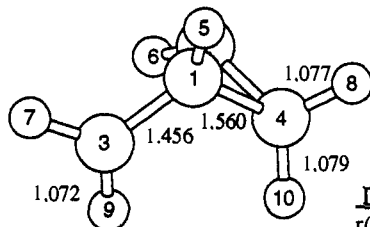**6** (C$_2$) *gauche*-Butadiene

1.078

1.499

1.075

1.075

125.4

1.360

Angles (in degrees)
α(7,3,2) = 121.0
α(9,3,2) = 122.0
α(5,1,4) = 116.0
ω(4,1,2,3) = 31.4

**7 (C₁) Concerted Conrotatory Transition State for
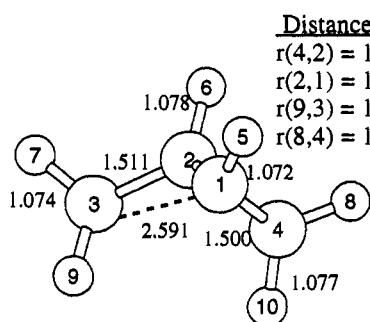the 1⇔ 6 Isomerization Reaction**

Angles (in degrees)
α(3,1,2) = 98.7
α(4,1,2) = 58.1
α(5,1,2) = 124.1
α(6,2,1) = 128.0
α(7,3,1) = 121.2
α(8,4,1) = 113.0
α(9,3,1) = 119.7
α(10,4,1) = 119.1
ω(3,1,2,4) = -108.4
ω(3,1,2,6) = 12.7
ω(5,1,2,4) = 110.5
ω(5,1,2,6) = 128.0
ω(2,1,3,7) = -105.0
ω(2,1,3,9) = 62.3
ω(3,1,4,8) = -166.5
ω(3,1,4,10) = -26.9

Distances (in Å)
r(1,2) = 1.518
r(2,3) = 2.258
r(2,4) = 1.495
r(1,5) = 1.074
r(2,6) = 1.074
r(3,7) = 1.075

8 (C₁) Concerted Disrotatory Transition state for the 1⇔ 6 Isomerization Reaction
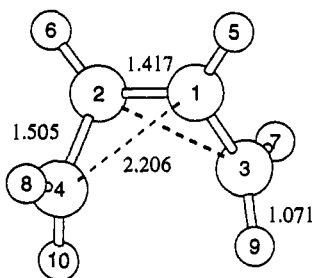

Distances (in Å)
r(4,2) = 1.558
r(2,1) = 1.507
r(9,3) = 1.075
r(8,4) = 1.077

Angles (in degrees)
α(3,2,1) = 118.3
α(4,1,2) = 62.4
α(5,1,2) = 129.9
α(6,2,1) = 117.4
α(7,3,2) = 119.2
α(8,4,2) = 117.6
α(9,3,2) = 118.6
α(10,4,2) = 117.2

ω(3,2,1,4) = 108.2
ω(5,1,2,4) = 121.2
ω(5,1,2,6) = 15.6
ω(6,2,4,1) = 107.5
ω(1,2,3,7) = 120.9
ω(1,2,3,9) = -33.6
ω(1,2,4,8) = 106.8
ω(1,2,4,10) = -106.3

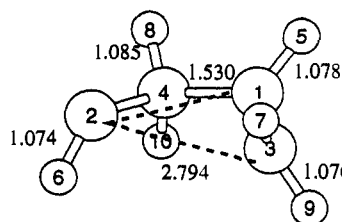**9 (C₂) Second Order Stationary Point (two imaginary frequencies)**

Distances (in Å)
r(7,3) = 1.074
r(6,2) = 1.079

Angles (in degrees)
α(3,1,2) = 98.0
α(6,2,1) = 129.0
α(5,1,2) = 129.1
α(7,3,1) = 117.7
α(9,3,1) = 118.1
ω(3,1,2,4) = 79.1
ω(5,1,2,6) = 18.4
ω(7,3,1,2) = 84.4
ω(9,3,1,2) = -94.9

**10 (C₁) Nonconcerted Transition State for the 1⇔ 4⇔ 6 Isomerization Reaction**

Distances (in Å)
r(1,3) = 1.506
r(1,2) = 2.535
r(2,4) = 1.527
r(7,3) = 1.076
r(10,4) = 1.089

Angles (in degrees)
α(3,1,4) = 117.1
α(5,1,3) = 119.0
α(6,2,4) = 128.8
α(7,3,1) = 120.2
α(8,4,1) = 110.8
α(9,3,1) = 120.1
α(10,4,1) = 110.6

ω(3,1,4,2) = 25.1
ω(5,1,4,2) = -128.8
ω(6,2,1,5) = -175.7
ω(6,2,4,1) = -99.7
ω(4,1,3,7) = -93.3
ω(4,1,3,9) = 107.4
ω(3,1,4,8) = 147.0
ω(3,1,4,10) = -94.4

