Quantum Mechanical Study of the Ring-Closing Reaction of the Hexatriene Radical Cation

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The ring-closing reaction of hexatriene radical cation $\mathbf{1}^{\bullet+}$ to 1,3-cyclohexadiene radical cation $\mathbf{2}^{\bullet+}$ was studied computationally at the B3LYP/6-31G* and QCISD(T)/6-311G*//QCISD/6-31G* levels of theory. Both, concerted and stepwise mechanisms were initially considered for this reaction. Upon evaluation at the B3LYP level of theory, three of the possible pathways—a concerted C_2-symmetric via transition structure $\mathbf{3}^{\bullet+}$ and stepwise C_1-symmetric pathways involving three-membered ring intermediate $\mathbf{5}^{\bullet+}$ and four-membered ring intermediate $\mathbf{6}^{\bullet+}$—were rejected due to high-energy stationary points along the reaction pathway. The two remaining pathways were found to be of competing energy. The first proceeds through the asymmetric, concerted transition structure $\mathbf{4}^{\bullet+}$ with an activation barrier $E_a = 16.2$ kcal/mol and an overall exothermicity of −23.8 kcal/mol. The second pathway, beginning from the cis,cis,trans rotamer of $\mathbf{1}^{\bullet+}$, proceeds by a stepwise pathway to the cyclohexadiene product with an overall exothermicity of −18.6 kcal/mol. The activation energy for the rate-determining step in this process, the formation of the intermediate bicyclo[3.1.0]hex-2-ene via transition structure $\mathbf{9}^{\bullet+}$, was found to be 20.4 kcal/mol. More rigorous calculations of a smaller subsection of the potential energy hypersurface at the QCISD(T)//QCISD level confirmed these findings and emphasized the importance of conformational control of the reactant.

Introduction

The study of the structure and reactivity of hydrocarbon radical cations has been a topic of interest for more than 20 years. Initially, the research in this field focused on the experimental exploration of new electron-transfer-catalyzed pericyclic reactions.[1] However, it became clear that an application of these methods as a tool in synthesis would not be possible without a better understanding of the mechanisms of the reactions. Therefore, the emphasis shifted during the past decade to mechanistic studies of these interesting reactive intermediates.[2] This was facilitated by major advances in mass spectrometry, a rapid increase in computational power, and the development of new quantum mechanical methods that were able to adequately treat radical cations.

Similar to the development of the mechanistic understanding of pericyclic reactions of neutral compounds, the study of electrocyclic reactions has been a starting point for the investigation of pericyclic reactions of radical cations. Due to the small size of the starting material and the relative simplicity of the reaction, the ring opening of the cyclobutene radical cation has been studied in detail. Several of the early experimental reports[3] and theoretical analysis[4] discussed this reaction. However, much of the experimental data was inconclusive. For example, estimates of the activation energy for the ring opening of the cyclobutene radical cation ranged from <7 kcal/mol to 16.5 kcal/mol.[3c,d,5] Computational studies[6] uncovered a remarkable richness of available reaction pathways, which can best be described as a reaction continuum crossing the so-called “Bauld plateau” rather than a single, distinct reaction pathway.

While the ring opening of the cyclobutene radical is well documented, the next higher homologue of this reaction, the ring-closing reaction of the hexatriene radical cation, is much less well-known. The different rotamers of the starting material, the hexatriene radical cation $\mathbf{1}^{\bullet+}$, have been characterized both experimentally and computationally.[7] The electrocyclic ring opening of

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(1) For summaries of this aspect, compare: (a) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307. (b) Linker, T.; Schmittel, M. *Radikale und Radikalionen in der Organischen Synthese;* VCH−Wiley: New York 1998. (c) Bauld, N. L. In *Advances in Electron-Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: New York, 1992; Vol. 2. (d) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550. (e) Bauld, N. L. *Radicals, Radical Ions, and Triplets*; Wiley-VCH: New York, 1997. (f) Müller, F.; Mattay, J. *Chem. Rev.* **1993**, *93*, 99.

