J. Phys. Chem. A **2007,** *111,* 734−742

Computational Investigation of the Conrotatory and Disrotatory Isomerization Channels of Bicyclo[1.1.0]butane to Buta-1,3-diene: A Completely Renormalized Coupled-Cluster Study

Armağan Kinal[†] and Piotr Piecuch*[,‡]

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received: September 4, 2006; In Final Form: November 4, 2006

The conrotatory and disrotatory mechanisms of the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene have been computationally investigated with the CASSCF, MCQDPT2, (U)B3LYP, CCSD(T), CR-CCSD(T), and CR-CC(2,3) approaches. The coupled-cluster (CC) methods, including the CC approach with singles, doubles, and noniterative triples (CCSD(T)), and its completely renormalized (CR) extensions called CR-CCSD(T) and CR-CC(2,3), and the density functional theory B3LYP approach do an excellent job of correctly predicting the activation barrier for the conrotatory pathway, which corresponds to a weakly biradical transition state (TS), producing values within experimental error bars. In particular, the recently developed CR-CC(2,3) method gives 40.8 or 41.1 kcal/mol, in perfect agreement with the experimental value of 40.6 ± 2.5 kcal/mol. The complete-active-space self-consistent-field (CASSCF) approach and the second-order multireference perturbation theory (MCQDPT2) are less accurate in describing the conrotatory barrier than CR-CC(2,3). The higher energy disrotatory pathway, which has not been characterized experimentally and which involves a strongly biradical TS, poses a great challenge for many methods. CCSD(T) fails, predicting the activation barrier for the disrotatory pathway significantly below the conrotatory barrier, contradicting the experimental result that the conrotatory pathway describes the mechanism. The strongly biradical character of the disrotatory TS, spin contamination, and the proximity of singlet and triplet potential energy surfaces cause difficulties for B3LYP, which does not link this TS with *gauche*-buta-1,3-diene. No such difficulties occur in the CASSCF calculations, which offer a proper description of the structure of the disrotatory TS that links it with the reactant and product molecules. The CR-CC(2,3) approach, which accurately balances dynamical and nondynamical correlations in systems containing closed-shell and biradical structures, predicts the activation enthalpy for the disrotatory mechanism of ∼66 kcal/mol. CR-CCSD(T) gives ∼69 kcal/mol. In agreement with experiment and earlier multireference configuration interaction calculations of Nguyen and Gordon, CR-CCSD(T) and CR-CC(2,3) favor the conrotatory mechanism. The CASSCF, MCQDPT2, and B3LYP methods correctly place the disrotatory barrier above the conrotatory one, but, on the basis of a comparison with the accurate CR-CC(2,3) results, they underestimate the activation energy for the disrotatory pathway. All CC approaches employed in this study produce very good estimates of the enthalpy of isomerization of bicyclo[1.1.0]butane into buta-1,3-diene, the experimental value of which is −25.9 ± 0.4 kcal/mol, giving about −28 kcal/mol, when *trans*-buta-1,3-diene is used as a product, and −25 kcal/mol, when the nearly isoenergetic *gauche*-buta-1,3-diene rotamer is used as a product. The CC reaction enthalpies are more accurate than those obtained with CASSCF, MCQDPT2, and B3LYP.

Introduction

The experiments[1] on the thermal pericyclic rearrangement of bicyclo[1.1.0]butane (bicbut) to *trans*-buta-1,3-diene (*t*-but), a prototype for the thermal reactions of bicyclobutane derivatives, were conducted in the late 1960s. They revealed that bicyclobutane undergoes a concerted process with its two methylene groups moving in a conrotatory manner,[1d,e] which agrees with the Woodward−Hoffmann orbital symmetry rules.[2] Over the next decades, several theoretical studies,[3] in which the concerted conrotatory and disrotatory paths[3b,c] (Scheme 1a) as well as the nonconcerted biradical process[3a] (Scheme 1b) were considered as possible mechanisms, had been performed. In particular, the expert multireference configuration interaction (MRCI) and second-order multireference perturbation theory (MRPT; specifically, PT2F) calculations by Nguyen and Gordon[3c] predicted that the concerted conrotatory process is the lowest energy pathway with an activation barrier of 41.5 kcal/mol, in excellent agreement with the experimental value of 40.6 ± 2.5 kcal/mol.[1a] They also showed that the orbital symmetry forbidden disrotatory path has a transition state (TS), dis_TS, located about 15 kcal/mol above the TS of the conrotatory path (con_TS), and that the nonconcerted biradical pathway, which was supported by the early semiempirical calculations,[3a] is much too high in energy to be considered as a plausible mechanism.

One of the interesting issues related to the bicbut → *t*-but isomerization reaction is the relative accuracy of the computed activation barriers characterizing the conrotatory and disrotatory mechanisms. In particular, because of a different nature of the species involved in the conrotatory and disrotatory pathways, the fact that a given method produces a very good agreement with experiment for the conrotatory path does not guarantee

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* To whom correspondence should be addressed. E-mail: piecuch@chemistry.msu.edu; www.cem.msu.edu/∼piecuch/group_web (internet).

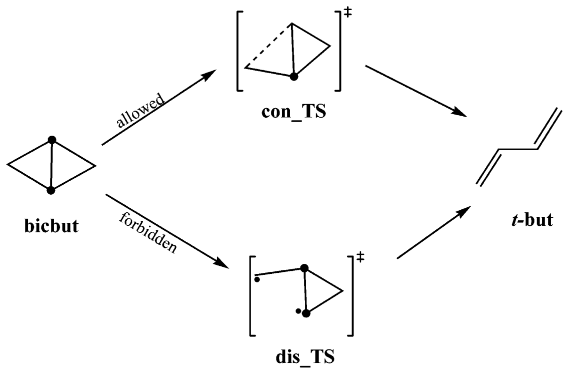
[†] NATO/TUBITAK Science Fellow.

[‡] Also at: Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824.

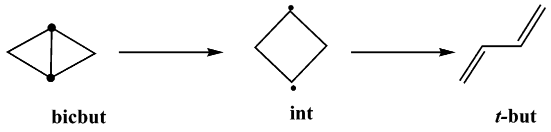
10.1021/jp065721k CCC: $37.00

SCHEME 1

a. Concerted Conrotatory and Concerted Disrotatory Mechanisms



b. Nonconcerted Biradical Mechanism



that the analogous results for the disrotatory process are of similar quality, particularly that no experimental data are available for the disrotatory pathway. As shown in this paper, this remark applies to several electronic structure methods.

