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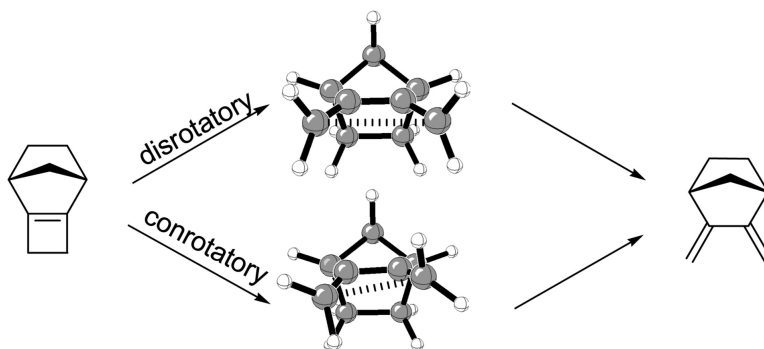
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A R T I C L E S

Altering the Allowed/Forbidden Gap in Cyclobutene Electrocyclic Reactions: Experimental and Theoretical Evaluations of the Effect of Planarity Constraints

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Abstract: The allowed conrotatory cyclobutene ring-opening has a distinctly nonplanar carbon skeleton. Classic experiments by Brauman and Archie, and by Freedman et al., placed the allowed/forbidden gap at greater than 15 kcal/mol. Wolfgang Roth proposed that a system forced to planarity might have a smaller preference for the conrotatory mode than unconstrained systems. Such systems have now been studied theoretically and experimentally, and results that confirm Roth's postulate are presented here. The experiments were performed in Bochum, and the calculations were carried out in Osaka and Los Angeles. As the cyclobutene ring-opening transition structure approaches planarity, the energy gap between allowed conrotatory and the forbidden disrotatory pathways decreases. For the ring-opening of a cyclobutene fused to norbornene, the energy gap between the forbidden and the allowed transition state is only 4.1 kcal/mol by CASSCF and 8.0 kcal/mol by CAS-MP2 as compared to 13.4 and 19.2 kcal/mol, respectively, for the parent cyclobutene. Experimental studies of 3,4-dimethylcyclobutenes fused to various ring systems are reported, and a trend is found toward a reduced allowed/forbidden gap as the planarity of the cyclobutene is enforced.

Introduction

The ring-opening of cyclobutene has been studied extensively both theoretically and experimentally as the prototype of thermal electrocyclic processes.[1−3] The four-electron electrocyclic ring-opening process is conrotatory under thermal conditions, where the termini rotate in the same direction in accord with the Woodward−Hoffmann rules (**1**).[1] The experimental $\Delta H^{\ddagger}$ for the electrocyclic opening of cyclobutene is 32.5 ± 0.5 kcal/mol, and the reaction is exothermic by 10.8 kcal/mol.[4] Cyclobutenes have played a major role in the understanding of such processes as torquoselectivity, the role of substituents on activation energies of clockwise and counterclockwise conrotatory ring-opening.[5,6]

The transition structures of the conrotatory (via **1**)[1−3] and disrotatory processes (via **2**)[7] have been elucidated in recent years. The allowed conrotatory cyclobutene ring-opening has a distinctly nonplanar carbon skeleton. Classic experiments by Brauman and Archie, and by Freedman et al., placed the allowed/forbidden gap at greater than 15 kcal/mol.

The late Wolfgang Roth proposed that a system forced to planarity might have a smaller preference for the conrotatory mode. The concept is as follows: as one destabilizes the conrotatory transition structure by minimizing the overlap between the σ orbital of the breaking bond and the π orbital which exists in the cyclobutene, the allowed−forbidden gap should decrease. This destabilization can be achieved by introducing constraints to force either the $H-C_1-C_2-H$ or the $C_4-C_1-C_2-C_3$ angle to approach 0°. This planarity constraint should play only a small role in the disrotatory process, because this process occurs through virtually a planar process. The primary overlap of the terminal orbitals of the conrotatory transition state is stabilizing, whereas this stabilization is decreased in the planar transition structure. Experimental work was undertaken under Roth's direction, and theoretical calculations were begun as a means to provide theoretical insights into

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|| Corresponding authors for CASSCF and CiLC-IRC calculations, experimental results, and overall interpretations, respectively.

⊥ Deceased, October 29, 1997.

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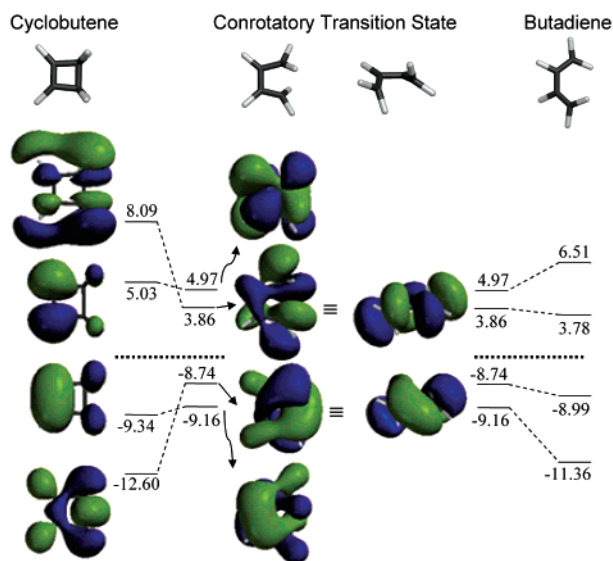
Figure 1. Orbital correlation diagram of cyclobutene and conrotatory transition state (HF/6-31G(d)). Correlations with butadiene π and π^* orbitals are also shown.

Scheme 1

Scheme 2. Newman Projections of Cyclobutene Ring-Opening TS and Several Constrained Geometries

Scheme 3

these processes. This work is the culmination of several decades of study and establishes the effect of planarity on the allowed−forbidden gap. Roth's hypothesis has been verified.

Background

Figure 1 illustrates an orbital correlation diagram of cyclobutene and the ring-opening transition state generated by HF/6-31G(d) calculations. This figure is an elaboration of the orbital correlations by Woodward and Hoffmann[1] and also by Longuet-Higgins and Abrahamson[8] that stereospecificity may be rationalized by correlations of the π and π^*, and the σ and σ^* orbitals of cyclobutene with the π and two π^* orbitals of butadiene. This correlation diagram has been also used to help explain torquoselectivity.[5,6,9] The conrotatory ring-opening, which retains C_2 symmetry throughout the reaction, correlates the σ bond of cyclobutene with the HOMO of the transition state. The HOMO of the transition state is essentially a distorted σ orbital of cyclobutene. Similarly, the σ^* orbital of the reactant correlates with the LUMO of the transition state.[10]

The ring-opening transition state occurs at the point where significant overlap of the breaking σ with the π^* orbitals and of the π with the σ^* begins, as illustrated in Scheme 2. Once the overlap is large, there is a rapid stabilization of the filled orbitals to give the product. Roth noted that if the cyclobutene were kept planar, this overlap would be quite small. If the resulting destabilization were large enough, then the allowed and forbidden transition states would have similar energies. The overlap decreases from the unconstrained transition state geometry to the H-planar geometry, which has constraints mentioned previously, and the overlap is the smallest in the all-planar geometry, as illustrated in Scheme 2.