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the 1,3-cyclohexadiene **2**$^{\bullet+}$ to give different rotamers of **1**$^{\bullet+}$ under photochemical conditions has been studied in some detail by a variety of techniques.[8] The reaction of **2**$^{\bullet+}$ was studied using the INDO and CNDO/S methods under the assumption of orbital symmetry conserving pathways, which predicted a disrotatory ring opening for the ground state and a conrotatory ring opening for the excited-state reaction.[8c,9] It was subsequently demonstrated that simple orbital symmetry arguments do not apply to the reaction of radical cations.[2,10] Rather, many formally pericyclic reactions of radical cations proceed via unsymmetric pathways, while the symmetry-preserving pathways proceed via second-order saddle points of higher energy due to Jahn–Teller distortions.[4]

It is well-known that **2**$^{\bullet+}$ does not undergo ring opening, but rather adds to neutral **2** in a [4 + 2] cycloaddition under thermal conditions.[1c,e] No ring opening occurs in the matrix or the mass spectrometer where this bimolecular pathway is not possible. To the best of our knowledge, there is only a single example of a thermal ring closure of a hexatriene radical cation, the somewhat special case of a α-phenyl-*o*-quinodimethane radical cation, described in the literature.[11] This is rather surprising given that the parent reaction is exothermic by more than 20 kcal/mol, as we will show later. Due to the generally flat hypersurfaces found for most hydrocarbon radical cations, the reaction pathways are largely determined by the thermochemistry of the reaction. The very similar closure of the 1,5-hexadiene radical cation to form the cyclohexane-1,4-diyl radical cation proceeds, for example, already at very low temperatures.[12] An understanding of the factors that distinguish the ring closure of the 1,3,5-hexatriene radical cation from the previously studied reactions would therefore add to our general understanding of radical cation chemistry.

In analogy to the homologous ring opening of the cyclobutene radical cation,[6] the five different pathways shown in Figure 1 are conceivable. The reaction could proceed through a concerted pathway involving either a symmetric or an unsymmetric transition structure, **3**$^{\bullet+}$ or **4**$^{\bullet+}$. Alternatively, stepwise pathways involving the cyclized intermediates **5**$^{\bullet+}$ –**7**$^{\bullet+}$ are possible. Here, we will report the results of our investigation of these pathways. After a brief discussion of the thermochemistry of the reaction, we will describe the broader exploration of the potential energy hypersurface. We will then discuss the relevant transition structures of the competing pathways in more detail using highly correlated MO calculations. Finally, we will address the origin of the apparent nonreactivity of *ccc*-**1**$^{\bullet+}$.

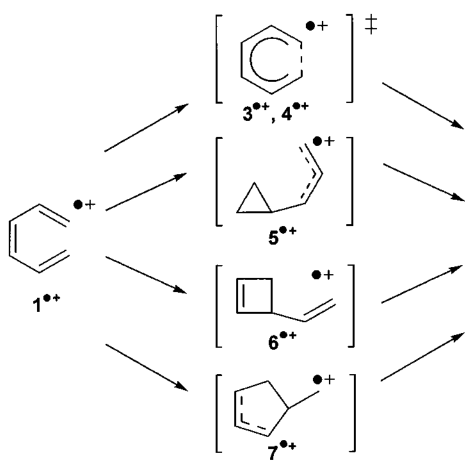

Figure 1. Possible reaction pathways for the ring closure of the hexatriene radical cation.

Computational Methodology

The extraordinary flatness of the hypersurfaces of hydrocarbon radical cations and the importance of electron correlation in these species makes the choice of an appropriate computational method crucial. Concern over this point has been, and continues to be, the focus of numerous studies in the literature. It is now generally accepted that UHF and MPn methods are not suitable for the calculation of hydrocarbon radical cations because they yield wave functions that are often severely spin contaminated.[2,13] This can lead to significant errors in geometries and energies, specifically of transition structures. The relative benefits and deficiencies of hybrid DFT methods have also come under scrutiny in recent years.[14] B3LYP has been quite successful in a number of recent studies of radical cations and gave results that were in excellent agreement with available experimental data and highly correlated MO-based methods.[2] However, the fact that B3LYP does not localize spin and charge gives it a bias toward delocalized structures. As a result, stationary points that are found on with other levels of theory sometimes cannot be found with B3LYP.