The problem is that, unlike the conrotatory pathway that involves a TS with a largely closed-shell character, the TS for the disrotatory path is practically a pure biradical, and it is well-known that the investigation of reaction mechanisms involving species with varying degrees of biradical character is a major challenge for many quantum chemical methods. Due to the multireference nature of the wave function characterizing biradical species, the standard single-reference approaches have severe difficulties with describing reaction mechanisms involving biradical TSs and intermediates. For instance, the commonly used single-reference coupled-cluster (CC) approach with singles, doubles, and noniterative triples (CCSD(T)),[4] which provides an accurate description of closed-shell molecules such as bicbut and *t*-but, fails dramatically for biradical species.[5] One can certainly improve the description of biradicals by making use of multireference methods, such as MCSCF or CASSCF (multiconfigurational or complete-active-space self-consistent-field), MRCI, and various types of MRPT, which are all designed to handle large nondynamical correlation effects present in biradical systems. Unfortunately, these methods may be insufficiently accurate in cases involving stronger dynamical correlation effects that dominate closed-shell systems. As a result, they may provide a less accurate description of the closed-shell reactant and product molecules relative to the biradical structures along the reaction pathway and this may lead to an artificial overestimation of the stability of the biradical species relative to the reactants and products. An extreme example of the difficulties the MCSCF (CASSCF) and MRPT methods have with balancing the dynamical and nondynamical correlation effects and a varying degree of biradical character along the reaction coordinate can be found in refs 5d,e. An alternative to the above ab initio methods is the density functional theory B3LYP hybrid approach,[6] which is often regarded as an inexpensive computational technique for examining the relative energetics of biradicals and the corresponding closed-shell species.[7] Unfortunately, for stronger biradicals the unrestricted B3LYP (UB3LYP) method may fail to produce accurate results, which is a result of the presence of the Hartree−Fock exchange in the B3LYP hybrid functional.[5d,8] To overcome the above difficulties and successfully describe reaction mechanisms involving biradical species, such as the disrotatory pathway of the bicbut → *t*-but isomerization reaction, one must use computational methods that can accurately balance dynamical and nondynamical correlation effects. It has recently been shown[5] that in spite of their formally single-reference character, the completely renormalized CC (CR-CC) methods,[9−11] including, in particular, the recently developed, rigorously size extensive CR-CC(2,3) approach,[11] satisfy this condition, at least when the biradical TSs and intermediates are involved, and so are among the most promising candidates for studying reaction mechanisms where the degree of biradical character of the electronic wave function changes along the reaction coordinate.

In this work, we apply the CR-CC, i.e., the original CR-CCSD(T)[9,10] and the newest CR-CC(2,3)[11] methods, to the conrotatory and disrotatory isomerization channels of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene, largely focusing on the relevant activation and reaction energies. We compare the CR-CCSD(T) and CR-CC(2,3) results with those produced by CASSCF,[12] the MCQDPT2[13] variant of MRPT, (U)B3LYP, and CCSD(T), and the available experimental data for the reaction enthalpy and conrotatory activation barrier. The analysis of the higher energy disrotatory pathway, which has not been characterized experimentally, is based on comparing the computational methods among themselves. This includes all of the methods listed above and the MRCI and PT2F results reported in ref 3c. As shown in this work, the easy-to-use, single-reference CR-CC approaches, particularly CR-CC(2,3), produce highly accurate activation and reaction energies, which very well agree with the available experimental data and which are overall better than the results of the multireference CASSCF and MCQDPT2 calculations. We also show that the CR-CCSD(T) and CR-CC(2,3) methods eliminate the dramatic failure of CCSD(T), which favors the disrotatory mechanism in spite of the fact that the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene is a conrotatory process. In agreement with experiment and multireference calculations, the single-reference CR-CCSD(T) and CR-CC(2,3) methods favor the conrotatory mechanism.

Computational Methods

The stationary points defining the conrotatory and disrotatory pathways that describe the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene, along with the energetics resulting from our best CR-CC(2,3) calculations and the available experimental data, are shown in Figure 1. Both pathways begin at bicbut, and, after passing through the corresponding conrotatory and disrotatory TSs (the con_TS and dis_TS structures, respectively) converge at the local minimum defining the gauche form of buta-1,3-diene (designated as *g*-but). The *gauche*-buta-1,3-diene system isomerizes via a low-energy rotational barrier, defined by the TS structure labeled in Figure 1 as *gt*_TS, to give the final reaction product, *t*-but.

All of the species involved in the conrotatory and disrotatory mechanisms (bicbut, *g*-but, *t*-but, con_TS, dis_TS, and *gt*_TS) were optimized by employing the 10-electron, 10-orbital (10,10) CASSCF method and the cc-pVDZ basis set.[14] To account for all changes in the bicyclobutane ring system along the conrotatory and disrotatory reaction pathways, five doubly occupied molecular orbitals (MOs) correlating with the C1−C2, C1−C3, C2−C3, C2−C4, and C3−C4 σ bonds and the corresponding antibonding MOs were used to construct the relevant active space (the atom numbering is available in Figure

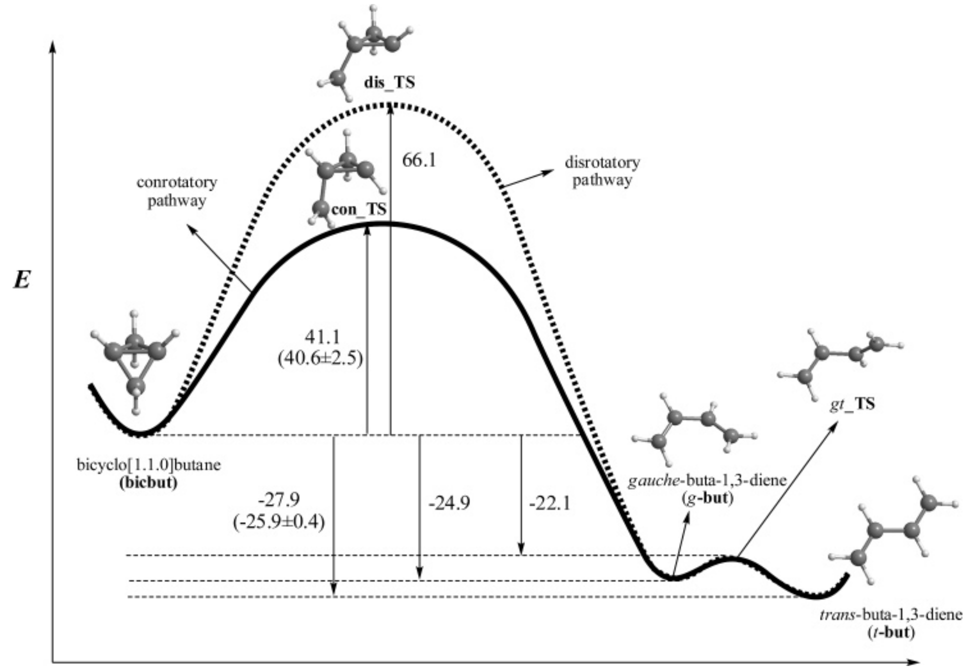


Figure 1. Conrotatory and disrotatory pathways describing the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene, along with the enthalpy values relative to the reactant for the relevant stationary points resulting from the CR-CC(2,3)/cc-pVTZ//CASSCF(10,10)/cc-pVDZ calculations (in kilocalories per mole). The available experimental enthalpies, also in kilocalories per mole, are given in parentheses.