The high stereospecificity associated with the conrotatory mode was confirmed by the pyrolysis of 3,4-dimethylcyclobutene by Brauman and Archie. They found approximately
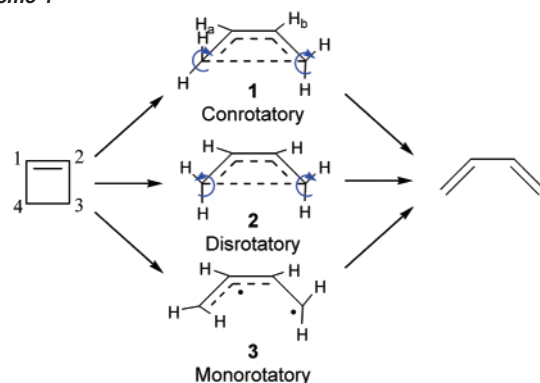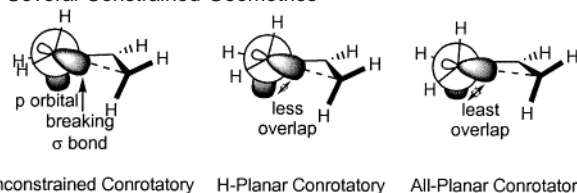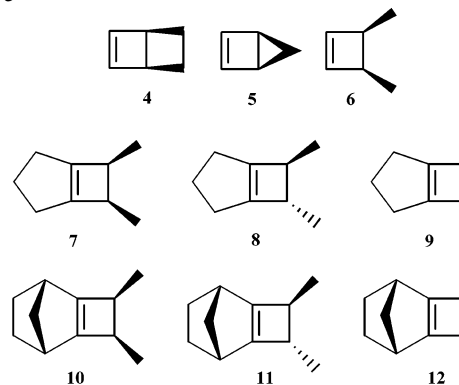
0.005% of the disallowed product, which equates to an allowed−forbidden gap of greater than 15 kcal/mol.[11] Freedman et al. found that *cis*-1,2,3,4-tetraphenylcyclobutene opens exclusively to the *cis,trans*-1,2,3,4-tetraphenylbutadiene, and the corresponding *trans*-cyclobutene opens exclusively to the *cis,cis*-butadiene.[12]

These studies and the overlap factors illustrated in Scheme 2 led Roth to propose that it is possible to destabilize **1** by inducing planarity on the dihedral angle of $H_a−C_1−C_2−H_b$ (Scheme 1). Closing the gap between the conrotatory and disrotatory pathways could be achieved by distorting the transition structure by inducing planarity on either $H_a−C_1−C_2−H_b$ or $C_4−C_1−C_2−C_3$. The cyclobutene ring-opening can, of course, be forced to proceed through the disrotatory pathway by fusing the ring such that a *cis*-bridge is introduced across $C_3−C_4$, as in **4** and **5**,[13] but this study involves systems **7−12**, where the constraints are at the double bond of cyclobutene instead (Scheme 3).

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There have been previous theoretical studies of the disrotatory cyclobutene ring-opening. Breulet and Schaefer utilized a two-configuration self-consistent field (TCSCF) ab initio calculation to characterize conrotatory and disrotatory stationary points.[14] They found that the conrotatory stationary point is a true transition state, whereas the disrotatory stationary point has two imaginary vibrational frequencies. This study was at the time an improvement of initial MINDO/3 calculations by Dewar and Kirschner who found a ground-state disrotatory transition state.[15] Robb et al. presented a detailed excited-state potential energy surface of butadiene using a multiconfigurational self-consistent field (MCSCF) and proposed that a disrotatory process proceeds through a conical intersection.[16] Buenker et al. have attempted to understand the role of ring torsion in the electrocyclic reaction of cyclobutene to butadiene and have found that the rotational phase of the process occurs over a narrow range of distance between C_3 and C_4.[17] Maier and Bothur also studied both theoretically (B3LYP/6-311G(d)) and experimentally the thermal and photochemical ring-openings of dichlorocyclobutenes.[18]

Only recently was the thermal disrotatory transition state for cyclobutene ring-opening found by Sakai with CASSCF calculations.[7] The forbidden pathway has an activation energy 19.5 kcal/mol higher than that of the allowed conrotatory pathway, according to MP2/CAS 6-311+G(d,p) calculations.[7]

The planarity effect on the allowed−forbidden gap was originally investigated experimentally by Roth and Hörstermann in 1979.[19] Houk and Kallel attempted theoretical studies of the system in the late 1980's, but they were unable to locate disrotatory transition states.[20] A collaborative manuscript between the Bochum and Los Angeles groups was begun at that time. Interest in these reactions recently resurfaced due to Sakai's successful location of transition states for disrotatory reactions of cyclobutenes and derivatives.[7] We have now combined modern computational work and the details of the original experimental study of the effect of planarity on the cyclobutene ring-opening transition states.

Results

Experimental. We summarize here the principal experimental results. Full experimental details are given in the Supporting Information.

1a. Synthesis of *cis*- and *trans*-6,7-Dimethylbicyclo[3.2.0]-hept-1(5)-ene (7 and 8). The target molecules were synthesized starting from ketone **13**, which was prepared in two steps from cyclopentanone according to Birkofer.[21] The reaction of 2-ethylidenecyclopentanone with the Wittig reagent prepared from ethyltriphenylphosphonium bromide and *n*-butyllithium gave a mixture of dienes **14** and **15** in a ratio of 1:7 in 15% yield. An analytical sample of the mixture was separated by preparatory gas chromatography, and the mixture of **14** and **15** was photocyclized without separation.[22] Under the reaction condi-

Scheme 4
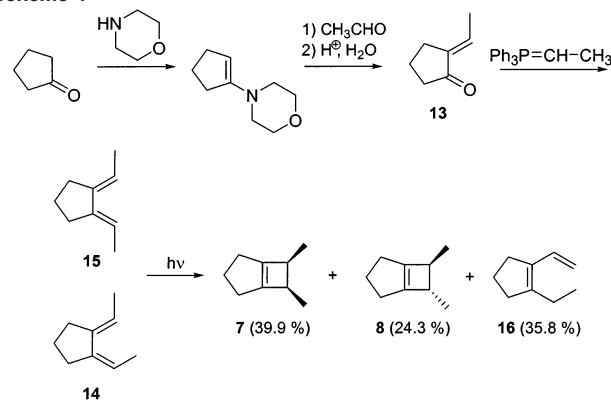
tions, a rapid equilibration to a ratio of **14**:**15** = 5:1 occurred. Further irradiation of the mixture gave three products which were separated by gas chromatography and identified as the expected cyclization products **7** and **8** and the diene **16** derived from **14** via a 1,5-hydrogen shift (Scheme 4).