We adopted a computational strategy whereby all structures were first fully optimized at the B3LYP/6-31G* level of theory. Stationary points were characterized by frequency analysis at the same level to ensure local minima for intermediates and first-order saddle points for transition structures. The imaginary frequency of the located transition structures was then animated using MOLDEN to ensure that it corresponded with the desired reaction coordinate. In some cases, IRC calculations were used to establish the nature of a transition structure. The optimized structures from the B3LYP level were then reoptimized at the QCISD/6-31G* level of theory and followed with QCISD(T)/6-311G* single point calculations for selected points of the potential energy hypersurface. All reported energies were corrected for zero-point vibrational energies from B3LYP calculations unless specified otherwise, and are given in kcal/mol relative to the 1,3-cyclohexadiene radical cation, **2**$^{\bullet+}$. Calculations were performed using the G98 series of programs[15] running on SGI Origin2000 computers at the High Performance Computing Complex at the University of Notre Dame.

Results and Discussion

Rotamers of the Hexatriene Radical Cation. The different possible rotamers of **1**$^{\bullet+}$ have been studied previously at the CASSCF level,[7a] thus providing a

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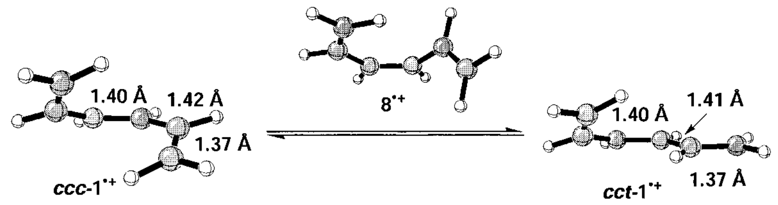

Figure 2. Structures of Rotamers of $\mathbf{1}^{\bullet+}$.

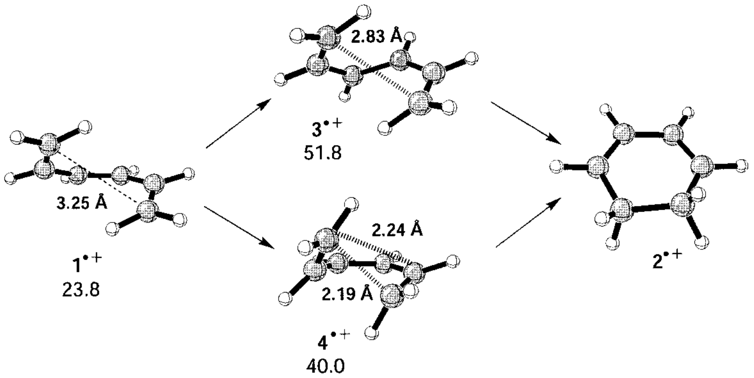

Figure 3. C_2-symmetric $\mathbf{3}^{\bullet+}$ and unsymmetric transition structure $\mathbf{4}^{\bullet+}$ for the concerted ring closure of $\mathbf{1}^{\bullet+}$.

convenient benchmark for our calculations. As a first step in the investigation of the ring closing reaction of 1,3,5-hexatriene radical cation $\mathbf{1}^{\bullet+}$, the rotational conformers of the reactant were thus studied. In its neutral state, *cis*-1,3,5-hexatriene is free to adopt three conformers, cis-cis-cis (ccc), cis-cis-trans (cct) and trans-cis-trans (tct), by rotation around a single bond with a barrier of only ~1 kcal/mol. Although the lowest energy conformation of these three is *tct*-$\mathbf{1}^{\bullet+}$, the species of importance for ring closure are *ccc*-$\mathbf{1}^{\bullet+}$ and *cct*-$\mathbf{1}^{\bullet+}$ (see Figure 2). The energy difference between *ccc*-$\mathbf{1}^{\bullet+}$ and *cct*-$\mathbf{1}^{\bullet+}$ of 5.2 kcal/mol calculated at the B3LYP/6-31G* level is very close to the CASSCF calculated value of 5.4 kcal/mol[7a] as well as the value for neutral *ccc*-**1** and *cct*-**1** of 5.6 kcal/mol obtained at the B3LYP/6-31G* level. The calculated geometries are also very similar to the ones obtained at the CASSCF level.