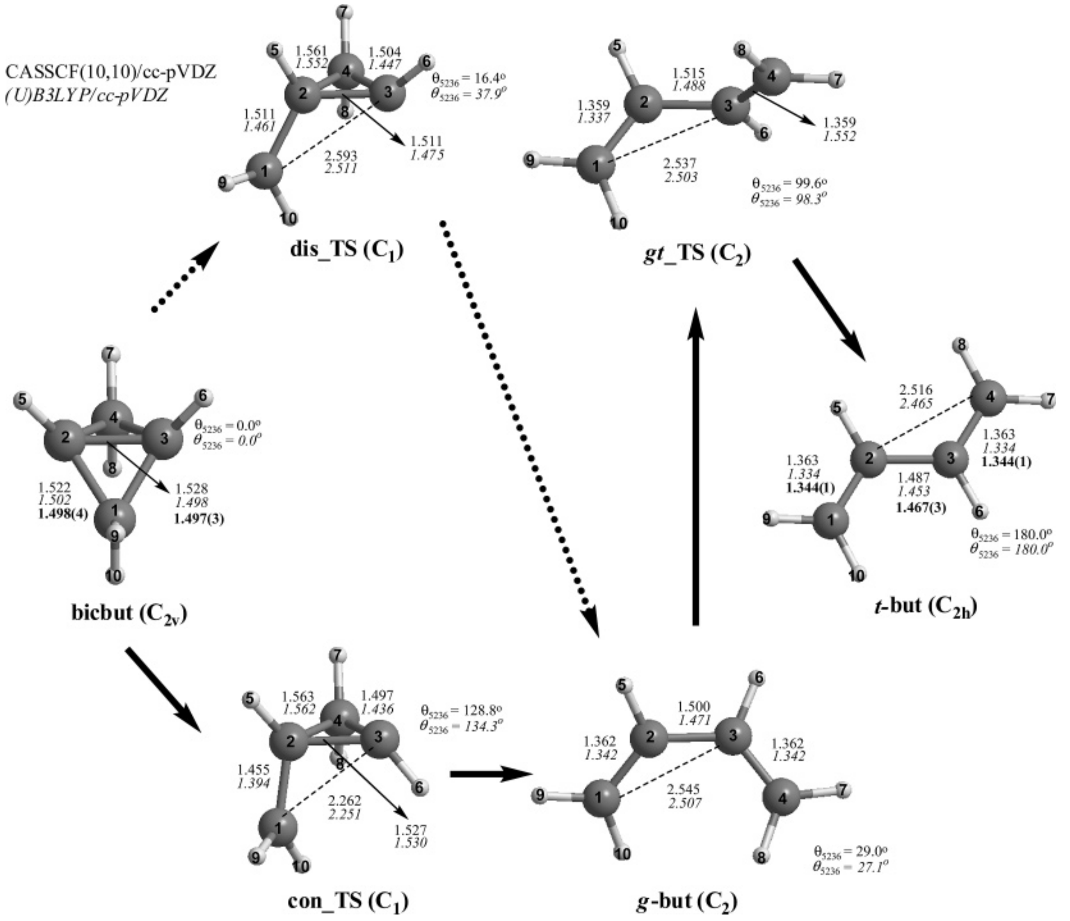


Figure 2. Selected geometrical parameters for the stationary points along the conrotatory and disrotatory pathways characterizing the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene resulting from the CASSCF(10,10)/cc-pVDZ (the Roman font) and (U)B3LYP/cc-pVDZ (the Italic font) levels of theory. The boldface values indicate the available experimental parameters. Distances are in angstroms, and angles are in degrees.

2). The nature of each species (a minimum or a TS) was examined by exploiting the usual harmonic vibrational frequency analysis. The intrinsic reaction coordinate (IRC) calculations[15] were carried out at the CASSCF(10,10)/cc-pVDZ level to verify that the TSs identified in geometry optimizations connect the correct minima on the potential energy surface (PES) shown in

TABLE 1: Electronic Energies Corrected for ZPVEs[a] (i.e., Enthalpies at 0 K) of the Conrotatory and Disrotatory TSs, con_TS and dis_TS, Respectively, the *g*-but Intermediate Product, the TS Connecting *g*-but and *t*-but (*gt*_TS), and the *t*-but Final Product, Relative to the bicbut Reactant, at Several Levels of Theory

method	con_TS	dis_TS	*g*-but	*gt*-TS	*t*-but
(U)B3LYP/cc-pVDZ	41.5	49.8	−26.3	−22.8	−29.9
CCSD(T)/cc-pVTZ//(U)B3LYP/cc-pVDZ	40.2	b	−24.7	−22.0	−27.6
CR-CCSD(T)/cc-pVTZ//(U)B3LYP/cc-pVDZ	42.4	b	−24.5	−21.9	−27.4
CR-CC(2,3)/cc-pVTZ//(U)B3LYP/cc-pVDZ	40.8	b	−24.6	−21.9	−27.5
CASSCF(10,10)/cc-pVDZ	38.5	52.0	−39.7	−37.2	−42.6
MCQDPT2/cc-pVDZ//CASSCF(10,10)/cc-pVDZ	37.0	53.7	−26.4	−23.4	−29.4
(U)B3LYP/cc-pVTZ//CASSCF(10,10)/cc-pVDZ	41.6	51.1	−28.2	−24.9	−31.8
CCSD(T)/cc-pVTZ//CASSCF(10,10)/cc-pVDZ	40.4	21.8	−25.1	−22.3	−28.0
CR-CCSD(T)/cc-pVTZ//CASSCF(10,10)/cc-pVDZ	42.8	68.8	−24.8	−22.1	−27.7
CR-CC(2,3)/cc-pVTZ//CASSCF(10,10)/cc-pVDZ	41.1	66.1	−24.9	−22.1	−27.9
$\langle S^2 \rangle^c$	0.12	0.96	0.00	0.00	0.00
% biradical character[d]	24	90	9	8	9
experiment	40.6 ± 2.5[e]				−25.9 ± 0.4[f]

[a] ZPVEs were calculated at the same levels of theory as those used in geometry optimizations. [b] Not calculated since, as explained in the text, the UB3LYP description of dis_TS is highly problematic. [c] Obtained at the UB3LYP/cc-pVDZ level. [d] Obtained at the CASSCF(10,10)/cc-pVDZ level. The bicbut reactant has a biradical character of 4%. [e] Reference 1a. [f] The reaction enthalpy at 298 K based on the enthalpies of formation of bicyclo[1.1.0]butane and buta-1,3-diene reported in ref 19.