**Figure 1.** MCSCF(10,10)/6-31G(d) structures of C₄H₆ isomers. Experimental values are in parentheses.
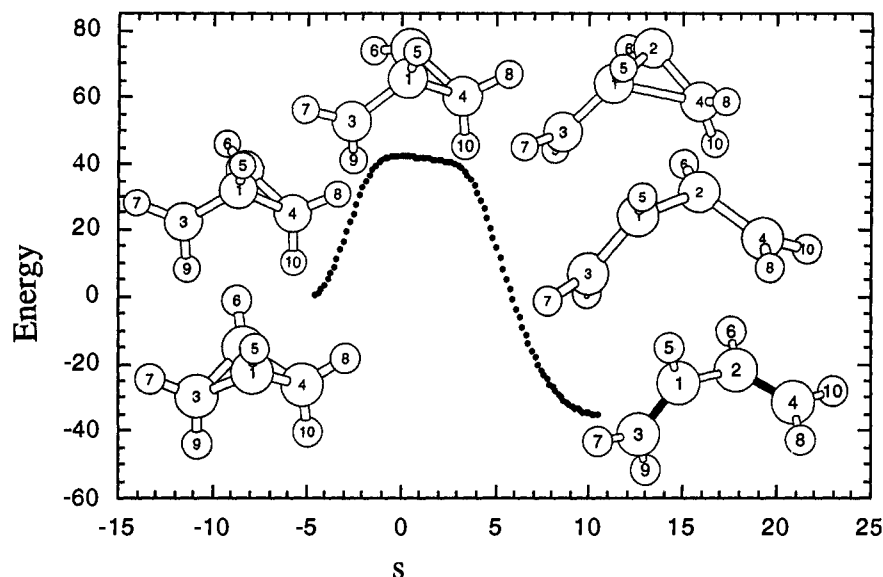
Figure 2. MCSCF(10,10)/6-31G(d) IRC for the bicyclobutane ⇌ *gauche*-1,3-butadiene reaction; energy in kcal/mol; *s* in amu$^{1/2}$-bohr. The structures displayed along the IRC are of the transition state (top): forward (*s* > 0), points 25, 45, and 64; backward (*s* < 0), points 14 and 28.
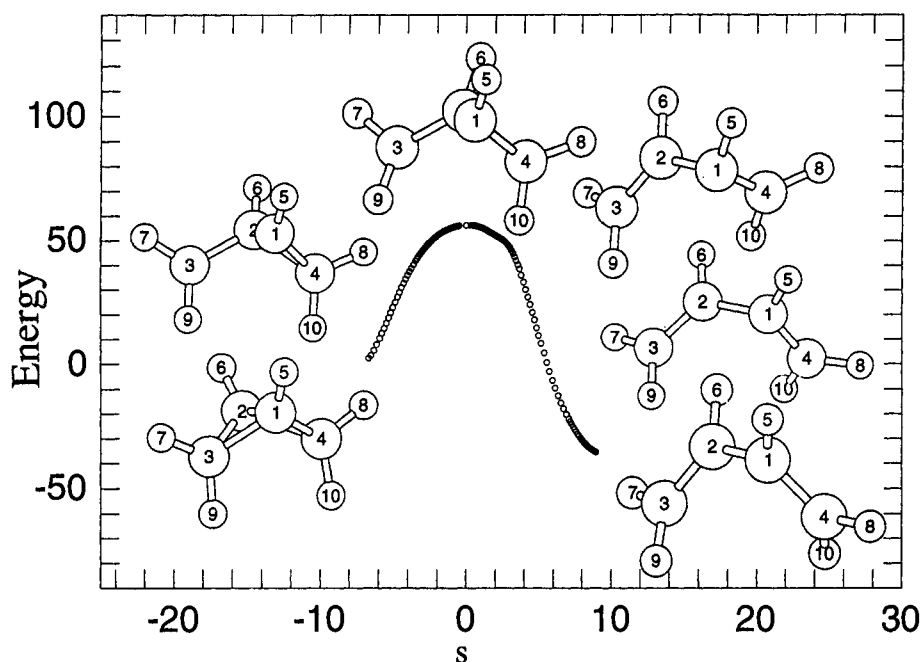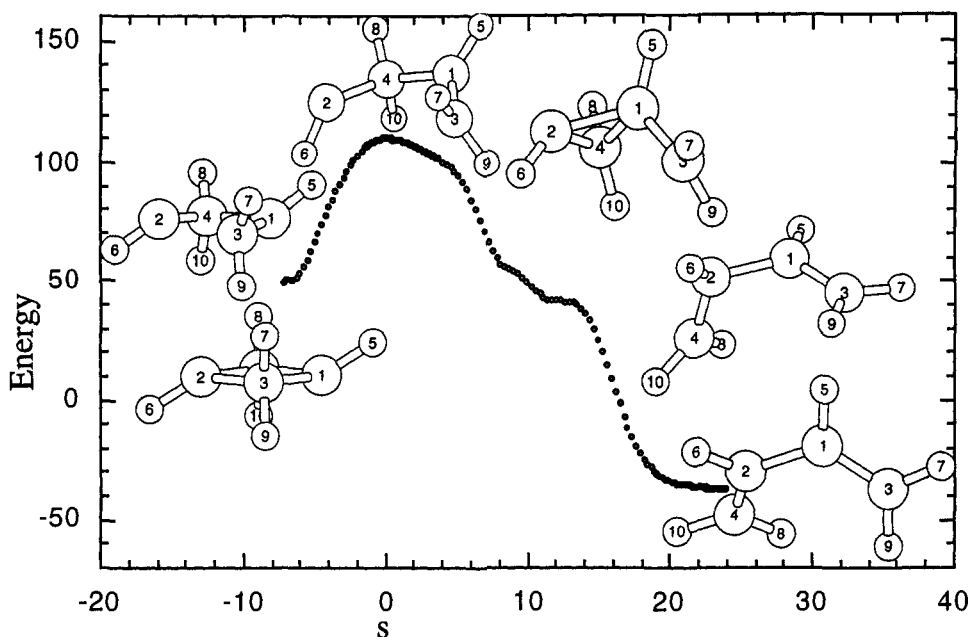

Figure 3. MCSCF(10,10)/6-31G(d) IRC for the bicyclobutane ⇌ *gauche*-1,3-butadiene reaction; energy in kcal/mol; *s* in amu$^{1/2}$-bohr. The structures displayed along the IRC are of the transition state (top): forward (*s* > 0), points 70, 80, and 100; backward (*s* < 0), points 60 and 75.

isomerization of **1** is a stepwise process involving the cyclo-propylcarbinyl biradical intermediate (**3**), based on results from the two configurational CI calculations within the MINDO/3 approximation. The rate determining step was predicted to be a ring opening of **1** to form **3** which subsequently dissociates into **2** without significant activation. The authors have argued that the stereochemistry of the reaction is maintained due to the rapid interconversion of **3** to **2** compared to the formation of **3** from **1**.

Based on *ab initio* MP2/3-21G calculations, Shevlin and McKee[9b] have suggested that ring opening of bicyclo[1.1.0]-butane (**1**) to form 1,3-butadiene (**2**) follows an asynchronous one-step pathway, with a transition state having one C−C peripheral bond lengthened by 0.783 Å and the other by 0.088 Å compared to **1**. The relative thermodynamic stabilities of various biradicals were also considered by Shevlin and McKee. Since all the biradicals investigated were found to be higher in energy relative to the transition state, the stepwise mechanism

3a   **3b**
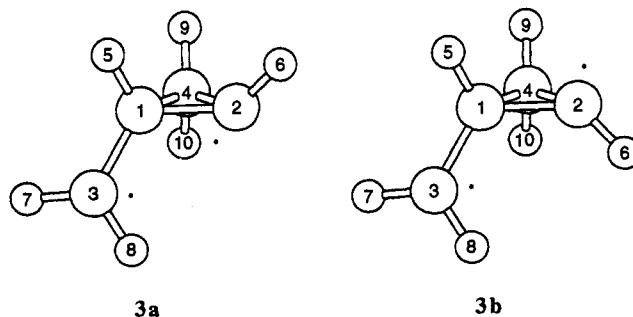
was ruled out. However, these calculations were performed at a modest level of theory using single determinant based methods that are inadequate for describing species having large diradical character.[9a,10] As a result, a consistent picture of the isomerization potential energy surface was not attainable. This point is disscussed in greater detail in the following sections. In the

Figure 4. MCSCF(10,10)/6-31G(d) IRC for the bicyclobutane ↔ *gauche*-1,3-butadiene reaction; energy in kcal/mol; s in amu$^{1/2}$·bohr. The structures displayed along the IRC are of the transition state (top), forward (s > 0)—points 60, 85, and 122; backward (s < 0)—points 36 and 43.

present work, the isomerization of bicyclo[1.1.0]butane to 1,3-butadiene is examined in detail using multiconfigurational wave functions. Multiconfigurational wave functions have the necessary flexibility to properly describe diradical intermediates such as **3**[9] and **4**.[4c–e,10c] In this way, structures **1**–**4** and the associated transition states can be described *in an accurate and consistent manner*. The intermediate **4** has been examined in our previous study of the inversion of bicyclo[1.1.0]butane.[10c]

4 (C2h)
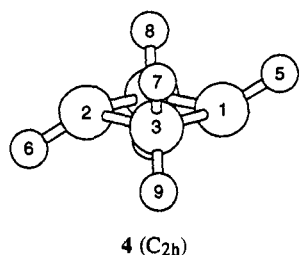
To gain a better understanding of the stereochemistry and to ensure proper connections of all transition states with the corresponding minima, we also apply the concept of intrinsic reaction coordinate (IRC)[14] to map out each reaction path by following the steepest descent paths from the transition states to reactants and products. This detailed analysis of each reaction path allows us to provide important new insights into the isomerization sterochemistry.

II. Methods of Calculation

Since the isomerization of bicyclo[1.1.0]butane to 1,3-butadiene involves breaking at least two opposite peripheral C—C bonds, our

multiconfigurational wave function for this process would require an active space of at least 4 orbitals and 4 electrons [i.e., MCSCF(4,4)]. To completely account for all changes in the bicyclo[1.1.0]butane ring system, the reference space is expanded by combining five doubly occupied C—C bonding MOs and their corresponding antibonding MOs, creating 19404 spin adapted configuration state (CFS) functions (for C_1 symmetry) making up the 10 orbitals and 10 electrons complete active space (CAS) MCSCF[14] [MCSCF(10,10)] wave function.

The MCSCF(10,10) determinations of geometries were performed using the 6-31G(d) basis set. Structures were obtained with the use of the analytically determined gradients encoded in the GAMESS[15] quantum chemistry program system. Minima and transition states were verified by evaluating the appropriate matrix of energy second derivatives (hessian), using finite differences of the analytically determined gradients. The final energetics were obtained from MRCI[11] calculations (including all single and double excitations from the active orbitals of the MCSCF(10,10) reference space), using the MCSCF wave functions to define the reference space. All MRCI calculations were done using the MOLPRO[16,11] codes.