The NMR spectrum of *cis*-6,7-dimethylbicyclo[3.2.0]hept-1(5)-ene (**7**) showed the doublet for the methyl groups at 1.0 ppm, whereas the corresponding signal of the *trans*-isomer **8** is shifted to a lower field (1.15 ppm). For the tertiary protons of the four-membered ring, the opposite effect is observed. The *cis*-product showed a multiplet at 2.9 ppm for the allylic protons separated from the other ring protons of the molecule. The corresponding signal of the *trans*-isomer overlaps with the other signals between 2.0 and 2.4 ppm. Similar effects have been observed with other systems having vicinal substituents such as 1,2-dimethylene-3,4-dimethylcyclobutane or 3,4-dimethyl-cyclobutene.[23] Furthermore, the stereochemistry can be properly assigned from the configuration of the products of the pyrolysis of **7** and **8**, respectively. Because the mode of the thermal ring-opening is clear (conrotatory), the main (allowed) product shows whether the starting material was cis or trans. Product **14** is derived from the *cis*-compound **7**, and **15** is derived from the *trans*-compound **8**. The stereochemistry of **14** (*Z,E*) and **15** (*E,E*) was assigned from the interpretation of their NMR spectra. The NMR of the unsymmetrical (*Z,E*)-compound **14** is more complex than the NMR of **15** (*E,E*).

1b. Thermal Ring-Opening of *cis*- and *trans*-6,7-Dimethylbicyclo[3.2.0]hept-1(5)-ene (7 and 8). For the investigation of the stereoselectivity of the ring-opening reaction, the isomeric cyclobutenes **7** and **8** were thermolized in the gas phase. To ensure the detection of the smallest amounts of the "forbidden" products, the starting materials for the thermolysis were purified by gas chromatography to an isomeric purity of >99.99%. The ring-opening of **7** was investigated at three temperatures between 125 and 200 °C. Besides the expected 1,2-diethylidenecyclopentanes **14** and **15**, diene **16** could be detected in various amounts depending on the reaction temperature. By thermolysis of pure **14** and **15**, it could be shown that only the *Z,E*-isomer (**14**) undergoes the H-shift reaction, whereas the *E,E*-isomer (**15**) was stable under the reaction conditions (Scheme 5). The results of the thermolyses are listed in Table 1.

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(20) Kallel, E. A.; Houk, K. N., unpublished and now obsolete results.
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Table 1. Products of the Thermolysis of **7**

		products		
reaction conditions	conversion [%]	**14** [%]	**15** [%]	**16** [%]
125 °C/120 min	45	98.76	0.27	0.97
160 °C/60 min	100	93.67	0.42	5.91
200 °C/60 min	100	33.15	0.61	66.25

Table 2. Products of the Thermolysis of **8**

		products		
reaction conditions	conversion [%]	**14** [%]	**15** [%]	**16** [%]
125 °C/30 min	100	0.05	99.95	
160 °C/10 min	100	0.06	99.94	
200 °C/10 min	100	0.03	99.93	0.04

Scheme 5
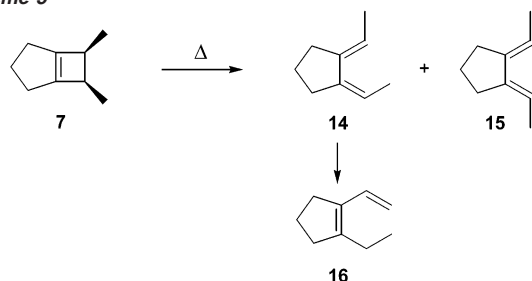
Scheme 6
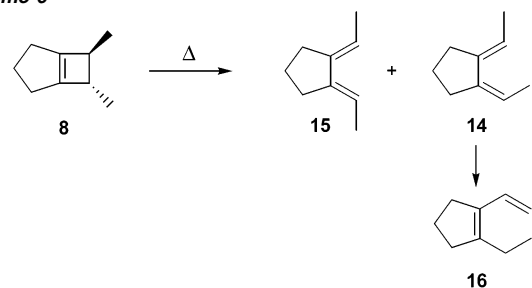
To eliminate any catalytic effects from the surface, the whole apparatus was silylated multiple times. However, no influence on the composition of the product mixture was observed in comparison to the nonsilylated apparatus, and the results do not appear to be influenced by secondary reactions. The average difference between free energies of activation can be calculated from the ratio of the products using eq 1, where k_1 is the sum of the products **14** and **15**, and k_2 is the percentage of **15**.

$$\Delta\Delta G^{\ddagger} = RT \ln(k_1/k_2) \qquad (1)$$

$$\Delta\Delta G_{160\,°C}^{\ddagger} = 4.7 \text{ kcal/mol}$$

The thermolysis of the *trans*-olefin **8** was performed under the same conditions used for the *cis*-isomer and gave identical products (Scheme 6 and Table 2).

The difference of the free energies of activation for allowed and forbidden paths was found to be $\Delta\Delta G_{160\,°C}^{\ddagger} = 6.4$ kcal/mol. The difference of 1.7 kcal/mol between the $\Delta\Delta G^{\ddagger}$ values can be explained by the steric hindrance of the methyl groups which assists the forbidden disrotatory reaction of the *cis*-isomer. A similar but opposite effect can be assumed for the allowed ring-opening, leading to an increased activation energy of the *cis*-diene **7** relative to the corresponding reaction of the

unsubstituted cyclobutene. The activation parameters of the electrocyclic ring-opening were determined to confirm this assumption.

1c. Kinetics of the Gas-Phase Thermolysis of *cis*- and *trans*-6,7-Dimethylbicyclo[3.2.0]hept-1(5)-ene (7 and 8). The thermolysis of the substituted cyclobutenes **7** and **8** was carried out in a hot air thermostat directly connected to a gas chromatograph. The reaction was monitored without condensation of the products for each analysis. The reaction rates were determined from the decrease of the starting material. The isomerization of the *cis*-dimethyl derivative, **7**, was monitored at six temperatures between 100 and 150 °C at a pressure of 1 Torr. Under these conditions, the reaction was first order.

The following activation parameters were obtained from the Arrhenius or Eyring plots (available in the Supporting Information): $E_a = 32.70 \pm 0.08$ kcal/mol, $A = (6.87 \pm 0.77) \times 10^{13}$/s, $\Delta H_{130\,°C}^{\ddagger} = 32.50$ kcal/mol, $\Delta S_{130\,°C}^{\ddagger} = 2.19$ cal/mol·K, and $\Delta G_{130\,°C}^{\ddagger} = 31.63$ kcal/mol.