Figure 1. To incorporate the dynamical electron correlation effects, which cannot be recovered by the CASSCF(10,10) approach, the single-point MCQDPT2 calculations employing the same basis set, i.e., cc-pVDZ, and the same active space, i.e., (10,10), as used in the CASSCF calculations were carried out.

To assess the applicability of the (U)B3LYP method to the conrotatory and disrotatory pathways describing the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene, the stationary points on the PES found with the CASSCF approach were reoptimized and characterized at the (U)B3LYP/cc-pVDZ level of theory. The IRC calculations were performed at this level as well. They revealed that the conrotatory TS, designated as con_TS, connects the bicbut reactant and the *g*-but intermediate species in a correct manner. However, the disrotatory TS, dis_TS, obtained with UB3LYP connects bicbut to a local minimum structure resembling con_TS rather than linking bicbut and *g*-but, as shown in Figure 1. Part of the problem is that the dis_TS species has a 90% biradical character [following ref 16, the degree of biradical character is defined in this paper as $(2 - n_H) \times 100$, where n_H is the occupation number of the natural orbital corresponding to the highest occupied molecular orbital (HOMO) level calculated with the CASSCF(10,10)/cc-pVDZ approach]. The singlet UB3LYP/cc-pVDZ calculations for the dis_TS structure produce an $\langle S^2 \rangle$ value of 0.96, which is also indicative of its strong biradical character. This huge spin contamination suggests that dis_TS may possess a low-lying triplet state, which is close in energy to (or even degenerate with) the singlet state, potentially complicating the situation. To get further insights and address this issue, in addition to the aforementioned singlet optimizations, the triplet-state CASSCF and UB3LYP optimizations were performed to determine the geometries and energies of the low-lying triplet-state species corresponding to the dis_TS and con_TS structures (see the next section for discussion).

An accurate account of the electron correlation effects is essential for obtaining reliable energies. For polyatomic systems, this is often achieved through the use of higher level ab initio methods and, if affordable, larger basis sets than those employed during geometry optimizations. To improve the description of electron correlation effects, particularly the dynamical correlations, in addition to the aforementioned MCQDPT2 calculations, the single-point energy calculations at the CASSCF(10,10)/cc-pVDZ and (U)B3LYP/cc-pVDZ optimized geometries were performed with the CCSD(T),[4] CR-CCSD(T),[9,10] and CR-CC(2,3)[11] methods and the larger cc-pVTZ basis set.[14] As pointed out in the Introduction, the latter two approaches, particularly CR-CC(2,3), provide a highly accurate and balanced description of dynamical and nondynamical correlation effects in systems containing biradical and closed-shell structures.

The GAMESS package[17] has been utilized in all computations, except for the (U)B3LYP calculations, which were carried out using GAUSSIAN 98.[18] In particular, the CCSD(T), CR-CCSD(T), and CR-CC(2,3) calculations were performed with the CC routines and algorithms described in refs 9b, g and 11a, which are part of GAMESS.

Results and Discussion

The energies relative to the reactant, bicbut, characterizing the stationary points along the conrotatory and disrotatory paths of the bicbut → *t*-but isomerization, obtained at various levels of theory and corrected for the zero-point vibrational energies (ZPVEs) resulting from the same types of calculations as used in geometry optimizations, are listed in Table 1. The ZPVE-corrected CR-CC(2,3)/cc-pVTZ//CASSCF(10,10)/cc-pVDZ energies and the available experimental activation and reaction enthalpies are also shown in Figure 1. Table 1 also includes the information about the expectation values of the S^2 operator ($\langle S^2 \rangle$) for the wave functions resulting from the singlet UB3LYP calculations, the percent biradical character of all species along the conrotatory and disrotatory pathways resulting from the analysis of the natural orbitals of CASSCF as described above (cf. footnote d in Table 1), as well as the available experimental activation and reaction enthalpies. The CASSCF and (U)B3LYP optimized geometries of all species involved in the conrotatory and disrotatory mechanisms are depicted in Figure 2.

As explained in the Introduction, it is well-established that the isomerization of bicyclo[1.1.0]butane into buta-1,3-diene is a conrotatory process. The experimental value of the corresponding activation barrier is 40.6 ± 2.5 kcal/mol.[1a] The important question is how well various methods, including the CR-CC approaches mentioned in a title, perform in reproducing the experimental barrier. Another important question is what various quantum chemistry methods do with the disrotatory pathway and the corresponding TS, dis_TS, which should be located significantly above the conrotatory pathway, if theory is to agree with experiment, and which has a strongly biradical character. We also discuss the performance of the CR-CC and other methods in describing the overall reaction enthalpy of the isomerization of bicyclo[1.1.0]butane into buta-1,3-diene, whose experimentally derived value is −25.9 ± 0.4 kcal/mol (see footnote f in Table 1). The isomerization of *g*-but into the final reaction product, *t*-but, which is the last step of the isomerization of bicyclo[1.1.0]butane into buta-1,3-diene, is mentioned in our discussion but not extensively analyzed, since *gauche*-buta-1,3-diene and the TS that connects it with *trans*-buta-1,3-diene, i.e., *gt*_TS, are largely closed-shell structures with energies only slightly above *trans*-buta-1,3-diene. Such structures are reasonably well described by all methods that account for dynamical correlation effects (in our case, all CC methods, B3LYP, and MCQDPT2) and are, as such, less challenging to modern methods of electronic structure theory. Clearly, the mechanism of the isomerization of bicyclo[1.1.0]butane into buta-1,3-diene is defined by the relative energetics of conrotatory and disrotatory TSs, con_TS and dis_TS, respectively. Thus, our discussion largely focuses on these TSs.