Upon single-electron oxidation by electron-transfer catalysis (ETC), the barrier to free rotation becomes with 11.6 kcal/mol quite high, thus making the interconversion of *ccc*-$\mathbf{1}^{\bullet+}$ and *cct*-$\mathbf{1}^{\bullet+}$ a slow process as compared to the interconversion of the conformers of neutral **1**. The formal single and double bonds C_2-C_3, C_3-C_4, and C_4-C_5 in $\mathbf{1}^{\bullet+}$ are essentially indistinguishable, as can be seen by the similarity of the carbon–carbon bond lengths shown in Figure 2. This phenomenon, which is due to delocalization of the SOMO across the entire polyene system, is well-known in the literature.[2,6,18,20] The formal C_3-C_4 double bond is weakened, leading to the experimentally observed isomerization of the central double bond.[7,8] The transition structure for the rotation around the C_2-C_3 bond can be readily located at the B3LYP/6-31G* level of theory, unlike the one for the smaller butadiene radical cation homologue.[14d,16] This is due to the lack of symmetry and the favorable localization of spin and charge in the diene unit. Therefore, the activation energy for interconversion of the rotamers is lower than the value of 28.1 kcal/mol calculated for the butadiene case at the QCISD(T) level of theory,[14d] explaining the experimentally observed formation of several rotamers of $\mathbf{1}^{\bullet+}$ in the matrix.[7,8] Since a concerted transition structure for the ring closure is only accessible from *ccc*-$\mathbf{1}^{\bullet+}$ and the interconversion at the radical cation stage is slow, the basic assumptions of the Curtis–Hammet principle are not fulfilled here. The energy difference between the two reactive rotamers thus needs to be considered in an analysis of the thermochemistry of the reaction.

The Concerted Pathways. For the reaction of $\mathbf{1}^{\bullet+}$ to $\mathbf{2}^{\bullet+}$ the concerted and stepwise pathways shown in Figure 1 have been proposed. We begin by investigating the possible concerted pathways. Figure 3 depicts two possible transition structures, the first of which is the C_2-symmetric structure $\mathbf{3}^{\bullet+}$. This stationary point is very similar to the structure that would be expected for the conrotatory transition structure of the electrocyclic ring closing of neutral **1**. According to the Woodward–Hoffmann rules, this pathway would be expected for the photochemical ring closure of **1**. However, it has been shown that this reaction is considerably more complex

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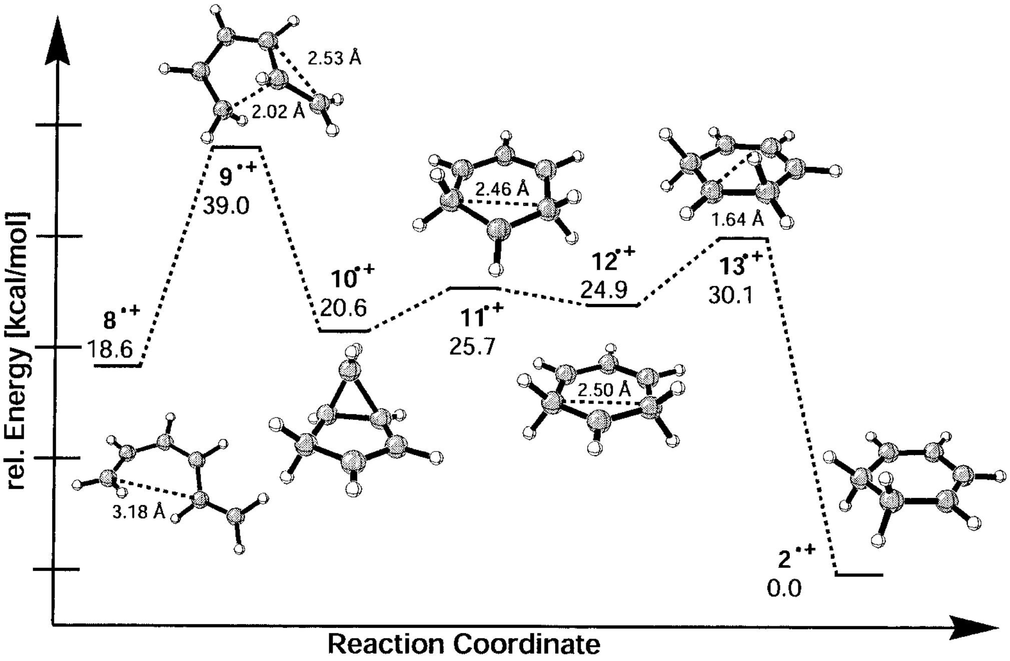