In addition, second-order perturbation theory calculations with the CASSCF(10,10) wave function as the reference space (PT2)[13] were also carried out to assess the effect of dynamic electron correlation that is not included in the MRCI(10,10). PT2 calculations of two different types of Møller—Plesset-like partitioning were carried out using the MOLCAS-2 program.[17] The PT2D partitioning includes only the diagonal part of the one-electron operator in the zeroth-order Hamiltonian while PT2F also includes all nondiagonal elements. Only PT2F is invariant to orbital transformations.

The IRC was traced by following the path of steepest descents in the mass-weighted Cartesian coordinates.[18,19] The reaction paths were generated using the second-order Gonzalez—Schlegel (GS2)[20] method encoded in GAMESS.[15] The initial step off the saddle point was taken by following the imaginary normal mode with a 0.12 amu$^{1/2}$·bohr step.

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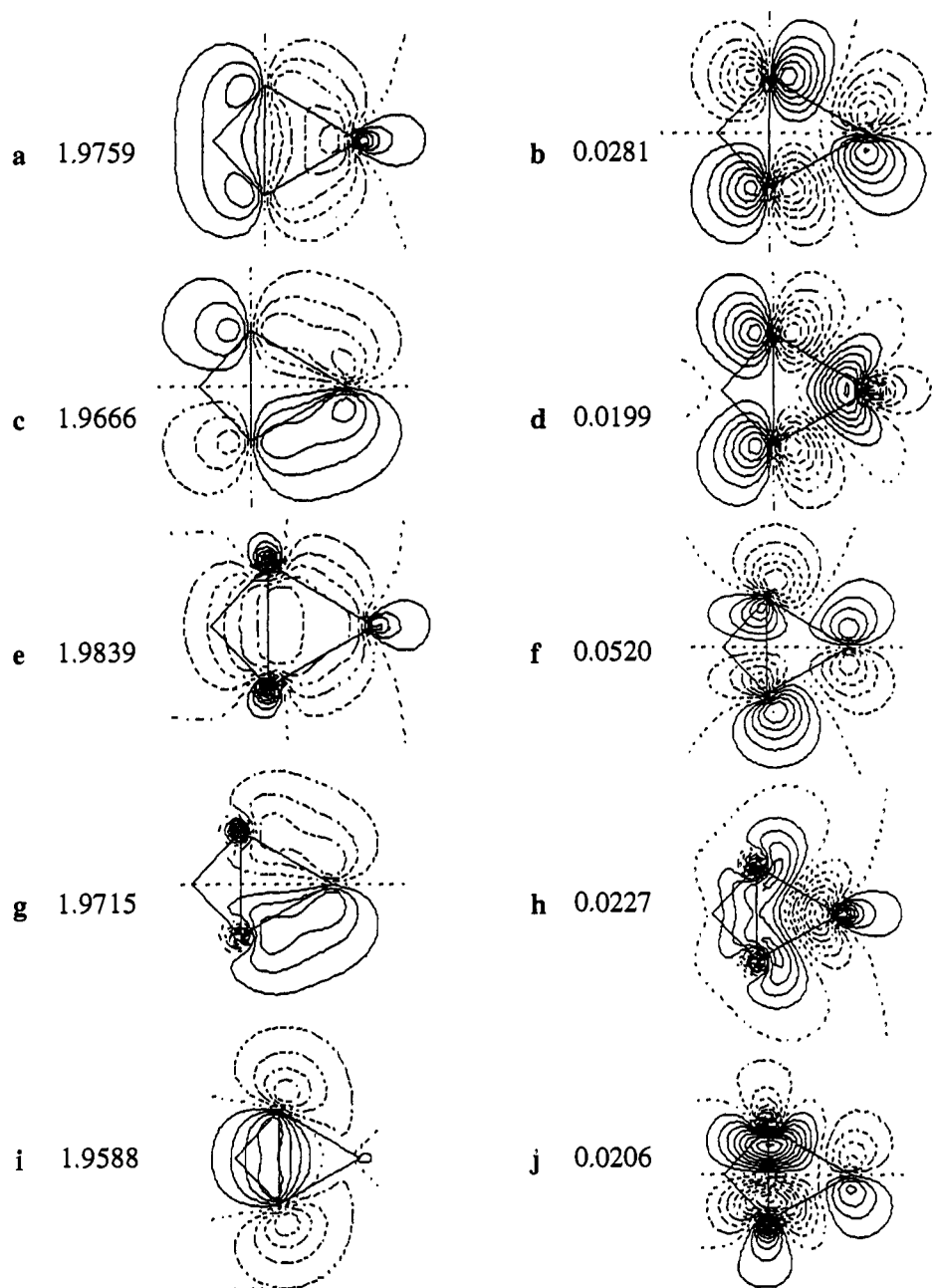
Figure 5. Contour plots of bicyclobutane (1) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the planes that are constructed from two bridgehead atoms and one of two peripheral atoms (numberical values = occupation numbers).

Other points on the IRC were located with a step size of 0.17 amu$^{1/2}$·bohr (Δs = 0.17 amu$^{1/2}$·bohr).

All geometry searches and IRC calculations were done with the 6-31G(d) basis set.[11] Since the basis set dependence upon going from 6-31G(d) to 6-311G(d,p)[21] was shown to be small in MRCI and PT2F calculations for the inversion process of bicyclo[1.1.0]butane,[10c] only the 6-31G(d) basis set is used for all correlated calculations in this study.

III. Results and Discussion

A. Structures and Reaction Energetics.
The MCSCF, MRCI, and PT2F total and relative energies of all stationary

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points on the isomerization surface are listed in Table 1. The MCSCF(10,10)/6-31G(d) geometric parameters of these species are given Figure 1. Whenever available, the experimental geometric parameters are given in parentheses for comparisons. In general, correlated MCSCF bond distances are slightly longer compared to the experimentally determined values. Our MC-SCF(10,10) calculations overestimate the experimental[22] bridgehead (C_1—C_2) and peripheral (C_1—C_3) distances of bicyclo-[1.1.0]butane (1) by 0.024 and 0.021 Å, respectively (see Figure 1). Similarly, MCSCF(10,10) bond distances for 1,3-butadiene (2) are about 0.01−0.03 Å longer than the experimental values.[23] Energetically, the exothermicity of the isomerization 1 → 2 has been experimentally measured to be 26 ± 2 kcal/mol.[24] The calculated MCSCF(10,10) exothermicity is 41.3 kcal/mol, including corrections for the vibrational zero-point energy (ZPE).