Since the accuracy of energy predictions depends on the use of reliable geometries, we begin our discussion with an analysis of the geometries of stationary points employed in this study. As shown in Figure 2, the RB3LYP (restricted B3LYP) and CASSCF geometry optimizations for the reactant and product molecules accurately reproduce the corresponding experimental geometries, with RB3LYP producing slightly better predictions for the bond lengths in bicbut and *t*-but than CASSCF. Clearly, both B3LYP and CASSCF perform quite well for the closed-shell minima on the PES corresponding to the reactant and product species. The same is true for the largely closed-shell *g*-but and *gt*_TS structures, for which CASSCF and B3LYP agree almost perfectly.

We now analyze the TS of the conrotatory mechanism, con_TS, which, according to the CASSCF calculations, has a 24% biradical character. In this case, the corresponding bond lengths and bond angles of the CASSCF and UB3LYP optimized structures remain quite similar. In fact, the only more substantial difference between these structures is in the value of the dihedral angle θ_{5236}, which in the UB3LYP optimized structure is about 6° larger than that in the CASSCF optimized structure of con_TS. Despite the fact that the discrepancies between the CASSCF and (U)B3LYP geometries for con_TS are more significant than in the case of the reactant and product molecules, the CASSCF and UB3LYP results are close enough to allow us to conclude that these methods agree rather well for con_TS. The characteristic feature of con_TS is that as the C1−C3 bond gets broken, the C1−C2 and C2−C3 bonds rotate in the same direction, so that the H5 atom forms a dihedral angle θ_{5236} of about 130° with the C2, C3, and H6 atoms, as opposed to a situation in the bicbut reactant where the H5 and H6 atoms are eclipsed (see Figure 2 for the atom numbering). Over the course of the reaction, the C2−C3 bond length remains essentially unchanged, while the C1−C2 bond shortens and gains a considerable π character, which explains why con_TS has a relatively small 24% biradical character in spite of the fact that the C1−C3 bond is completely broken in it.

The IRC calculations performed with CASSCF and UB3LYP indicate that the conrotatory TS, con_TS, connects the correct structures, the reactant bicbut and the intermediate product *g*-but (cf. Figure 1). As explained above, the (U)B3LYP method performs rather well in the geometry predictions for bicbut, con_TS, *g*-but, *gt*_TS, and *t*-but. This is not the case when the disrotatory TS, dis_TS, is studied using UB3LYP. First, it is important to note that dis_TS is almost a pure biradical (its biradical character resulting from the analysis of the CASSCF wave function equals 90% and the value of $\langle S^2 \rangle$ obtained with UB3LYP is 0.96; see Table 1). When the CASSCF and UB3LYP geometries of dis_TS are compared with each other, significant discrepancies are observed. The largest deviation between these geometries is in the value of the dihedral angle θ_{5236}. The UB3LYP value of θ_{5236} is greater than the corresponding CASSCF value of 16.4° by 21.5°. Furthermore, all of the C−C bonds in the UB3LYP optimized structure of dis_TS (the C1−C2, C2−C3, C2−C4, C3−C4, and broken C1−C3 bonds) are shorter than the corresponding bonds in the CASSCF optimized geometry. In addition to these substantial differences between the CASSCF and UB3LYP geometries, the IRC calculations with UB3LYP indicate that dis_TS connects the bicbut reactant to a local minimum structure which is geometrically close to con_TS rather than connecting bicbut to *g*-but, as shown in Figure 1. All of this implies that the UB3LYP optimized geometry of dis_TS is not a reliable prediction.

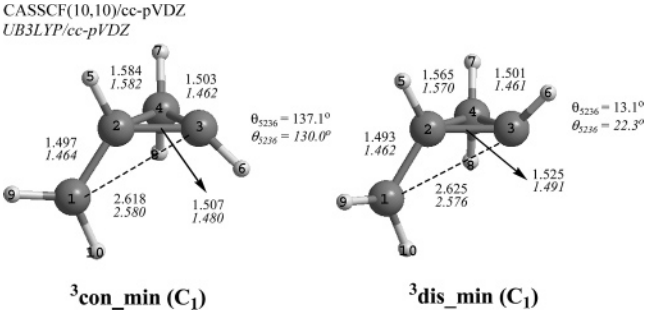
TABLE 2: Electronic Energies, Relative to the bicbut Reactant (in kilocalories per mole), of the Conrotatory and Disrotatory TSs, con_TS and dis_TS, Respectively, on the Singlet PES (S_0) and the Corresponding Conrotatory and Disrotatory Minima on the Triplet PES (T_1), ^{3}con_min and ^{3}dis_min, Respectively, Obtained in the CASSCF and UB3LYP Optimizations[a]

	con_TS/^{3}con_min		dis_TS/^{3}dis_min	
	S_0	T_1	S_0	T_1
CASSCF(10,10)/cc-pVDZ	41.2	52.8	55.8	51.7
UB3LYP/cc-pVDZ	44.4	53.4	54.4	52.4
ΔE^{S-T}(CASSCF)	−11.6		4.1	
ΔE^{S-T}(UB3LYP)	−9.0		2.0	

[a] The ΔE^{S-T} values (in kilocalories per mole) are the adiabatic singlet−triplet (S_0−T_1) energy differences characterizing the con_TS/^{3}con_min and dis_TS/^{3}dis_min pairs.

The underlying reason for this failure of the UB3LYP method in predicting the dis_TS geometry is related to the fact that strong biradicals have singlet and triplet states that are almost degenerate because of the weak coupling between unpaired electrons. Since dis_TS is an almost pure biradical, we expect the singlet and triplet states to be close in energy in that region. This is, indeed, the case. For example, the energy difference between the triplet and singlet states at the singlet dis_TS geometry predicted at the UB3LYP/cc-pVDZ level is only 0.3 kcal/mol, which confirms our expectation. As a result, the wave function resulting from the singlet UB3LYP calculations is significantly triplet-contaminated ($\langle S^2 \rangle \sim 1$), so the geometry of dis_TS, predicted by UB3LYP, contains the triplet characteristics along with the singlet features, making the UB3LYP description of the dis_TS structure unreliable.