Figure 4. Stepwise pathway for the ring closure of **1**$^{\bullet+}$.

and involves a conical intersection.[17] The computed distance between the bond-forming terminal carbons of *ccc*-**1**$^{\bullet+}$ is 2.83 Å. A normal-mode analysis shows that **3**$^{\bullet+}$ is a true first-order saddle point on the hypersurface, which is at an energy 28.0 kcal/mol higher than *ccc*-**1**$^{\bullet+}$. Due to the high energy and ^{2}A electronic state for which there is no adiabatic connection to the ^{2}B ground state of *ccc*-**1**$^{\bullet+}$, **3**$^{\bullet+}$ is not part of the reaction pathway for cyclization of **1**$^{\bullet+}$. Nevertheless, **3**$^{\bullet+}$ is noteworthy because it is not subject to a second-order Jahn–Teller distortion, unlike the symmetric species in previous studies of hydrocarbon radical cation reactions.[6a,e18] This demonstrates that symmetric structures cannot automatically be excluded for consideration when studying these reactions.

The concerted pathway from **1**$^{\bullet+}$ to **2**$^{\bullet+}$ involving the unsymmetric transition structure **4**$^{\bullet+}$, which is 11.8 kcal/mol lower in energy than the symmetry-preserving pathway, is a much more viable option. The terminal carbons of this structure are at a distance of 2.19 Å. C_2 through C_5 are approximately planar (the dihedral $C_2-C_3-C_4-C_5$ is 4.3°) while C_1 sits above this plane at an angle of 53.0° and C_6 is 14.3° below the plane. The activation energy of the C_1-symmetric pathway is 16.2 kcal/mol relative to *ccc*-**1**$^{\bullet+}$. The reaction is exothermic by 23.8 kcal/mol. These values should be compared with an activation energy of 29.0 kcal and a reaction energy of -14.5 kcal/mol for the neutral reaction.[19] The radical cation reaction is therefore favored both kinetically and thermodynamically over the thermal reaction. Geometrically and electronically, **4**$^{\bullet+}$ resembles the conical intersection found for the photochemical ring closure of **1**.[17] The C_1-C_6 and the C_1-C_5 distances are nearly identical at 2.19 and 2.24 Å, respectively, while the C_2-C_4 is an almost planar allyl radical system. The largest positive charge is found on the terminal carbons. These similarities reemphasize the relationship between the many radical cation reactions and the corresponding neutral, biradical pathways that was already noticed in several other formally pericyclic reactions of radical cations.[2]

The Stepwise Pathways. We will now turn to the possible stepwise pathways leading from **1**$^{\bullet+}$ to **2**$^{\bullet+}$. As a point of departure, the cyclic species **5**$^{\bullet+}$–**7**$^{\bullet+}$ shown in Figure 1 were proposed as possible candidates for cyclic intermediates along a given reaction pathway in analogy to the cyclopropyl carbinyl radical cation intermediate originally proposed by Bauld for the cyclobutene radical cation ring opening.[6d] By calculating the energies of these species, their legitimacy as valid intermediates in the ring closing reaction was readily assessed. The three-membered ring intermediate **5**$^{\bullet+}$ was located as a local minimum with a relative energy of 60.6 kcal/mol. The four-member ring intermediate **6**$^{\bullet+}$ was also located as a local minimum with a relative energy of 50.9 kcal/mol. Since both of these structures are significantly higher in energy than **4**$^{\bullet+}$, which is a first-order saddle point, we concluded that they would not play a significant part in any energetically viable reaction pathway. Therefore, they will not be discussed any further here.