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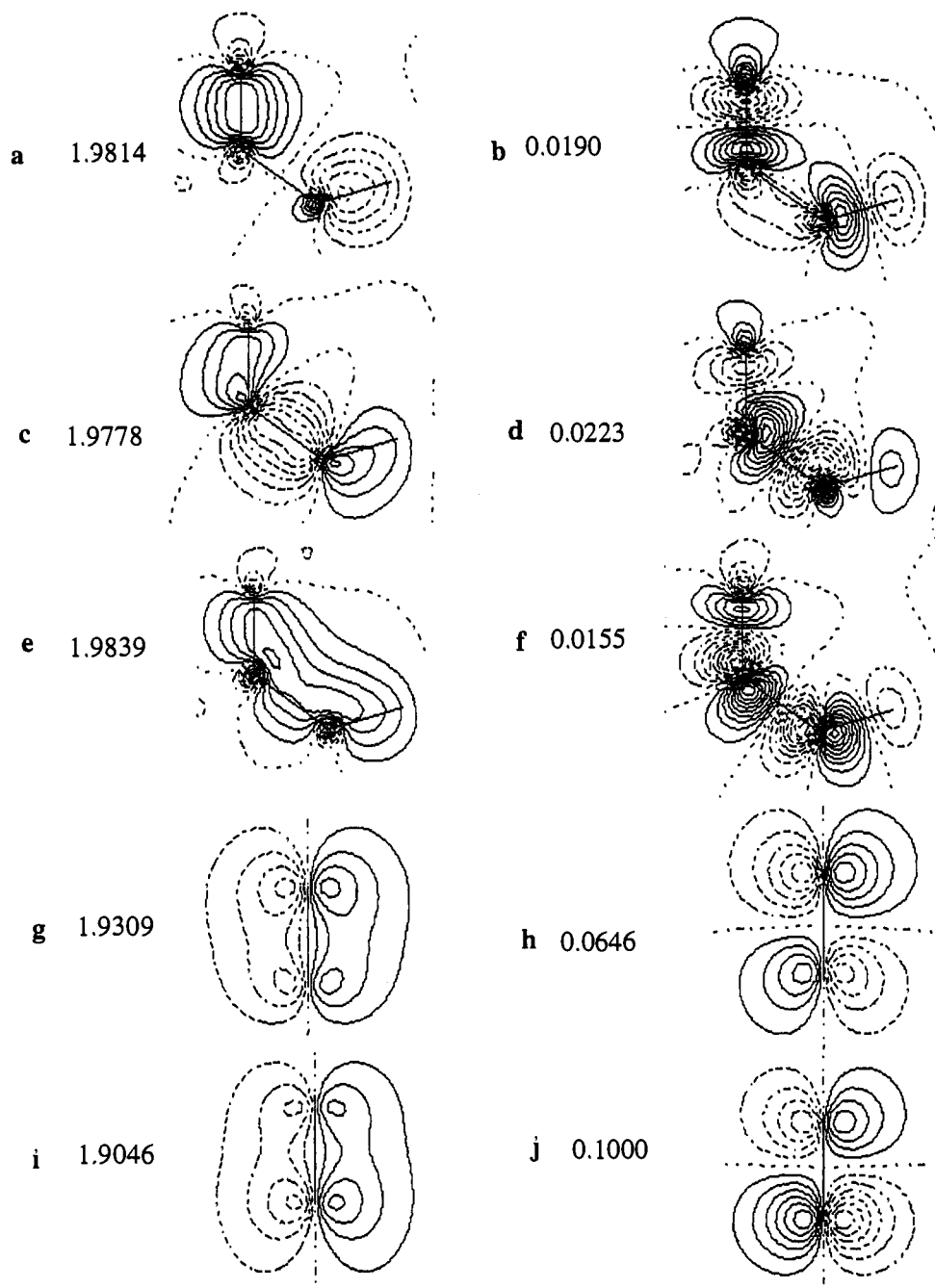
Figure 6. Contour plots of the *gauche*-butadiene (**6**) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the $C_1-C_2-C_3$ plane (a—h) and the planes bisecting $H_{10}-C_4-H_8$ (g—h) and $H_9-C_3-H_7$ (i—j) (numerical values = occupation numbers).

To include dynamic electron correlation, MRCI(10,10)//MC-SCF(10,10) calculations with all CH MOs frozen were carried out, resulting in an exothermicity of 32.4 kcal/mol. The full PT2 based on the same MCSCF(10,10) wave function has the advantage that all valence MOs are correlated. This level of theory, PT2F//MCSCF(10,10), yields an isomerization enthalpy of −26.0 kcal/mol. This PT2F result is in excellent agreement with the experimental exothermicity value.

The *cis*-1,3-butadiene conformation (**5**) is not a minimum on the MCSCF(10,10)/6-31G(d) potential energy surface. Rather, this structure, with one imaginary frequency of 130i cm^{-1}, corresponds to the rotational transition state leading to the *gauche*-1,3-butadiene (**6**) isomer. This is in agreement with earlier *ab initio* calculations.[24] At the PT2F level of theory, the *cis*-1,3-butadiene transition state is predicted to be 3.6 kcal/

mol (with ZPE correction) above the *trans*-1,3-butadiene (**2**) conformer. A similar ΔH value is obtained with MRCI (see Table 1). The *gauche* conformer of 1,3-butadiene (**6**) is a minimum on the MCSCF(10,10)/6-31G(d) potential energy surface. The *gauche* isomer is predicted to be 0.8 (0.7) kcal/mol below the *cis* and 2.8 (2.6) kcal/mol above the *trans* at the PT2F (MRCI) level of theory. So, the orbitals that are frozen in the MRCI calculations have little effect on the relative energies of the three 1,3-butadiene conformers. The relative energies are essentially identical to the MP2/6-31G(d)//MP2/6-31G(d) predictions by Wiberg et al.[25]

B. Transition Structures and Barrier Heights. Three transition states, **7**, **8**, and **10**, were located on the MCSCF-(10,10)/6-31G(d) potential energy surface. Structures **7** and **8** correspond to the transition states for the asynchronous concerted

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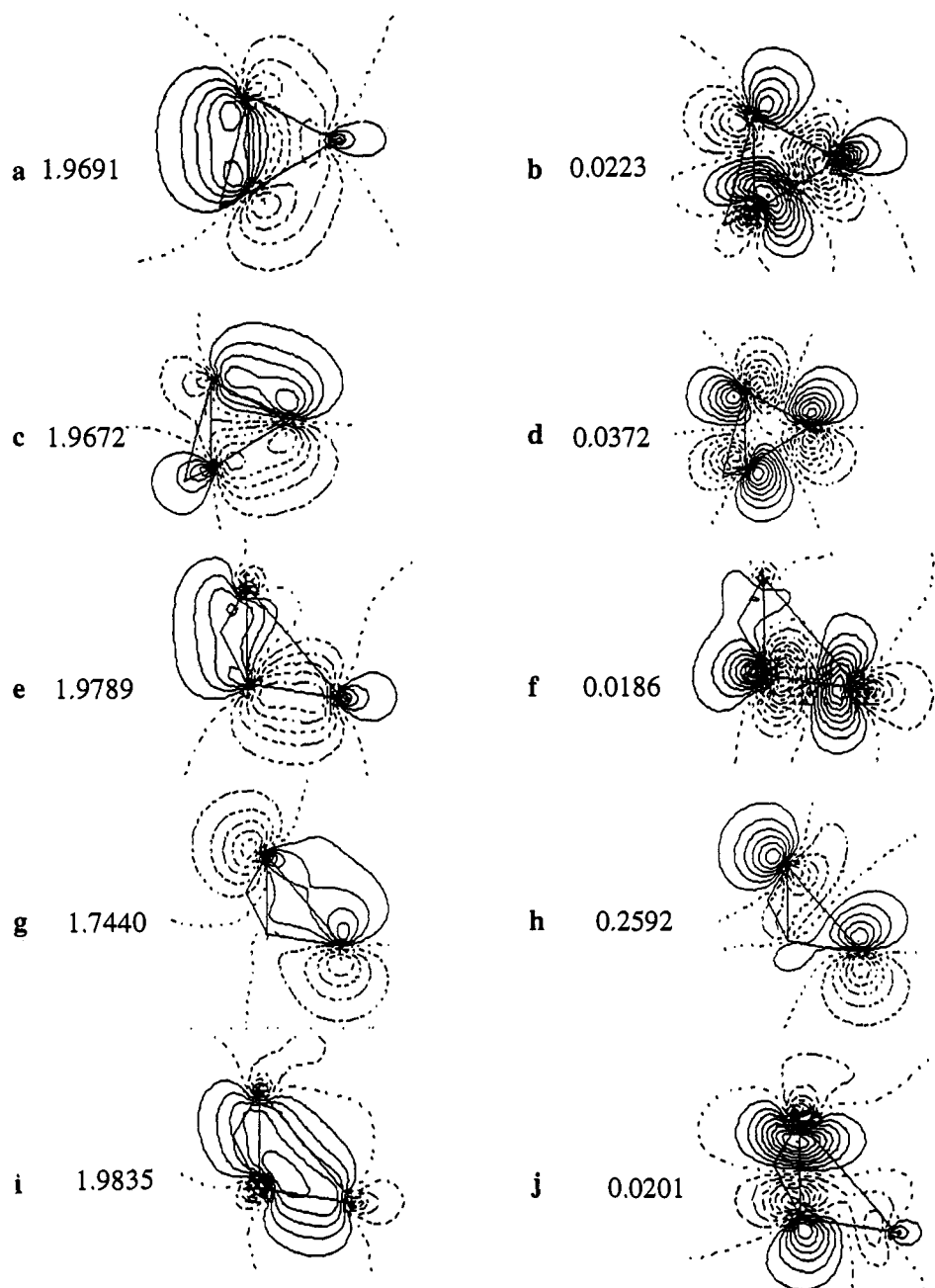
Figure 7. Contour plots of the conrotatory transition state (**7**) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the planes that are constructed from two bridgehead atoms and one of two peripheral atoms, 1−2−4 plane (a−d), 1−2−3 plane (e−j) (numerical values = occupation numbers).