A similar reasoning also explains the observed failure of UB3LYP in the IRC calculations, in which the dis_TS structure resulting from the singlet UB3LYP optimization connects bicbut to a con_TS-like local minimum structure rather than to the *g*-but intermediate product. Our CASSCF calculations enabled us to find two local minima on the triplet PES in the region of the coordinate space defined by the con_TS and dis_TS structures, which we designate as ^{3}con_min and ^{3}dis_min and which are located only 3.0 and 4.1 kcal/mol, respectively, below the singlet dis_TS structure according to CASSCF (see Table 2 and Figure 3 for their energies and geometrical parameters). The UB3LYP triplet calculations predict the existence of similar two minima as well, but because of the significant spin contamination of the wave functions resulting from the singlet and triplet UB3LYP calculations, the IRC path obtained with UB3LYP that originates at the dis_TS state optimized in singlet UB3LYP calculations does not stay on the PES generated in the formally singlet, but in reality considerably triplet-



^{3}con_min (C_1) **^{3}dis_min (C_1)**

Figure 3. Selected geometrical parameters for the local minima on the triplet PES, ^{3}con_min and ^{3}dis_min, which appear in the vicinity of the singlet con_TS and dis_TS structures, optimized at the CASSCF(10,10)/cc-pVDZ (the Roman font) and UB3LYP/cc-pVDZ (the Italic font) levels. Distances are in angstroms, and angles are in degrees.

contaminated, UB3LYP calculations. The IRC path of UB3LYP that originates at the dis_TS structure obtained in the triplet-contaminated singlet UB3LYP calculations switches to the PES that results from the singlet-contaminated triplet UB3LYP calculations which heads toward the ^{3}con_min-like local minimum instead of going toward the *g*-but intermediate product. This is a signature of the singlet−triplet PES crossing in the vicinity of the dis_TS structure, which cannot be properly handled by the severely spin-contaminated UB3LYP calculations. Our CASSCF calculations show that the singlet and triplet PESs indeed cross, but this is not a problem for CASSCF. The wave functions obtained in the CASSCF calculations are pure multiplets, so that the IRC path corresponding to the singlet PES does not switch to the IRC path corresponding to the triplet PES. As a result, the con_TS and dis_TS saddle point structures on the singlet PES obtained with CASSCF connect the bicbut and *g*-but minima in a proper manner shown in Figure 1. We conclude that the CASSCF geometry of the singlet dis_TS structure, which does not contain any triplet contaminants, is the correct geometry. The geometry of dis_TS resulting from the heavily spin-contaminated UB3LYP calculations cannot be trusted. This is why we employed the CASSCF optimized geometry of dis_TS in the single-point energy calculations using the MCQDPT2 and CC methods. For consistency, we also used the CASSCF geometries of the bicbut, con_TS, *g*-but, *gt*_TS, and *t*-but structures in the MCQDPT2 and CC single-point calculations.

As already mentioned, the experimental activation enthalpy for the bicbut → *t*-but isomerization has a value of 40.6 ± 2.5 kcal/mol within a temperature range of 476−502 K.[1a] Since it is established that the bicbut → *t*-but isomerization is a concerted reaction with the relevant methylene groups moving in a conrotatory manner, this value corresponds to the activation barrier of the conrotatory pathway (see Figure 1). Thus, we can assess the accuracy of methods employed in this study by comparing the energies of the con_TS structure corrected for ZPVEs with the experimental activation energy. As mentioned earlier, the con_TS structure has a partly biradical character and the CASSCF method gives extra stability to structures having biradical character relative to the corresponding closed-shell structures (in our case, the bicbut reactant), since it neglects dynamical correlation effects which are relatively large in closed-shell systems.[5a−c] Our CASSCF value of the conrotatory activation barrier of 38.5 kcal/mol, which is 2.1 kcal/mol below the experimental result, confirms this. Similar remarks apply to the MCQDPT2 results for con_TS. The MCQDPT2 method describes the nondynamical correlation effects accurately, but the treatment of dynamical correlation effects, which are particularly important for closed-shell structures, is a low-order treatment. As a result, the MCQDPT2 value of the conrotatory activation energy of 37.0 kcal/mol is below the experimental activation energy. It is not much below the experimental result, because the degree of biradical character of con_TS is relatively small (24%), but it is below. On the basis of a similar analysis, we expect that the CASSCF and MCQDPT2 energies of dis_TS, which is a much stronger biradical when compared with con_TS, relative to the corresponding energies of the bicbut closed-shell reactant, are underestimated even more. A comparison of the CASSCF and MCQDPT2 results for dis_TS with the corresponding highly accurate CR-CC(2,3) result confirms this. The UB3LYP method, which seems relatively insensitive to variations in the basis set and geometry in our calculations (see Table 1) and which can handle structures with a modest degree of biradical character, such as con_TS, performs quite well for con_TS, only slightly overestimating the actual activation barrier corresponding to the conrotatory pathway. The conrotatory activation barriers predicted by all CC methods are also within the experimental error bars. In particular, the CCSD(T) and CR-CC(2,3) methods reproduce the experimental activation barrier almost exactly, giving, depending on the geometries employed ((U)B3LYP or CASSCF), 40.2 or 40.4 and 40.8 or 41.1 kcal/mol, respectively. The CR-CCSD(T) approach overestimates the experimental activation energy, but only by ∼2 kcal/mol, which is still within the experimental error bars. Since the CASSCF and (U)B3LYP geometries of con_TS are similar and the analogous statement applies to bicbut, the use of either set of geometries produces essentially the same CC results, as shown in Table 1. This gives us confidence in the ability of CC methods to describe the conrotatory pathway. The fact that the CR-CC(2,3) approach reproduces the experimental activation energy defining the conrotatory mechanism to within 0.5 kcal/mol illustrates the types of accuracies the CR-CC(2,3) approach can offer in mechanistic considerations.

Unlike the conrotatory TS, the description of the disrotatory TS, dis_TS, poses a much greater challenge for most of the methods employed in this study, due to the almost purely biradical character of dis_TS which calls for an accurate and balanced treatment of dynamical and nondynamical correlation effects. Among all of the methods employed here, the one that is expected to produce the most reliable activation barrier for the disrotatory mechanism, which is defined by the dis_TS structure, is CR-CC(2,3). This statement is based on the well-established ability of the CR-CC(2,3) approach to provide a highly accurate and balanced description of dynamical and nondynamical correlation effects in systems containing biradical and closed-shell structures.[5d,e,11]