All attempts to locate structure **7**$^{\bullet+}$, which would structurally be similar to the methylene cyclopentene diradical located on the hypersurface of neutral C_6H_8,[17] as a stationary point at the B3LYP level failed. Geometry optimization of an input structure like **7**$^{\bullet+}$ proceeded barrierlessly downhill to the stable bicyclic species **10**$^{\bullet+}$, which has a relative energy of 20.6 kcal/mol. Alternatively, a hydrogen shift would lead to the dihydro fulvene radical cation described previously.[20] However, further consideration of a structure similar to **7**$^{\bullet+}$ led to calculations on **9**$^{\bullet+}$, which resembles what would be expected as a transition structure for the closing of a five-member ring beginning from *cct*-**1**$^{\bullet+}$. The fact that intermediate **10**$^{\bullet+}$ lies much lower energy than either concerted transition structure stimulated further study into a possible stepwise reaction pathway from *cct*-**1**$^{\bullet+}$ to **2**$^{\bullet+}$.

The results of this investigation are summarized in Figure 4. This stepwise pathway starts from *cct*-**1**$^{\bullet+}$, which as mentioned earlier is at a relative energy of 18.6 kcal/mol. The critical distance in this first step of the reaction is between C_1 and C_5, the two carbon centers involved in formation of the five-member ring-like transition structure. The distance from C1 to C_5 in *cct*-**1**$^{\bullet+}$ was found to be 3.18 Å. The pathway then proceeds to transition structure **9**$^{\bullet+}$ with an activation energy of 20.4 kcal/mol at the B3LYP level of theory. Here, the C_1−C_5 distance has shortened substantially to 2.02 Å. Also, the shortening of the C_1−C_5 distance is attended by a concurrent decrease in the C_4−C_6 distance. This C_4−C_6 bond-forming mode anticipates the formation of the bicyclic intermediate **10**$^{\bullet+}$, which then can undergo ring opening via transition structure **11**$^{\bullet+}$ to yield the cyclohexadiene-1,3-diyl **12**$^{\bullet+}$. Transition structure **11**$^{\bullet+}$ was found to be only 5.1 kcal/mol higher in energy than bicyclic **10**$^{\bullet+}$ and represents an extremely late transition state. It is only 0.8 kcal/mol higher than **12**$^{\bullet+}$. The imaginary frequency corresponding to the reaction coordinate for this transformation was found to be −89.7 cm^{-1}, describing an extremely flat hypersurface curvature in the region of the transition structure. As would be expected for the endothermic formation of **12**$^{\bullet+}$, the structure of the transition state **11**$^{\bullet+}$ strongly resembles **12**$^{\bullet+}$. The carbon−carbon bond being broken in this step is at a distance of 2.46 Å in **11**$^{\bullet+}$ and increases to only 2.50 Å in the intermediate **12**$^{\bullet+}$. **12**$^{\bullet+}$ lies in a very shallow well on the hypersurface, and it can be expected that substituent effects could substantially stabilize or destabilize this species. A [1,2]-hydrogen shift via transition structure **13**$^{\bullet+}$ is the final step in the transformation of *cct*-**1**$^{\bullet+}$ to the cyclohexadiene radical cation **2**$^{\bullet+}$. Energetically, **13**$^{\bullet+}$ is 5.2 kcal/mol higher than is **12**$^{\bullet+}$ and is 30.1 kcal/mol higher than **2**$^{\bullet+}$. The bond length of the breaking C−H bond in **13**$^{\bullet+}$ is 1.64 Å.

Two of the structures along the reaction pathway intersect with other parts of the $C_6H_8^{\bullet+}$ hypersurface that have been studied previously. A substituted analogue of **10**$^{\bullet+}$ has been located at the UMP2 level of theory by Roth and Herbertz in association with the ring opening of bicyclic vinyl cyclopropane radical cations.[21] It resides in a local minimum on the hypersurface at an energy 18.4 kcal/mol lower than **9**$^{\bullet+}$. In a recent study of the Diels−Alder reaction of the butadiene radical cation to acetylene, Bouchoux et al. published findings on the conversion of **10**$^{\bullet+}$ to **12**$^{\bullet+}$ via transition structure **11**$^{\bullet+}$ at the UMP2 level of theory.[20] We present here calculations on similar species, exploring a different part of the C_6H_8 hypersurface. The use of B3LYP/6-31G* in our study, though, affords the ability to compare and contrast the results of calculations at a level of theory that is less affected by the problems with spin contamination mentioned earlier. Bouchoux et al. found that **11**$^{\bullet+}$ is 13.2 kcal/mol higher in energy than **10**$^{\bullet+}$ with the overall conversion being endothermic by 8.6 kcal/mol. The results at the B3LYP level show a considerably flatter reaction profile. This is in agreement with other studies that found the hypersurfaces obtained by B3LYP calculations tend to be generally flatter than the ones obtained by MP2 calculations.