mechanisms in which the methylene groups move in conrotatory and disrotatory fashions, respectively. Transition state **10** corresponds to the non-concerted isomerization process with a diradical intermediate **4** which can be readily converted to bicyclo[1.1.0]butane without significant activation.[10c] The geometric parameters and relative energies of these transition states are also given in Table 1 and Figure 1, respectively. The IRCs traced from these transition states to the corresponding minima are displayed in Figures 2 and illustrate that the three transition states do indeed connect the appropriate minima.

At all levels of theory, ring opening of bicyclo[1.1.0]butane (**1**) via the conrotatory transition state **7** is predicted to be the lowest in energy among the three barriers found. At the MCSCF(10,10) level of theory, the conrotatory barrier (**7**) is located at 39.7 kcal/mol above the reactant bicyclo[1.1.0]butane, with ZPE included. PT2F//MCSCF(10,10) and MRCI/MCSCF-(10,10) slightly increase this barrier to 41.5 kcal/mol. This is

in excellent agreement with the experimentally measured barrier of 40.6 kcal/mol.[4]

At the transition state (**7**), the C_2-C_3 peripheral bond (2.258 Å) is completely broken while the other C_1-C_3 peripheral distance (1.456 Å) is only 0.063 Å shorter than the C−C peripheral distance in the reactant bicyclo[1.1.0]butane. The ring opening is accompanied by a distortion of the $H_5-C_1-C_2-H_6$ dihedral angle to 128° away from the eclipsed position at the equilibrium structure (**1**) (see **7**, Figure 1). In the opposite ring, the C_1-C_4 distance increases to 1.560 Å, and C_2-C_4 decreases to 1.495 Å.

The disrotatory ring opening transition state (**8**) is located at 52.4 kcal/mol above bicyclo[1.1.0]butane on the MCSCF(10,-10)/6-31G(d) potential energy surface. MRCI and PT2F dynamic electron correlation corrections give 56.7 and 56.3 kcal/mol, respectively, for this barrier when ZPE corrections are included. This is about 15 kcal/mol higher than the conrotatory
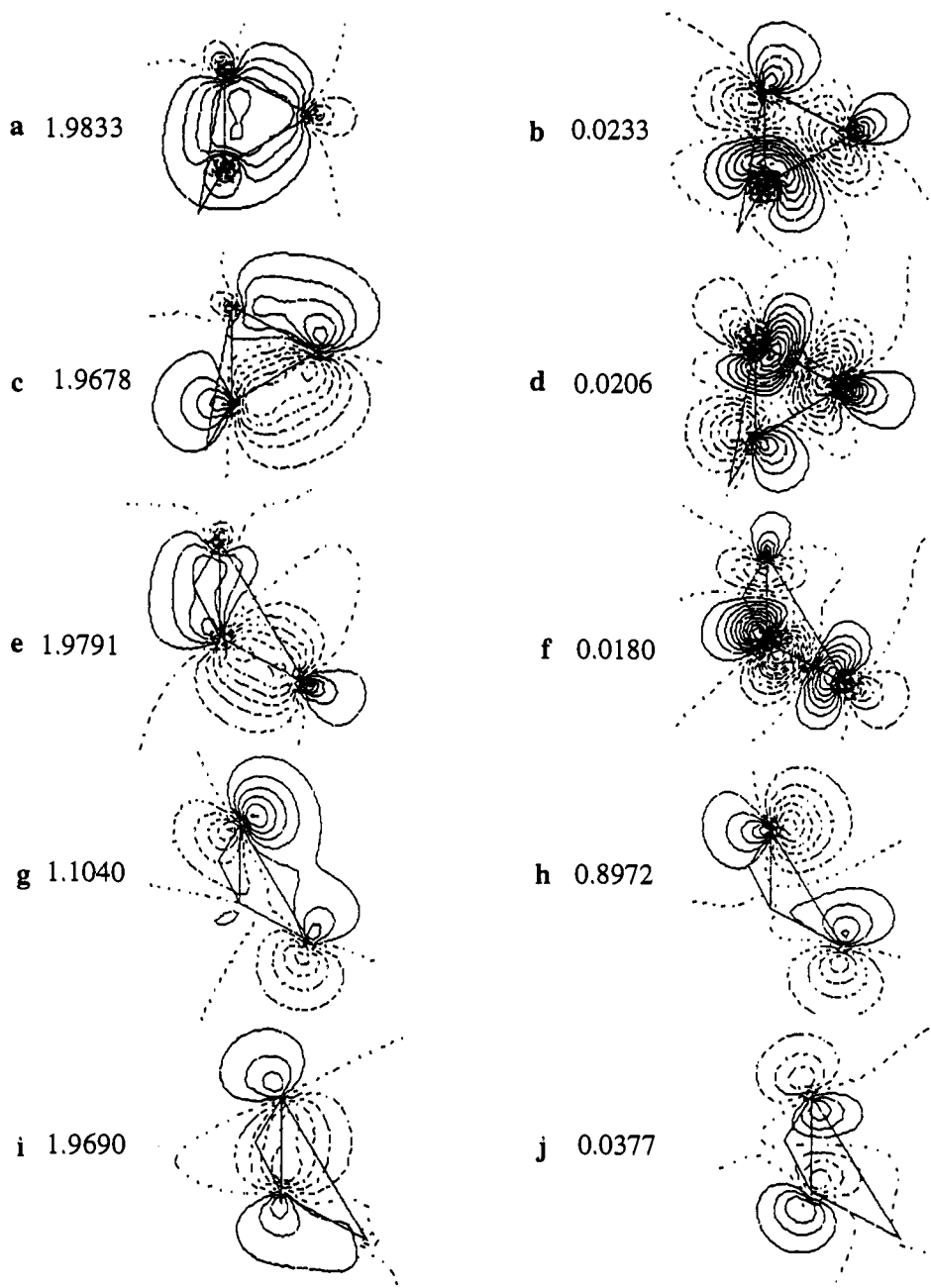
Figure 8. Contour plots of the disrotatory transition state (**8**) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the planes that are constructed from two bridgehead atoms and one of two peripheral atoms, 1−2−4 plane (a−d), 1−2−3 plane (e−j) (numerical values = occupation numbers).

isomerization barrier, obtained at the same levels of theory. At the transition state (**8**), the C_1-C_3 bond in one cyclopropane ring is completely broken (C_1-C_3 = 2.591 Å), while all C−C distances in the opposite cyclopropane ring are only slightly changed from their values in bicyclo[1.1.0]butane (Figure 1). In contrast to the conrotatory transition state (**7**), **8** has two bridgehead hydrogens (H_5 and H_6) nearly eclipsed with each other.