The corresponding kinetics of the *trans*-dimethyl derivative **8** were investigated at eight temperatures between 60 and 135 °C, and the following activation parameters were obtained from the Arrhenius or Eyring plots: $E_a = 29.02 \pm 0.04$ kcal/mol, $A = (4.32 \pm 0.28) \times 10^{13}$/s, $\Delta H_{97\,°C}^{\ddagger} = 28.28$ kcal/mol, $\Delta S_{97\,°C}^{\ddagger} = 1.44$ cal/mol·K, and $\Delta G_{97\,°C}^{\ddagger} = 27.72$ kcal/mol.

The ring-opening of *cis*-6,7-dimethylbicyclo[3.2.0]hept-1(5)-ene (**7**) has a 1.4 kcal/mol higher activation energy than the 1,2-dimethylcyclobutene ring-opening and 4.9 kcal/mol higher activation energy than the parent cyclobutene ring-opening, whereas the activation energy of the *trans*-6,7-dimethylbicyclo[3.2.0]hept-1(5)-ene (**8**) ring-opening is decreased by 2.4 kcal/mol as compared to the 1,2-dimethylcyclobutene ring-opening. These results are consistent with analogous systems shown in Table 3. Trans substitution results in lower activation energies than cis substitution. In general, cis substitution results in an increase in activation energy as compared to the unsubstituted systems, except in benzocyclobutene ring-opening. This series is the only endothermic process of the systems listed in Table 3 due to the loss of aromaticity upon ring-opening. The methyl substitution stabilizes the transition state that results in loss of aromaticity, and therefore there is a drop in activation energy for the cis and trans substituted benzocyclobutene ring-opening as compared to the parent benzocyclobutene to *o*-xylylene process.

2a. Strain and Stereochemistry of the Thermal Isomerization of Tricyclo[4.2.1.0²·⁵]non-2(5)-ene (12) and the *cis*- and *trans*-3,4-Dimethyl Derivatives. The experiments described above show that bridging the 1,2 positions in bicyclo[3.2.0]hept-1(5)-ene (**9**) leads to a significant decrease of the activation barrier for the forbidden disrotatory ring-opening, but there is only little effect of ring strain on the activation energy in the case of the allowed conrotatory ring-opening. Another highly strained cyclobutene is the tricyclo[4.2.1.0²·⁵]non-2(5)-ene (**12**) described by Aue[28] which reacts to form 2,3-dimethylenebicyclo-

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Table 3. Activation Energies of the Ring-Opening of 3,4-Disubstituted Cyclobutenes

Reaction	E_a kcal/mol	references
	32.5	4
	36.0	24
	37.4	25
	33.6	25
	25.0	12
	21.0	12
	40.0	26
	36.9	27
	34.8	27
	31.6	31, 32
	32.7	this work
	29.0	this work

Scheme 7
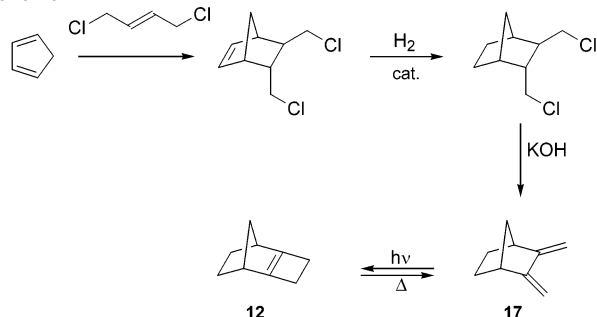
[2.2.1]heptane (**17**) (Scheme 7). We explored the strain in this system and the stereochemistry of ring-opening in substituted derivatives.

2b. Heat of Hydrogenation and Kinetics of the Gas-Phase Thermolysis of Tricyclo[4.2.1.0²·⁵]non-2(5)-ene (12). Lennartz found a heat of hydrogenation of 44.9 kcal/mol for **12**.[29] This

Table 4. Activation Energies of Strained Cyclobutenes

cyclobutene	relative ring strain (kcal/mol)	E_a (kcal/mol)	Reference
18	0	32.67	28, 27
9	11.26	31.57	28, 32
12	15.36	30.89	28, this paper

alkene is 4.1 kcal/mol more strained than **9**. Analogous to the results found with the bicyclo[3.2.0] system, the activation energy for the disrotatory ring-opening of **12** should be further decreased. On the other hand, there should be no net effect of the ring strain on the conrotatory ring-opening activation energy. The activation energy is expected to be approximately 31 kcal/mol. Aue had published an activation energy of only 26.6 kcal/mol for this system, but this experiment was carried out in solution and monitored by NMR spectroscopy. In solution, compound **12** tends to polymerize, so the activation barrier might not be reliable. Consequently, the ring-opening of **12** was explored in the gas phase. Dimerization products were ruled out because the gas chromatogram of the reaction mixture showed no byproducts. Work by Aue and Reynolds reports details of the problems with dimerization at the NMR concentrations used, and they conclude that the reaction has a barrier closer to 30.5 kcal/mol.[30]

Compound **12** was synthesized from the diene **17** by photochemical ring closure.[28] Compound **17** can be prepared easily by the Diels−Alder reaction of cyclopentadiene with (*E*)-1,4-dichlorobutene.[31] Because of the air-sensitivity of the olefin **12**, the workup of the crude reaction mixture was carried out under an argon atmosphere. The product was purified by preparative gas chromatography. Thermolysis of **12** was carried out at eight different temperatures between 92 and 165 °C in the same equipment used for the rearrangement of the olefins **7** and **8**.

The following activation parameters were taken from the Arrhenius and Eyring plots (available in the Supporting Information): $E_a = 30.89 \pm 0.08$ kcal/mol, $A = (2.57 \pm 0.30) \times 10^{13}$/s, $\Delta H_{128\,°C}^{\ddagger} = 30.08$ kcal/mol, $\Delta S_{128\,°C}^{\ddagger} = 0.25$ cal/mol·K, and $\Delta G_{128\,°C}^{\ddagger} = 29.98$ kcal/mol.

The activation energy of 30.9 kcal/mol in the gas phase is 4.3 kcal/mol higher than the activation energy determined by Aue in solution.[28] The E_a value found for the ring-opening of **12** supports the hypothesis that the activation energy for the conrotatory reaction depends very little on the ring strain of the cyclobutene, which is obtained by the difference in heat of hydrogenation of the compounds (Table 4).