Competition of Concerted and Stepwise Pathways. In the previous section we established that the activation energy E_a for the lowest energy concerted reaction pathway is 16.2 kcal/mol and that for the stepwise reaction pathway is 20.4 kcal/mol while several of the other pathways considered are not competitive. This would seem to suggest that the concerted pathway is the preferred pathway of reaction. However, the two relevant transition structures have energies identical within the accuracy that can be expected from the B3LYP/6-31G* methodology used. The difference in activation energies is rather due to the fact that the pathways begin from different starting points, *ccc*-**1**$^{\bullet+}$ and *cct*-**1**$^{\bullet+}$. Although *ccc*-**1**$^{\bullet+}$ is 5.2 kcal/mol higher in energy than *cct*-**1**$^{\bullet+}$, the Curtin−Hammett principle does not apply since they are not in rapid equilibrium. Since the barriers for rotation are substantially different from the ones in neutral **1**, other possibly nonreactive conformations may also have to be considered. Finally, different redox potentials of the neutral conformers might lead to the preferential formation of one of the radical cation rotamers. Therefore, to assess which is the preferred pathway, it is necessary to consider the energetic requirements for the different transformations starting from the neutral hexatrienes **1** at a higher level of theory.

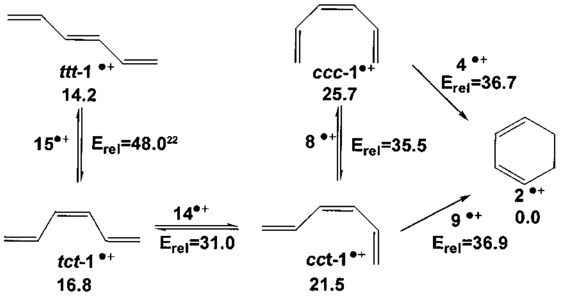

Figure 5. Reaction pathways and relative energies (QCISD(T)/6-311G**//QCISD/6-31G*) for ring closure and isomerization of **1**$^{\bullet+}$.

Before single-electron oxidation of neutral hexatriene, rotation around single bonds occurs readily and the conformers *ccc*-**1** and *cct*-**1** are free to interconvert with a barrier of only 1 kcal/mol. *cct*-**1** is 5.9 kcal/mol lower in energy than *ccc*-**1**, so a substantially larger population of 1,3,5-hexatriene would exist as the conformer *cct*-**1** in the equilibrium. The difference in the adiabatic gas phase oxidation potential calculated at the B3LYP/6-31G* level of theory is only 0.7 kcal/mol, making *cct*-**1** the most readily oxidized of the two conformers by a small margin. It can therefore be expected that the relative population of the two rotamers *ccc*-**1**$^{\bullet+}$ and *cct*-**1**$^{\bullet+}$ is similar to the equilibrium in neutral **1**. However, other rotamers of **1**$^{\bullet+}$ also need to be considered, as discussed below.

To obtained more accurate insights into the two competing pathways, we calculated selected points of the $C_6H_8^{\bullet+}$ hypersurface using the QCISD(T)/6-311G*//QCISD/6-31G* method. This highly correlated MO method has been used frequently for reference calculations[2] and does not suffer from some of the problems of hybrid DFT calculations discussed earlier, but is computationally significantly more demanding. Figure 5 summarizes our results for the concerted and stepwise pathways as well as the relative energies of the relevant rotamers including the activation energies for their interconversion.