In particular, as shown in ref 11 and as demonstrated in a large number of benchmark calculations performed by our group, the CR-CC(2,3) theory provides highly accurate and rigorously size extensive results of the very high, full CCSDT-like, quality for single-bond breaking and reaction pathways involving biradicals. An example that illustrates the ability of the CR-CC(2,3) approximation to provide a highly accurate and robust description of biradical TSs has been presented in ref 11b, where it has been shown that CR-CC(2,3) can reproduce the experimental enthalpy of stereomutations of cyclopropane involving the trimethylene biradical as a TS to within 0.5 kcal/mol. For comparison, the MCQDPT2 and MRCI calculations underestimate the enthalpy of stereomutations of cyclopropane by a few kilocalories per mole.[11e] Additional arguments in favor of the high accuracy of the CR-CC(2,3) result for the disrotatory activation energy characterizing the bicbut → *t*-but process are as follows: (i) As previously mentioned, and as verified by the calculations of the activation barrier for the conrotatory path defined by a partly biradical con_TS structure, the CASSCF and MCQDPT2 methods produce barrier estimates which are too low, since they artificially exaggerate the stability of biradical species relative to the corresponding closed-shell structures. The CR-CC(2,3) approach does not do this, balancing dynamical and nondynamical correlations in biradicals and closed-shells in a more accurate manner.[5d,e,11] In fact, even the older CR-CCSD(T) approach, which is generally somewhat less accurate than CR-CC(2,3), provides a better balance than CASSCF and MCQDPT2 in calculations involving closed-shell and biradical species.[5,11] (ii) It is well-known that the standard single-reference CCSD(T) method fails when biradicals are examined, since it produces the unphysically negative triples corrections to CCSD energies, particularly when the degree of biradical character is high.[5b,c,9−11] We observe this behavior here as well. As shown in Table 1, CCSD(T) places the dis_TS energy considerably below the energy of con_TS**,** contradicting experiment. The CR-CC(2,3) approach (CR-CCSD(T) as well) eliminates this problem. (iii) In cases of very strong biradicals, (U)B3LYP fails due to the presence of the Hartree−Fock exchange in the B3LYP hybrid functional. The UB3LYP results for strong biradicals are significantly contaminated by triplet contributions, which artificially lower the energies of biradicals relative to the corresponding closed-shell structures that are not spin-contaminated in RB3LYP calculations. An issue of spin contamination is not even present in CR-CC(2,3) calculations, which use the spin- and symmetry-adapted restricted Hartree−Fock reference. Although the CASSCF and MCQDPT2 methods underestimate the energies of biradicals relative to closed-shell structures for the entirely different reasons than in the (U)B3LYP case, the fact that the single-point CASSCF, MCQDPT2, and (U)B3LYP energies of dis_TS are similar (see Table 1) only reinforces our claim that the CASSCF, MCQDPT2, and (U)B3LYP activation energies for the disrotatory pathway are all too low. For all these reasons, the activation barrier obtained with CR-CC(2,3) can be used as the benchmark value for the assessment of the disrotatory barriers predicted by other methods employed in this study.

Let us, therefore, discuss the relative performance of various methods in describing the disrotatory barrier. The CCSD(T) activation enthalpy for the disrotatory path is 21.8 kcal/mol, which is approximately half of the conrotatory barrier. If we believed the CCSD(T) result, the reaction should proceed along the disrotatory path, completely contradicting the experiment.[1d] This is yet another example of the dramatic failure of the CCSD(T) method in mechanistic studies involving biradicals. The disrotatory activation barriers obtained with the CASSCF and MCQDPT2 methods are 52.0 and 53.7 kcal/mol, respectively. As already explained, we expect these values to be too low compared to the actual disrotatory barrier. Indeed, our CASSCF and MCQDPT2 calculations underestimate the activation enthalpy characterizing the disrotatory pathway by as much as 12−14 kcal/mol when compared to the best CR-CC(2,3) estimate. The (U)B3LYP prediction for the disrotatory barrier is 15 kcal/mol below the CR-CC(2,3) result as well, confirming the fact that the B3LYP functional cannot handle strong biradicals, as described above. The CR-CCSD(T) method slightly overestimates the disrotatory barrier. This is in agreement with all earlier CR-CCSD(T) calculations for biradicals reported in the literature.[5,9,10] The discrepancy between the CR-CCSD(T) and CR-CC(2,3) results is in this case 2.7 kcal/mol or 4%.

On the basis of the CR-CC(2,3) calculations, we predict that the actual activation enthalpy of the disrotatory mechanism of the bicbut → *t*-but (or, to be precise, bicbut → *g*-but**)** isomerization is on the order of 66 kcal/mol (see Table 1 and Figure 1). The earlier MRCI and PT2F calculations,[3c] which employed a rather small basis set [6-31G(d)] compared to the one used here (cc-pVTZ), produced the barrier for the disrotatory path of about 56−57 kcal/mol, which is ∼9−10 kcal/mol below our best CR-CC(2,3) result. The 9−10 kcal/mol discrepancy between our CR-CC(2,3) and earlier MRCI and PT2F results for the disrotatory activation energy can be, at least in part, attributed to the smaller basis set used in the MRCI and PT2F calculations reported in ref 3c. In addition, we expect the MRCI and PT2F values of the barrier defining the disrotatory mechanism to be below the actual value of this barrier due to the somewhat less accurate treatment of the dynamical correlation effects by the MRCI and PT2F approaches compared to CR-CC(2,3). It is probably safe to say that the actual value of the disrotatory barrier is somewhere between 57 and 66 kcal/mol, most likely closer to 66 kcal/mol than to 57 kcal/mol. Note, for example, that our MCQDPT2 calculation gives 53.7 kcal/mol and the MRCI approach, which offers a better treatment of dynamical correlation effects compared to MCQDPT2, gives a higher disrotatory activation barrier by a few kilocalories per mole.[3c] This only strengthens our belief that our CR-CC(2,3) result for this barrier is quite close to reality, since CR-CC(2,3) offers an even better treatment of dynamical correlation effects, while providing an accurate description of nondynamical correlation effects in biradicals. It would be very interesting to determine the disrotatory activation energy experimentally to see if our predictions are correct.