3a. Synthesis of *cis*- and *trans*-3,4-Dimethyltricyclo-[4.2.1.0²·⁵]non-2(5)-ene (10 and 11). To determine the relative activation energies of the allowed and forbidden disrotatory ring-

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Scheme 8
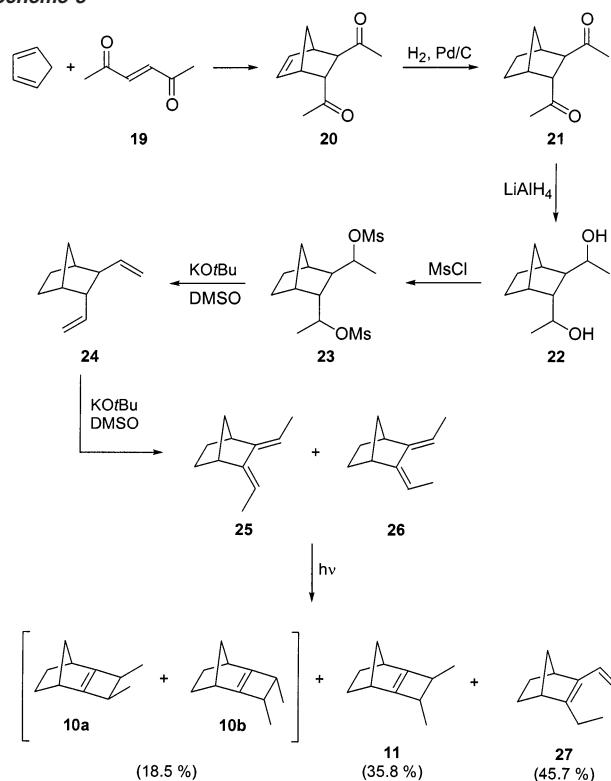
openings of the tricyclo[4.2.1.0$^{2.5}$]non-2(5)-ene system, the dimethyl derivatives **10a**, **10b**, and **11** were synthesized.

Compounds **10** and **11** were synthesized in seven steps starting from cyclopentadiene and (*E*)-hex-3-en-2,5-dione (**19**) as shown in Scheme 8. The Diels—Alder reaction of cyclopentadiene and **19** gave *trans*-5,6-diacetylbicyclo[2.2.1]hept-2-ene (**20**) in almost quantitative yield as a single product. Subsequent catalytic hydrogenation of **20** with Pd/C in glacial acetic acid led to *trans*-2,3-diacetylbicyclo[2.2.1]heptane (**21**) in 96% yield. Both the reduction of the diketone **21** using lithium aluminum hydride and the esterification of the resulting diol **22** with methanesulfonyl chloride to the corresponding bis-mesylate **23** gave yields higher than 95%. Elimination of **23** with potassium *tert*-butylate in dimethyl sulfoxide at temperatures below 40 °C gave the corresponding *trans*-2,3-divinylbicyclo[2.2.1]heptane **24** in ca. 80% yield. Treatment of **24** with potassium *tert*-butylate in dimethyl sulfoxide at 60 °C led to isomerization and gave a quantitative mixture of the dienes **25** and **26** in a ratio of 5:1.

Separation of the mixture of **25** and **26** on the preparative scale by gas chromatography was difficult, so a photocyclization was carried out using the 5:1 mixture. A solution of the mixture in pentane was irradiated at temperatures between −5 and 0 °C, and the reaction was monitored by gas chromatography. The cyclization of the dienes **25** and **26** was preceded by fast equilibration (**25**:**26** = 27:73) similar to the reaction of the 1,2-diethylidenecyclopentanes, **14** and **15**. The photoreaction gave three major products separated by gas chromatography and identified as compounds **10**, **11**, and **27** (Scheme 8).

The stereochemical assignment of the *cis*-product **10** to one of the two possible structures **10a** (exo) and **10b** (endo) by spectroscopic means was not possible. However, this is irrelevant for the following investigation as both compounds would give the same product (**26**).

Table 5. Thermolysis of the *cis*-Olefin **10**

reaction conditions	conversion [%]	products 25 [%]	26 [%]
140 °C/60 min	83	0.97	99.03
150 °C/30 min	91	1.08	98.92
150 °C/100 min	>99	1.04	98.96

Table 6. Thermolysis of the *trans*-Olefin **11**

reaction conditions	conversion [%]	products 25 [%]	26 [%]
93 °C/30 min	96	99.94	0.06
110 °C/25 min	100	99.92	0.08
125 °C/35 min	100	99.90	0.10

3b. Thermolysis of *cis*- and *trans*-3,4-Dimethyltricyclo-[4.2.1.0$^{2.5}$]non-2(5)-ene (10 and 11). The dienes **10** and **11** were purified by repeated gas chromatography to an isomeric purity greater than 99.98%. The thermal isomerization of the compounds was carried out at temperatures between 93 and 150 °C. The only products observed were the expected dienes **25** and **26**. To exclude isomerization of these dienes, both **25** and **26** were separately subjected to the thermolysis conditions. Both appear to be completely stable. The thermolysis of the *cis*-isomer **10** under different reaction conditions between 140 and 150 °C gave the product ratios shown in Table 5.

From these results, the free energy of activation for reaction of **10** is $\Delta\Delta G_{150\,°C}^{\ddagger} = 3.8$ kcal/mol. Thermolysis of the corresponding *trans*-isomer **11** at temperatures between 93 and 125 °C gave the results shown in Table 6.

In this case, the free energy of activation of **11** is $\Delta\Delta G_{110\,°C}^{\ddagger} = 5.4$ kcal/mol. Comparison of the $\Delta\Delta G^{\ddagger}$ values of **10** and **11** shows that the disrotatory ring-opening of the *cis*-isomer **10** is favored by 1.6 kcal/mol more than for the analogous reaction of the *trans*-isomer **11**. The effect is of the same magnitude as observed at the bicyclo[3.2.0]hept-1(5)-ene system and can be explained by steric interactions between the methyl groups of the *cis*-olefin **10**.

Theoretical. All of the systems studied experimentally were also studied theoretically. All stationary points were initially optimized with RHF with 3-21G and 6-31G(d) basis sets, then optimized again at the CASSCF and MP2 levels with the 6-31G-(d) basis set using the GAUSSIAN 98[33] and GAMESS[34] programs, respectively. For the CASSCF calculation, four active orbitals corresponding to two π and two π* orbitals of the butadienes were included. All configurations in the active space were generated. The force-constant matrix and vibrational frequencies were calculated with analytical second derivatives.

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Table 7. Products of Conrotatory and Disrotatory Ring-Opening of 3,4-Dimethylcyclobutenes and Derived Differences in Free Energies of Activation

	% con	% dis	$\Delta\Delta G^{\ddagger}$ (kcal/mol)	T (°C)
6	99.995	0.005	10.7	280
7	99.58	0.42	4.7	160
8	99.94	0.06	6.4	160
10	98.92	1.08	3.8	150
11	99.92	0.08	5.4	110

Additional calculations were performed to obtain improved energy comparisons: calculations with the CASSCF optimized structures with electron correlation incorporated through the multiconfigurational second-order Møller−Plesset perturbation theories (CAS-MP2) with the 6-31G(d) basis set. The intrinsic reaction coordinate (IRC) was followed from the transition state toward both reactants and products.