The geometries of the different species and the overall picture of the $C_6H_8^{\bullet+}$ hypersurface that emerges from these calculations are very similar to the ones obtained by the B3LYP/6-31G* calculations. The two reactive rotamers of the hexatriene radical cation, *ccc*-**1**$^{\bullet+}$ and *cct*-**1**$^{\bullet+}$, differ by 4.2 kcal/mol in energy and are separated

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[21] (a) Herbertz, T.; Blume, F.; Roth, H. D. *J. Am. Chem. Soc.* **1998**, *120*, 4591. (b) Weng, H. X.; Sheik, Q.; Roth, H. D. *J. Am. Chem. Soc.* **1995**, *117*, 10655. (c) Roth, H. D.; Weng, H. X.; Herbertz, T. *Tetrahedron* **1997**, *53*, 10051.

by a small barrier. The transition structures **4**$^{\bullet+}$ and **9**$^{\bullet+}$ leading to the product radical cation **2**$^{\bullet+}$ are basically identical in energy. Thus, the reaction pathway will be determined by the relative population of the two reactive rotamers.

In addition to *ccc*-**1**$^{\bullet+}$ and *cct*-**1**$^{\bullet+}$, other rotamers such as *tct*-**1**$^{\bullet+}$ and *ttt*-**1**$^{\bullet+}$ have been detected experimentally.[7,8] A direct ring closure is not possible for these rotamers due to the large distance of the carbon termini. Our QCISD(T)/6-311G*//QCISD/6-31G* calculations show that *tct*-**1**$^{\bullet+}$ is 4.7 kcal/mol more stable than *cct*-**1**$^{\bullet+}$. The transition structure connecting this species is lower in energy than the transition structures for ring closure or isomerization to *ccc*-**1**$^{\bullet+}$. The formation of the most stable isomer, *ttt*-**1**$^{\bullet+}$ is a relatively high-energy process,[22] even though the formation of this isomer was observed in the matrix under photochemical conditions.

Summary and Conclusions

The ring-closing reaction of the hexatriene radical cation proceeds via a stepwise pathway involving transition structure **9**$^{\bullet+}$ in the rate determining step. The origin of this pathway is, however, not the lower energy of **9**$^{\bullet+}$ relative to the transition structure of the concerted pathway, **4**$^{\bullet+}$, but rather the lower energy of the starting material for the stepwise pathway. A steady-state approximation for the concerted pathway according to the Curtin−Hammett principle is not justified since the energy of the transition structure for the interconversion of the two rotamers *ccc*-**1**$^{\bullet+}$ and *cct*-**1**$^{\bullet+}$ is comparable in energy to the activation energy for cyclization.

Despite the concerns over the applicability of hybrid density functional methods to radical cations in the literature, the geometries and relative energies obtained from the B3LYP calculations are close to the ones from the computationally much more demanding QCISD(T)//QCISD calculations. An exploration of the hypersurface by B3LYP calculations, followed by more detailed studies of the important portions of the hypersurface at a higher level of theory therefore appears to be a reasonable method for the study of hydrocarbon radical cation reactions. Several of the species on the $C_6H_8^{\bullet+}$ hypersurface resemble the corresponding biradical species on the C_6H_8 hypersurface which has been studied previously.[20,21]

Finally, the origin of the apparent nonreactivity of the hexatriene radical cation is the rapid formation of a rotamer, *tct*-**1**$^{\bullet+}$ where the carbon termini are too far away from each other to close to **2**$^{\bullet+}$. In the sole example of the reaction described in the literature,[11a] the formation of the unreactive rotamer is prevented by locking of a diene unit as a o-quinodimethane unit. Alternative methods would include the use of a conformational bias by appropriate substitution[23] or the incorporation of the diene portion into a di-exomethylene moiety.[11a] Experimental studies to test this hypothesis are currently in progress.

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Supporting Information Available: Cartesian coordinates, total energies, S^2 values, and zero-point corrected energies of all structures as well as imaginary frequencies, where applicable, are available in ASCII format. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] It is interesting to note that **15**$^{\bullet+}$ could not be located at the B3LYP/6-31G* level of theory. For a discussion of the origins of this, compare ref 14 and 16. The zero-point energy correction for this species was thus taken from BH and H calculations, where the localization of the transition structure was easily possible.

[23] Such a conformational bias has been successfully used in the case of the vinylcyclopropane rearrangement: (a) Houk, K. N.; Nendel, M.; Wiest, O.; *J. Am. Chem. Soc.* **1997**, *119*, 10545. (b) Nendel, M.; Sperling, D.; Wiest, O.; Houk, K. N. *J. Org. Chem.* **2000**, *65*, 3259.