The diradical structure **4** has been speculated to be an intermediate for the stepwise isomerization of bicyclo[1.1.0]-butane to 1,3-butadiene in photolysis studies.[10c-e] Structure **4**—a minimum on the MCSCF(10,10)/6-31G(d) potential energy surface and lying about 50 kcal/mol above bicyclo[1.1.0]-butane—has been found to isomerize back to bicyclo[1.1.0]-butane without any significant barrier.[10c] Despite careful searches, the diradical intermediates **3a** and **3b** were not found.

Since the isomerization of bicyclo[1.1.0]butane to 1,3-butadiene via intermediate **4** requires the breaking (at least

partially) of another C−C peripheral bond in addition to the central bridgehead C_1-C_2 bond, the barrier may be significantly higher than the concerted pathways. This barrier (**10**) is indeed found by PT2F to lie 116.4 kcal/mol (including ZPE correction) above bicyclo[1.1.0]butane. The barrier predicted by MRCI is about 1 kcal/mol higher than that of PT2F.

The relative barrier heights of the three transition states corresponding to the conrotatory process (**7**: 41.5 kcal/mol), disrotatory process (**8**: 56.3 kcal/mol), and stepwise process (**10**: 116.4 kcal/mol) may be understood by considering the transition state structures (Figure 1) and the nature of the corresponding wave functions. As noted above, the transition state structures **7** and **8** that correspond to concerted mechanisms each have one CC bond (2−3 in **7**; 1−3 in **8**) that has been stretched considerably relative to the normal CC bond distance in the parent bicyclobutane (**1**). The C_1-C_3 bond in **8** has in fact been stretched 0.34 Å more than the C_1-C_2 bond in **7**, suggesting that the former bond is more completely broken. In
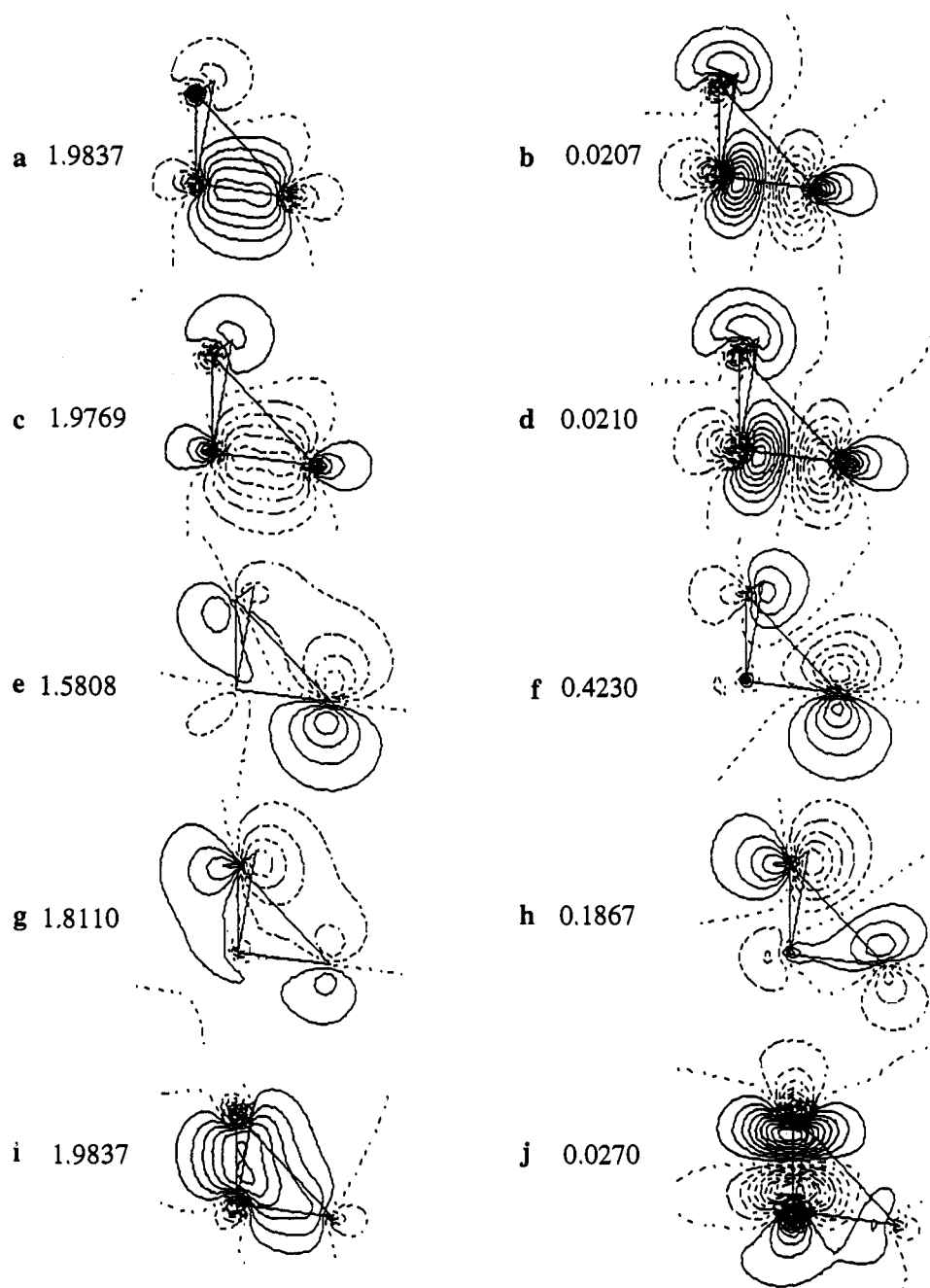
Figure 9. Contour plots of the second-order stationary point (**9**) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the planes that are constructed from two bridgehead atoms and one of two peripheral aotms (numerical values = occupation numbers).

addition, those bonds which will become double bonds in butadiene (C_1-C_3 and C_2-C_4 in **7**) are much shorter than the corresponding bonds in **8**. These two factors will tend to stabilize **7** relative to **8**. Support for this speculation may be drawn from the nature of the MCSCF wave functions for these two species. The large increase in $C-C$ bond distances at the transition states suggests significant configurational mixing may occur. The amount of configurational mixing in the transition states may be assessed by examining the natural orbital occupation numbers (NOONs) of the MCSCF wave functions. For RHF wave functions, the NOONs are 2 for occupied orbitals and 0 for virtual orbitals. The deviations from these values in multiconfigurational wave functions may therefore be taken as a measure of "diradical character".

The MCSCF(10,10) natural orbitals (NOs) of bicyclo[1.1.0]-butane, 1,3-butadiene, transition states, and other structures of interest are displayed in Figures 5-11. The orbitals labeled **g** and **h**—displayed in the plane containing two bridgehead atoms

and one peripheral atom—correspond to the bonding and antibonding orbitals of the broken $C-C$ peripheral bond in the transition states **7** and **8**. The NOONs for these NOs are nearly 1.0 (true diradicals) in structure **8** (Figure 8), whereas for structure **7**, these occupation numbers are ~1.75 and 0.25, respectively. The diradical character of **7** is lower compared to **8** (0.36 vs 1.00 electrons outside of the closed shell Hartree—Fock configuration), due in part to the greater stretching of the peripheral CC bond in **8** and in part to the developing π-bond character nearly perpendicular to the plotting plane in **7**. While there is still significant configurational mixing in the conrotatory transition state **7** compared to the relatively closed shell nature of bicyclo[1.1.0]butane (**1**) and 1,3-butadiene (**6**) (see Figures 5 and 6), it is much less than that in **8** and this serves to destabilize **8** more than **7**.