To interpret the reaction mechanisms of the conrotatory and disrotatory pathways, a configuration interaction localized molecular orbital CASSCF calculation along the intrinsic reaction coordinate (CiLC-IRC) was performed following a method described elsewhere:[35] (1) A four-orbital and four-electron CASSCF calculation is carried out to obtain a starting set of orbitals for the localization procedure. (2) After the CASSCF procedure is carried out, the CASSCF-optimized orbitals are localized by the Boys localization procedure.[36] The calculated localized orbitals are atomic in nature. (3) By using the localized MOs as a basis, we used a full CI with the determinant level to generate electronic structures and their weights in the atomic orbital-like wave functions. (4) The calculation procedures from (1) to (3) are repeated along the IRC path. The relative weights of the electronic configurations are used for the analysis of the reaction mechanisms. The CiLC-IRC calculations were also performed with the GAMESS program package.[34]

Discussion

Table 7 summarizes the temperature of pyrolysis and the ratios of products obtained for a series of 3,4-dimethylcyclobutenes (**6−8**, **10**, and **11**).[11,19] The major product of ring-opening is always the result of a conrotatory ring-opening, but variable amounts, up to 1% of the forbidden product, were observed. From the observed percentage of disrotatory product, it is possible to calculate a $\Delta\Delta G^{\ddagger}$ between the allowed conrotatory pathway and a pathway which gives the disrotatory product. For such systems, the disrotatory product could come from a concerted disrotatory path, or from a monorotatory pathway, either of which could produce a mixture of conrotatory and disrotatory stereochemistries. While the selectivities found earlier for the unconstrained cyclobutene, **6**, and the trans dimethyl compounds, **8** and **11**, are quite high in accord with expectation, the stereoselectivities found with **7** and **10** are low. Some other substituents may also tip the balance in favor of a stepwise or disrotatory mechanism. For example, the *cis*-dichloro analogue of **10** is estimated to have only a 2.5 kcal/mol preference for the conrotatory pathway.[10,39] To better understand the mechanism of the forbidden pathway, theoretical explorations of all of these systems were carried out.

Table 8. Computed Activation Energies (Relative Energies) of Conrotatory Cyclobutene Ring-Opening in kcal/mol

transition state	RHF/3-21G	RHF/6-31G(d)	MP2/6-31G(d)	CAS/6-31G(d)	CAS-MP2
unconstrained	41.6 (0.0)	46.9 (0.0)	37.6 (0.0)	36.6 (0.0)	40.4 (0.0)
H-planar	45.5 (3.9)	51.1 (4.2)	40.7 (3.1)	38.1 (1.5)	42.7 (2.3)
C-planar	50.8 (9.2)	55.7 (8.8)	45.2 (7.6)	40.5 (3.9)	46.2 (5.8)
all planar	56.7 (15.1)	62.4 (15.5)	50.8 (13.2)	42.6 (6.0)	49.3 (8.8)

Parent System. Table 8 lists the computed activation energies and relative energies for the unconstrained and several constrained cyclobutene ring-opening processes.[37] The constraints imposed are as follows. H-planar has a constrained $H_a-C_1-C_2-H_b$ dihedral angle of 0°. C-planar has a constrained $C_4-C_1-C_2-C_3$ dihedral angle of 0°. Finally, all-planar has both of the aforementioned dihedral angles constrained to 0°. The H-planar structure is destabilized by 3.1 kcal/mol as compared to the unconstrained system at MP2/6-31G(d) and 2.3 kcal/mol at CAS-MP2. Inducing C-planarity increases the activation energy by 7.6 kcal/mol as calculated by MP2/6-31G(d) and 5.8 kcal/mol by CAS-MP2. The all-planar activation barrier is destabilized by 13.2 kcal/mol for the MP2/6-31G(d) calculation and 8.8 for the CAS-MP2 calculation when compared to the unconstrained transition state.

These were compared with the disrotatory transition state and singlet diradical transition states. First, a singlet diradical was formed by 90° rotation of one terminal methylene assuming C_s symmetry and optimized with this constraint at the CAS calculation level, which is found to be a stationary point. The energy of this singlet diradical is only 1.7 or 7.2 kcal/mol above the conrotatory transition state at the CASSCF and CAS-MP2 levels, respectively. Another singlet diradical was formed by 90° rotation of both terminal methylenes assuming C_{2v} symmetry, at an angle of CCC = 124.7°, which is equal to the optimized angle of the above-mentioned singlet diradical with one terminal methylene constrained to 90°. The energy of the doubly constrained singlet diradical is 13.8 and 19.6 kcal/mol at the CASSCF and CAS-MP2 levels, respectively, above the conrotatory transition state, and is only 0.4 kcal/mol above the disrotatory transition state at both the CASSCF and the CAS-MP2 levels. Therefore, the disrotatory transition state is a biradical state as examined in a previous paper by the CiLC-IRC method with the configurational state function level.[35a] The electronic state of this disrotatory transition state will be discussed in a later section.

The geometries of the constrained cyclobutene openings are compared to the unconstrained ring-opening transition structure in Figure 2. In the unconstrained conrotatory ring-opening transition structure, the hydrogens at the C_1 and C_2 are out of plane, allowing for the p orbitals of these carbons to overlap with the breaking C_3-C_4 σ bond as illustrated previously in Scheme 2. The destabilization of the H-planar transition state is caused by the reduced overlap between these p and σ orbitals. The outward and inward rotating hydrogens increase their degrees of rotation ($\angle HC_4C_1C_2$) from 131° and −76° with the MP2 calculation (143° and −65° with the CASSCF calculation) in the unconstrained transition structure to 133° and −70° (146°

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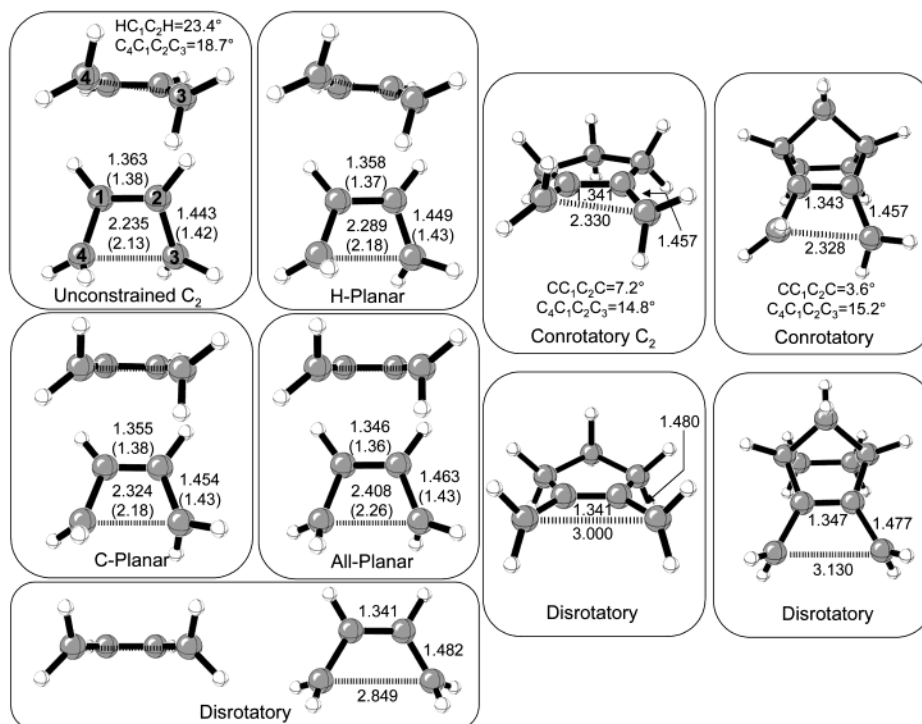
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Figure 2. Bond distances (Å) and angles of constrained cyclobutenes optimized by MP2 (CASSCF).