Finally, the experimentally derived reaction enthalpy of the isomerization of bicyclo[1.1.0]butane into buta-1,3-diene is −25.9 ± 0.4 kcal/mol at 298 K.[19] The CASSCF result is −43 kcal/mol, which is 17 kcal/mol below the experimental reaction enthalpy (see Table 1). Clearly, one needs to account for the dynamical correlation effects in the reactant and product molecules to improve the CASSCF result. The MCQDPT2 method, which accounts for the dynamical electron correlation effects in the second order, brings the poor CASSCF result for the reaction enthalpy to a much more reasonable value of about −29 kcal/mol. A similar degree of improvement is offered by the B3LYP method, which gives the reaction enthalpy of about (−30) to (−32) kcal/mol. The best values of the reaction enthalpy are obtained with the CC approaches, which all give about −28 kcal/mol, if we use the *trans*-buta-1,3-diene as a final product, and about −25 kcal/mol, if we use the nearly isoenergetic *gauche*-buta-1,3-diene rotamer which is separated from the *trans*-buta-1,3-diene structure by a low-energy barrier, as a product in the reaction enthalpy calculations (see Table 1). We can see once again that an accurate treatment of the dynamical correlation effects, which the CCSD(T), CR-CCSD(T), and CR-CC(2,3) methods offer and which are the dominant correlations in the reactant and product molecules, leads to improvements in the results. Similar is true for the *gt*_TS saddle-point structure that connects the gauche and trans rotamers of buta-1,3-diene. The *gt*_TS species has a largely closed-shell character, and we observe a great deal of consistency among all CC approaches, which give about −22 kcal/mol for the enthalpy of *gt*_TS relative to the bicbut reactant (see Table 1). The MCQDPT2 and B3LYP approaches, which offer a less accurate treatment of the dynamical correlation effects compared to CC methods, provide somewhat more negative, albeit still quite reasonable, values of (−23) to (−25) kcal/mol, and the CASSCF approach, which neglects the dynamical correlations, gives −37 kcal/mol, which cannot be regarded as a reliable result.

Summary and Concluding Remarks

In the present study, the disrotatory and conrotatory mechanisms of the isomerization of bicyclo[1.1.0]butane to *trans*-buta-1,3-diene have been computationally investigated with the CASSCF, MCQDPT2, (U)B3LYP, CCSD(T), CR-CCSD(T), and CR-CC(2,3) methods. The CASSCF(10,10)/cc-pVDZ optimizations located one TS for the conrotatory path, con_TS, which has a 24% biradical character, and one TS for the disrotatory path, dis_TS, which is an almost pure biradical. (U)B3LYP located both TSs as well, but, unlike CASSCF, it failed to provide a reliable description of the dis_TS saddle-point structure. The main reason for the failure of (U)B3LYP in describing the TS for the disrotatory pathway is a significant spin contamination and the proximity of the singlet and triplet PESs in the region of the dis_TS structure.

With an exception of CCSD(T), all methods used in this study agree that the thermal rearrangement of bicyclo[1.1.0]butane into buta-1,3-diene is a concerted conrotatory process, confirming the experimental findings and earlier MRCI and PT2F calculations.[3c] The CCSD(T) approach contradicts experiment and favors the disrotatory mechanism, since it fails to provide a reliable description of the TS along the disrotatory pathway, which is an almost pure biradical.

The activation barrier for the conrotatory pathway, whose experimental value is 40.6 ± 2.5 kcal/mol, is best described by the CCSD(T), CR-CC(2,3), and B3LYP methods, which give 40.2 or 40.4, 40.8 or 41.1, and 41.5 or 41.6 kcal/mol, respectively. The CR-CCSD(T) value of 42.4 or 42.8 kcal/mol is almost as good. The CASSCF and MCQDPT2 results are reasonable, but they underestimate the conrotatory activation barrier by 2−3 kcal/mol. This is related to the insufficiently accurate treatment of dynamical correlation effects by the CASSCF and MCQDPT2 approaches, which dominate electron correlations in the closed-shell reactant and product molecules and which are significant for the conrotatory TS whose biradical character is relatively small.

The situation changes when the disrotatory pathway is examined. The strongly biradical character of the disrotatory TS causes a failure of CCSD(T), which places it ∼20 kcal/mol below the conrotatory TS. The CASSCF and MCQDPT2 methods behave much better in this regard, placing the disrotatory TS above the conrotatory TS, but the activation barriers resulting from the CASSCF and MCQDPT2 calculations for the disrotatory pathway, of about 52 and 54 kcal/mol, respectively, seem too low. They are lower by a few kilocalories per mole than the MRCI result reported in ref 3c and considerably lower than the CR-CC(2,3) result of ∼66 kcal/mol. The CR-CC(2,3) approach is known to provide a highly accurate and balanced description of the dynamical and nondynamical correlation effects in calculations for single-bond breaking and reaction mechanisms involving biradical and closed-shell structures (cf., e.g., refs 5d,e and 11). The CASSCF and MCQDPT2 methods do not offer the same level of accuracy in balancing dynamical and nondynamical correlations in similar situations. Thus, the CR-CC(2,3) value of the disrotatory activation barrier of about 66 kcal/mol is expected to be more reliable than the analogous values obtained with CASSCF and MCQDPT2. On the basis of the prior experience, the CR-CCSD(T) result for the disrotatory activation barrier of ∼69 kcal/mol is expected to be somewhat too high. The (U)B3LYP results for the same barrier of ∼50−51 kcal/mol are too low, since B3LYP fails to describe the strongly biradical TS defining the activation barrier for the disrotatory mechanism.

With an exception of CASSCF, all methods employed in this work provide an accurate description of the enthalpy of isomerization of bicyclo[1.1.0]butane into buta-1,3-diene, whose experimentally derived value at 298 K is −25.9 ± 0.4 kcal/mol. Of all methods exploited in this work, the best results for the reaction enthalpy are obtained with the CCSD(T), CR-CCSD(T), and CR-CC(2,3) approaches, which give about −28 kcal/mol, if we use the *trans*-buta-1,3-diene as a product, and about −25 kcal/mol, if we use as a product the nearly isoenergetic *gauche*-buta-1,3-diene rotamer which is separated from *trans*-buta-1,3-diene by a low-energy barrier. The B3LYP and MCQDPT2 methods give somewhat less accurate (more negative) reaction enthalpy values.

In summary, the single-reference, "black-box", CR-CC(2,3) approach offers a highly accurate and well-balanced description of the conrotatory and disrotatory reaction pathways and reaction enthalpies for the isomerization of bicyclo[1.1.0]butane into buta-1,3-diene, making it a viable alternative for mechanistic studies involving closed-shell and biradical species. The CR-CCSD(T) approach, which has similar ease of use and costs, is almost as accurate, but the CR-CC(2,3) approach seems to be a preferred option.

Acknowledgment. This work has been supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy (Grant No. DE-FG02-01ER15228). The calculations were performed on the computer systems provided by the High Performance Computing Center and Department of Chemistry at Michigan State University. The authors would like to thank Mr. Jeffrey R. Gour for reading and commenting on the manuscript.

Supporting Information Available: Cartesian coordinates and electronic energies for all stationary points along the conrotatory and disrotatory reaction pathways. This material is available free of charge via the Internet at http://pubs.acs.org.

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