In the stepwise transition state **10** two CC bonds (2—3 and 1—2) have been largely broken and little new significant double bond character has been attained. So, one expects this transition

Isomerization of Bicyclo[1.1.0]butane to Butadiene

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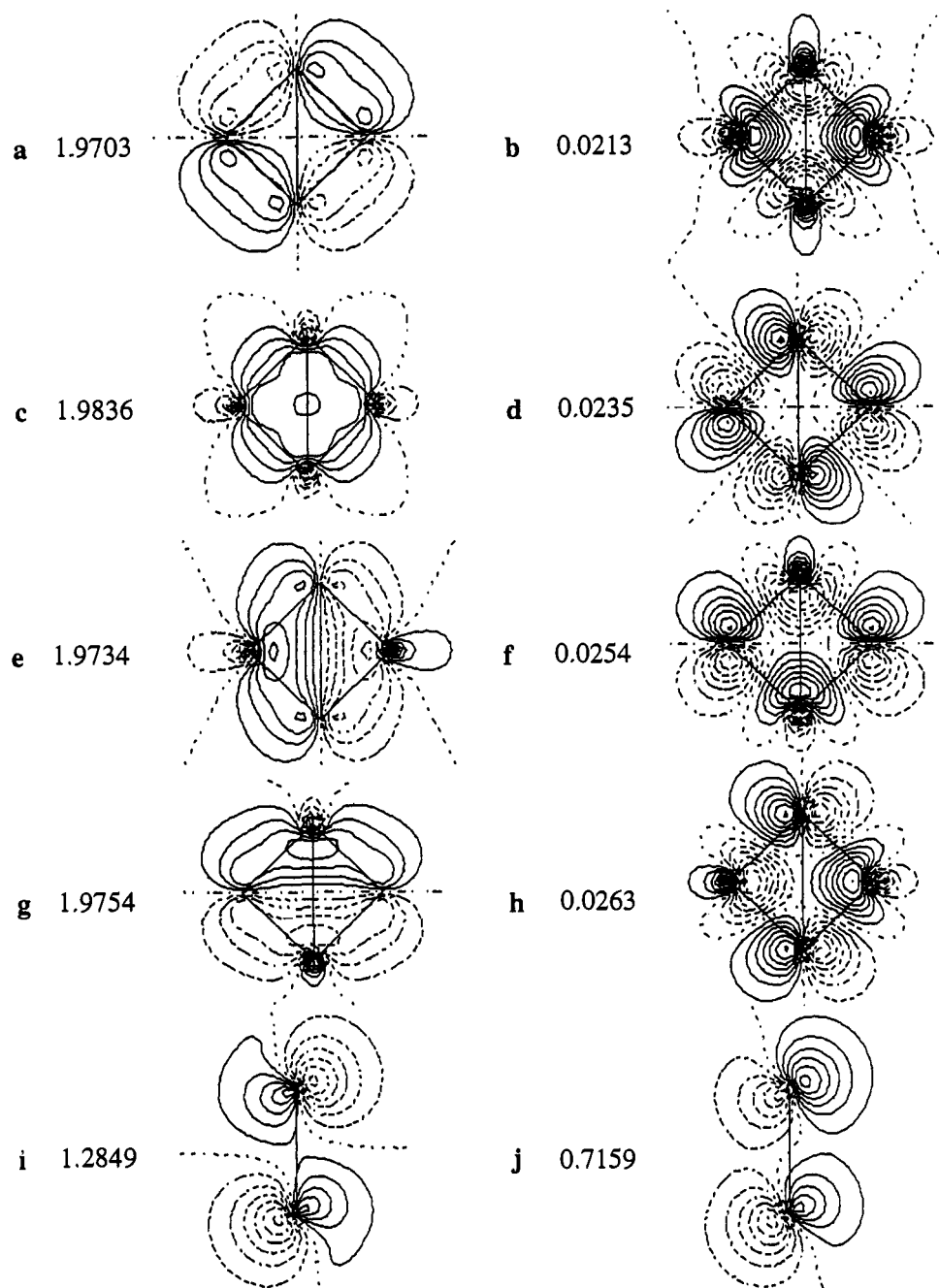
Figure 10. Contour plots of the bicyclobutane bond stretch isomer (**4**) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the YZ (a—h) and $\sigma_h(x,y)$ (i—j) (numerical values = occupation numbers).

state to be particularly unstable. Indeed, the NOONs of orbitals **i** and **j** become nearly 1 in the bond stretch isomer (**4**, Figure 10) and the nonconcerted transition state (**10**, Figure 11). The NOONs of orbitals **g** and **h** corresponding to the C_3—C_2 peripheral bond are also close to 1 at the transition state structure **10**. As a result, in structure **10** there are 1.85 electrons outside of the Hartree—Fock closed shell configuration (that is, in antibonding orbitals). So this stepwise transition state is essentially a double diradical because two bonds are nearly broken. So, it is not surprising that this is a particularly high energy transition state. In view of the varying degrees of diradical character in the three transition states, it is clear that the competing isomerization mechanisms of bicyclo[1.1.0]butane cannot be treated in a consistent manner with single configuration-based methods.

C. Reaction Paths. (i) **Conrotatory Ring Opening.** The connection of bicyclo[1.1.0]butane with the conrotatory transi-

tion state **7** and gauche-1,3-butadiene (**6**) is verified by the IRC calculations. Figure 2 displays the structural rearrangements along the IRC in this isomerization process. Notice that while one bridgehead hydrogen (H_5) bends away from an eclipsed position relative to H_6, the two methylene groups move in a conrotatory fashion in the ring-opening process. This leads to the final stereochemistry of 1,3-butadiene with H_8 and H_7 (exohydrogens of bicyclo[1.1.0]butane) having H—C—C—C dihedral angles of 0° (cis) and 180° (trans), respectively (see Figure 2). So if both peripheral exo-hydrogens (H_8, H_7) were labeled with deuteriums, the final product would be referred to as gauche-1,3-butadiene-1-cis-4-trans-d_2, as predicted by the IRC calculation in Figure 2, where the "1" and "4" refer to the carbons vicinal to H_8 and H_7, respectively. If one of the peripheral exo-hydrogens (H_8, H_7) was deuterated, an equal mixture of gauche-1,3-butadiene-cis-1-d (for D_8) and gauche-1,3-butadiene-trans-1-d (for D_7) would be obtained. Furthermore, since the gauche-
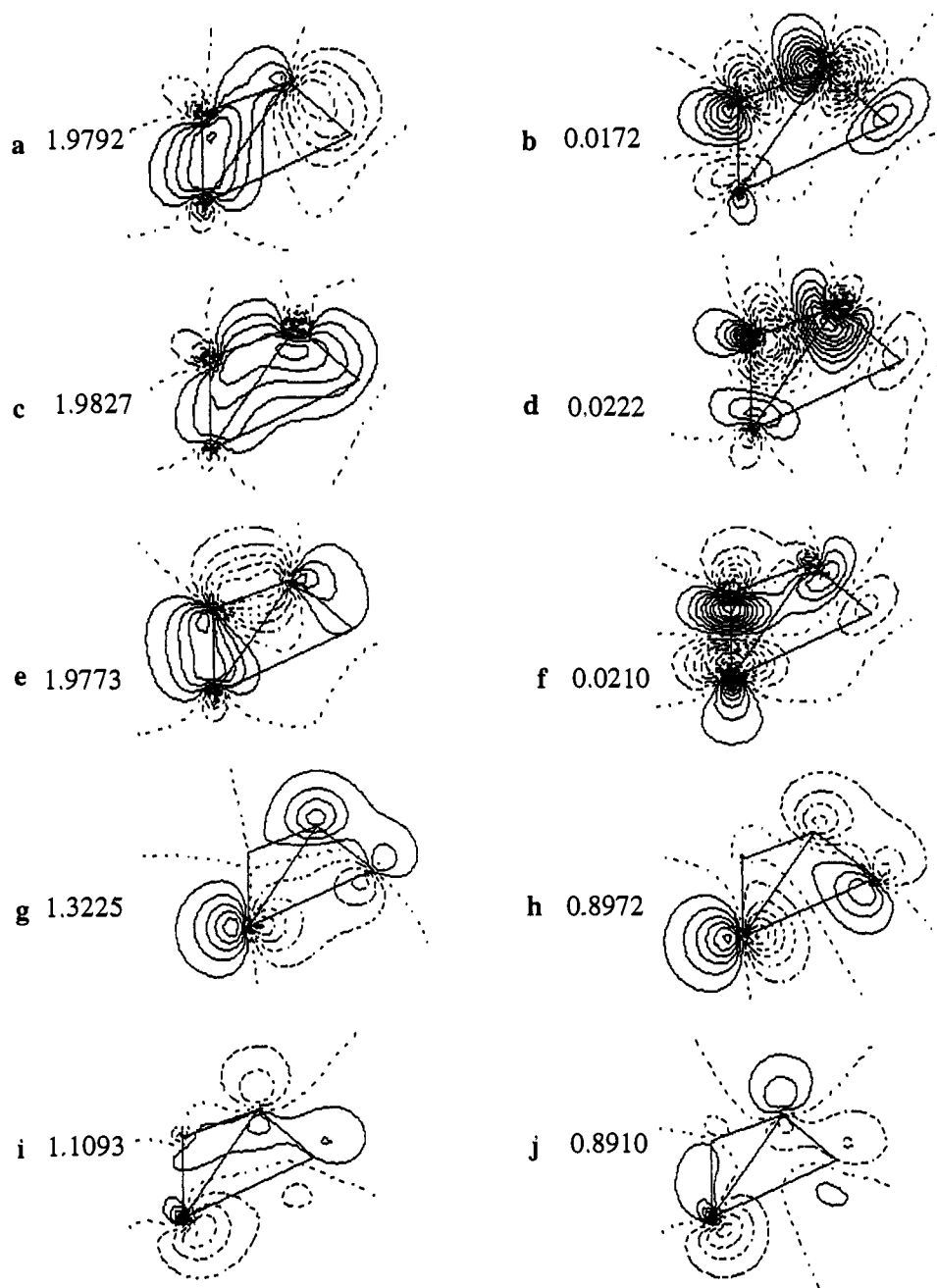
Figure 11. Contour plots of the nonconcerted transition state (10) correlated reaction orbitals of the optimized MCSCF(10,10)/6-31G(d) wave function in the planes that are constructed from two bridgehead atoms and one of two peripheral atoms, 1−2−4 plane (a−h), 1−2−3 plane (g−j) (numerical values = occupation numbers).