and −61°) in the H-planar structure (Figure 2). In the C-planar structure, a decrease in overlap of the breaking σ orbital with the π bond is achieved by even greater bending of the H's at C_1 and C_2 away from planarity. The dihedral angle of the hydrogens at C_1 and C_2 increases from 23° in the unconstrained transition structure to 26° in the C-planar structure. The outer and inner hydrogens now rotate to 136° and −71° at the MP2 (133° and −76° at CASSCF), respectively. The all-planar transition structure has the least overlap of the orbitals and exhibits the highest energy conrotatory ring-opening transition state. The breaking C−C bond is elongated to 2.26 Å at the MP2 and 2.41 Å with CASSCF. More rotation is seen in the outward and inward rotating hydrogens (138° and −67° at the MP2 (133° and −74° at the CASSCF), respectively) in the all-planar transition structure.

Transition Structure of Substituted Cyclobutenes. Forcing the bonds attached to alkene carbons C_1 and C_2 of the cyclobutene to be coplanar should narrow the gap between the biradical and the allowed transition state from 7.5−9.5 kcal/mol to 4−7 kcal/mol according to these model calculations. Substituents can also further narrow this gap. For example, Curry and Stevens have shown that the electrocyclic opening of *cis*-3,4-dimethylcyclobutene has a 1.5 kcal/mol higher activation energy than cyclobutene as a result of the stabilization by outward rotating methyl, but destabilization by inward rotation.[38] Consequently, a *cis*-3,4-dimethyl and planar-constrained structures, such as **7** and **10**, should have conrotatory transition structures destabilized by a sum of 4.6 kcal/mol using the MP2 calculation and experimental values, which results from 3.1 kcal/mol (for H-planar constraint) and 1.5 kcal/mol (for cis dimethyl substitution). The stabilization resulting from substitution of a methyl group on a primary radical center is 3.3 kcal/mol.[39] The other biradical center becomes a secondary terminus of an allyl radical, which should be stabilized by about 1.7 kcal/mol. Because of the similar destabilizing and stabilizing factors, this

Table 9. Activation Energies of Conrotatory and Disrotatory Electrocyclic Ring-Opening Reactions (kcal/mol)

	conrotatory		disrotatory		energy gap		ΔH_{rxn}	
	CAS	CAS-MP2	CAS	CAS-MP2	CAS	CAS-MP2	CAS	CAS-MP2
cyclobutene	36.6	40.4	50.0	59.7	13.4	19.2	16.0	8.9
9 (C_2)	33.0	38.9	38.3	48.2	5.4	9.2	28.0	20.7
9 (C_1)	32.7	38.4						
12 (C_1)	31.7	37.2	35.9	45.2	4.1	8.1	36.7	29.4

would make the conrotatory and monorotatory pathways about the same in energy. Consequently, some "forbidden" product could be produced through the biradical pathway. The trans isomers **8** and **11** should still have a 4.0 kcal/mol allowed mechanistic advantage.

The activation energies of ring-opening reactions of cyclobutene (**1** and **2**), bicyclo[3.2.0]hept-1(5)-ene (**9**), and tricyclo[4.2.1.02,5]non-2(5)-ene (**12**) are listed in Table 9. The geometries of stationary points were calculated by the CAS-(4,4)/6-31G(d) level. The disrotatory transition states of these compounds have two negative eigenvalues for their force-constant matrix. The eigenvector of one negative eigenvalue corresponds to the reaction coordinate, and the other corresponds to an a′ symmetry coordinate. The second-order saddle point of **9** with C_2 symmetry has two negative eigenvalues in the force constant matrix. By reducing the symmetry to C_1, we obtained the real transition state. The energy of the transition state with C_1 symmetry is only 0.5 kcal/mol lower that that with C_2 symmetry.

The conrotatory stationary state of **9** with C_2 symmetry is 1.5 kcal/mol more stable than **1** at the CAS-MP2 calculation level. On the other hand, the disrotatory ring-opening of **9** has an activation energy that is 11.5 kcal/mol more stable than that for **2**. The energy of reaction of **9** is −20.7 kcal/mol according to the CAS-MP2 calculation and is 11.8 kcal/mol more exothermic than that for cyclobutene. The similar activation
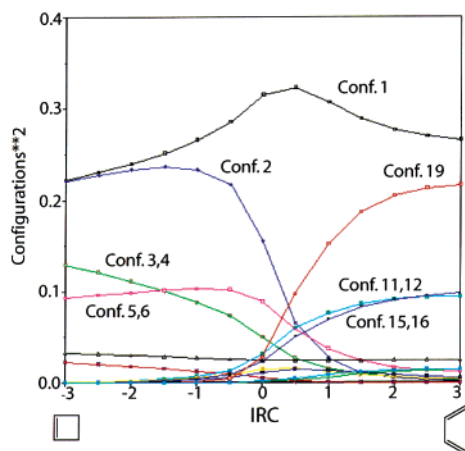
Figure 3. Square of CI coefficients of the CiLC-IRC along the conrotatory pathway of butadiene.

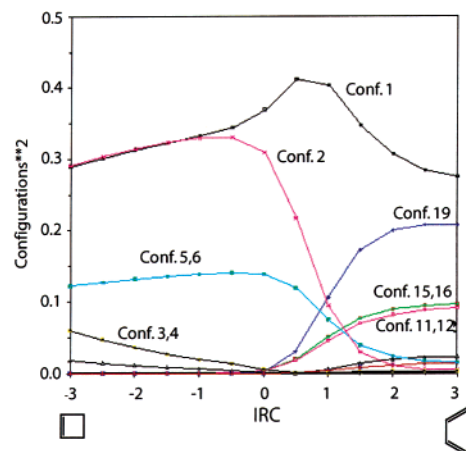**Figure 4.** Square of CI coefficients of the CiLC-IRC along the disrotatory pathway of butadiene.

energy of the disrotatory pathway and the energy of reaction between **9** and the parent system suggest that there is only a small effect on the disrotatory pathway when planarity is introduced to the system and that only the conrotatory pathway is affected by this distortion.