trans rotational barrier is less than 3 kcal/mol,[24] the final experimentally observed products are likely to contain an equal mixture of *trans*-1,3-butadiene-*cis-1-d* and *trans*-1,3-butadiene-*trans-1-d*, as has been found in labeling studies.[6] The predicted stereochemistry of the products is also consistent with experimental observations in the pyrolysis studies of *exo,exo-* and *exo,-endo*-dimethyl-substituted bicyclo[1.1.0]butane derivatives.[5]

(ii) **Disrotatory Ring Opening.** The IRC displayed in Figure 3 connects bicyclo[1.1.0]butane (1) with *gauche*-1,3-butadiene via transition state 8. In the disrotatory ring opening, the methylene groups rotate in opposite directions asynchronously. The disrotatory rotation of the two methylene groups gives rise to the *gauche*-1,3-butadiene-*1-trans-4-trans-d₂* (H_8—C_4—C_1—C_2 and H_7—C_3—C_2—C_1 dihedral angles are 180°) if the two *exo*-hydrogens are deuterium labeled. The opposite (*cis*) stereochemistry would be obtained for *endo*-deuterated bicyclo[1.1.0]butane. The reaction mechanism resulting in this

type of stereoselectivity for the disrotatory ring opening of bicyclo[1.1.0]butane is likely to be a minor path, since the competing conrotatory process with different stereoselectivity has a significantly lower barrier (15 kcal/mol lower). Furthermore, the *exo-* and *endo*-hydrogens of bicyclo[1.1.0]butane can be scrambled by the inversion process[10c] with a barrier about 8 kcal/mol lower than the disrotatory ring-opening barrier.

The barrier for disrotatory ring opening constrained to C_2 symmetry (9) is located at 85.7 kcal/mol above bicyclo[1.1.0]-butane. This structure (9, Figure 1) is not a true transition state, since it has two imaginary frequencies.

(iii) **Stepwise Mechanism.** The reaction path for the 4 ↔ 6 isomerization via transition state 10 is displayed in Figure 4. At the transition state (10), the bridgehead hydrogens (H_5 and H_6) remain staggered, and the bridgehead C_1—C_2 and the peripheral C_2—C_3 bonds are lengthened to 2.535 and 2.794 Å, respectively.

The initial descent from the transition state **10** toward 1,3-butadiene involves, mostly, the shortening of the bridgehead C_1-C_2 bond and the rotation of one methylene group. This is followed by the conrotatory rotations of the two methylene groups. Since the intermediate **4** scrambles the peripheral hydrogens via an inversion barrier of less than 1 kcal/mol,[10c] this isomerization process is not stereoselective.

D. Comparison with Previous Caclculations. Finally, it is important to compare our calculations with the previous studies of Shevlin and McKee (SM).[9b] In these earlier *ab initio* calculations,[9b] a concerted conrotatory barrier of 43.6 kcal/mol was estimated at the MP4(SDTQ)/6-31G(d) level of theory based on a series of additivity assumptions. While this barrier estimate is in reasonable agreement with our best (MRCI and PT2F) value of 41.5 kcal/mol, the SM estimate of 97 kcal/mol for the disrotatory process is more than 30 kcal/mol *larger* than our prediction of ca. 56 kcal/mol. Likewise, SM predict a barrier for the stepwise mechanism that is more that 50 kcal/mol *too small*. This illustrates the need for an adequate level of theory, such as that provided in the present work, to obtain a *consistent* picture of the potential energy surface.

IV. Summary and Conclusion

In the present work, three isomerization channels have been considered, and in each case, the reaction paths have been verified by following the corresponding minimum energy paths (MEP's). For the first time, this provides a direct comparison of the competing mechanisms, all explored at the same (reliable) level of theory. In addition, this comparison, with the aid of the MEP's, has allowed us to consider the stereochemistry of the observed products. Previous studies have speculated that bicyclo[1.1.0]butane isomerizes into either *cis* or *trans* 1,3-butadienes, whereas we have shown that the isomerization proceeds through *gauche*-1,3-butadiene. Since all of these calculations have been done at a consistent level of theory, comparisons can be made among the three isomerization processes, the role of the inversion processes, and the thermal and photolysis experiments.

The isomerization process of bicyclo[1.1.0]butane has been examined using multiconfigurational based wave functions. The ca. 42 kcal/mol conrotatory barrier obtained by PT2F/6-31G(d)//MCSCF(10,10)/6-31G(d) and MRCI(10,10)/6-31G(d)//MCSCF(10,10)/6-31G(d) is within 1 kcal/mol of experiment and of one another. Barriers for the concerted disrotatory and stepwise isomerization processes are ca. 56 and 116 kcal/mol, respectively, so the bicyclo[1.1.0]butane to 1,3-butadiene isomerization is predicted to proceed primarily via the concerted conrotatory mechanism. This conclusion is in agreement with the experimental observations[5,6] that the reaction proceeds in a concerted manner, but disagrees with previous semiempirical calculations that predict a stepwise mechanism.[9a]

Excellent agreement with the experimental exothermicity of the isomerization of bicyclo[1.1.0]butane to 1,3-butadiene was obtained for PT2F, but not for MRCI(10,10), since the frozen core approximation for CH bonds is less valid in the latter. The predicted stereochemistry is in agreement with the experimental observations. For this system, there appears to be a correlation between the amount of diradical character in the transition state (conrotatory < disrotatory < nonconcerted) and the height of the associated energy barrier. This emphasizes the need for multiconfigurational based methods for a consistent treatment of the isomerization process.

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