The conrotatory pathway activation energy of **12** is 1.2 kcal/mol more stable than that of **9** with C_1 symmetry. The disrotatory activation energy of **12** is 3.0 kcal/mol lower than that of **9**. The ring-opening process of **12** is 8.7 kcal/mol more exothermic than that of **9**. The energy difference of the disrotatory pathway between **12** and **9** is smaller than the difference between **2** and **9**. This suggests that the mechanism of the disrotatory pathway of **12** may be different from that of **9** and/or **2**. These mechanisms will be discussed in a subsequent section.

To investigate the constraints imposed on the system, we compare the transition structures for the conrotatory electrocyclic openings of **9** and **12**. These transition structures are shown in Figure 2. The $C-C_1-C_2-C$ torsion angle of the cyclopentene fused system is 7.2° in the transition structure for **9**, as compared to 23.4° in the unconstrained transition structures. Fusion to norbornene reduces this dihedral angle to 3.6°. The 3.8 kcal/mol $\Delta\Delta G^{\ddagger}$ conrotatory preference for **10** is somewhat lower than expected, which may indicate that there is a small barrier to formation of the biradical analogue to **3** and hence the thermodynamically more stable, disrotatory product.

CiLC-IRC Analysis. To study the mechanisms for the electrocyclic reactions of butadiene, **9** and **12**, the CiLC-IRC analysis was performed for the conrotatory and the disrotatory pathways of three of the molecules studied here. This method examines the nature of the electronic state along the path from cyclobutene to butadiene. The relative weights of the electronic configurations along the IRC pathways for the parent system are shown in Figures 3 and 4. The results for **9** and **12** are given in the Supporting Information. The most important electronic configurations in these figures are depicted in Figure 5. In Figure 5, a dotted line denotes a triplet coupling (antibonding) between the orbitals, and an ellipse denotes an ionic coupling (polarization). As shown previously,[7,35] a chemical bond can be described as the singlet coupling between two orbitals plus two polarization terms as shown in Figure 6.

Configuration 19 represents the singlet coupling part of the π orbitals for C_1-C_4 and C_2-C_3, or could be described as the
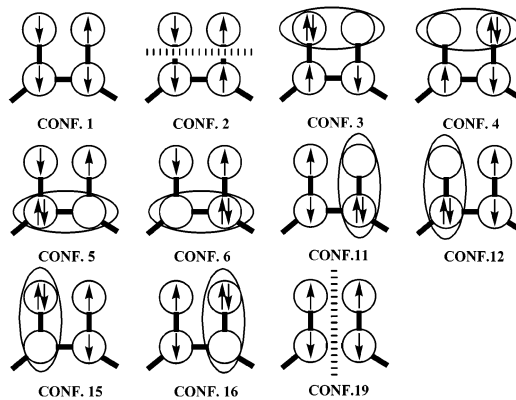
Figure 5. Some electronic configurations of the reaction pathway.

Figure 6. Coupling and polarization representations.

$C_1=C_4$ and $C_2=C_3$ double bonds (Figure 5). As shown in Figure 3, the square of the coefficient for this configuration increases dramatically as cyclobutene opens to butadiene. Each configuration set of 12 and 15 and 11 and 16 represent the polarization parts of the π orbitals for C_1-C_4 and C_2-C_3, respectively. Therefore, two sets of configurations, {19, 12, 15} and {19, 11, 16}, can be described as the π bonds for C_1-C_4 and C_2-C_3, respectively. Configuration 2 can be described as the $C_1=C_2$ double bond and C_3-C_4 σ bond. Therefore, the configuration sets {2, 5, 6} and {2, 3, 4} can be described as the π bond for C_1-C_2 and the σ bond for C_3-C_4. For the ring-opening of cyclobutene, Figures 3 and 4 show that the π bonds for C_1-C_4 and C_2-C_3 (primarily configuration 19) increase smoothly from the cyclobutene side to the transition state, and the π bond for C_1-C_2 and the σ bond for C_3-C_4 (primarily configuration 2) decreases from the cyclobutene to the butadiene. The relative weights of these bonds cross at a point on the butadiene side of the transition state. The "electronic transition state", reflected in this crossing, occurs after the "energetic transition state", which has the highest energy barrier on the reaction pathway.

For the comparison of the conrotatory and disrotatory pathways, the exchange of old π bonds of C_1-C_4 and C_2-C_3 with the new σ bond of C_3-C_4 occurs in a "concerted" fashion

for the conrotatory pathway and a "stepwise" fashion for the disrotatory pathway. For the conrotatory pathway, the relative weights of configurations 3 and 4, which are the polarization terms of σ bond for C_3-C_4, fade out after the appearance of the C_1-C_4 and C_2-C_3 π-bonds of butadiene. On the other hand, the relative weights of configurations of the π bonds for C_1-C_4 and C_2-C_3 and the polarization terms of σ bond for C_3-C_4 are almost zero at the transition state for the disrotatory pathway. The mechanisms for conrotatory and disrotatory pathways of **9** and **12** were analyzed in the same way (see the Supporting Information for correlation diagrams).

Conclusion

This study supports both experimentally and theoretically that the allowed−forbidden gap of cyclobutene ring-opening is dependent on the planarity of the ring-opening transition structure, as initially proposed by Roth and Hörstermann in the late 1970s. As planarity is introduced for the conrotatory transition structure for *cis*-3,4-dimethylcyclobutene fused to either norbornene or cyclopentene, the energy gap between the allowed and forbidden pathway is reduced. The reduction in energy difference between the allowed and forbidden processes is evidenced by the experimental $\Delta\Delta G^{\ddagger}$ obtained from the amount of disrotatory products formed: 3.8 kcal/mol for **10** and 4.7 kcal/mol for **7**, a reduction from 10.7 kcal/mol from the *cis*-3,4-dimethylcyclobutene studied by Brauman and Archie.[11] These experimental values are further supported by the activation energies obtained by CAS calculations for the unmethylated systems (4.1 kcal/mol for **12** and 5.4 kcal/mol for **9**). The decrease in the energy gap between the allowed and forbidden pathway is attributed to the decrease in favorable orbital interaction between both the σ and π^* orbitals and the π and σ^* orbitals in the conrotatory transition state upon introduction of planar constraints. The Roth hypothesis explains how the large energy of concert in the electrocyclic ring-opening of cyclobutene can be eroded by geometric constraints. In general, skeletal structures that prevent the transition state from achieving the cyclic delocalization that is intrinsic to pericyclic transitions states[40] will reduce, or even eliminate, the energy of concert of a pericyclic reaction.

Supporting Information Available: Cartesian coordinates of transition structures of the parent system, cyclopentyl, and norbornyl fused systems optimized by CASSCF and MP2. List of experimental techniques, NMR and IR data for intermediates and products, Arrhenius plots, and CiLC-IRC analysis for conrotatory and disrotatory ring-opening of cyclobutene fused to cyclopentane and norbornene (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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