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CASSCF and CASPT2 Calculations on the Cleavage and Ring Inversion of Bicyclo[2.2.0]hexane Find that These Reactions Involve Formation of a Common Twist-Boat Diradical Intermediate

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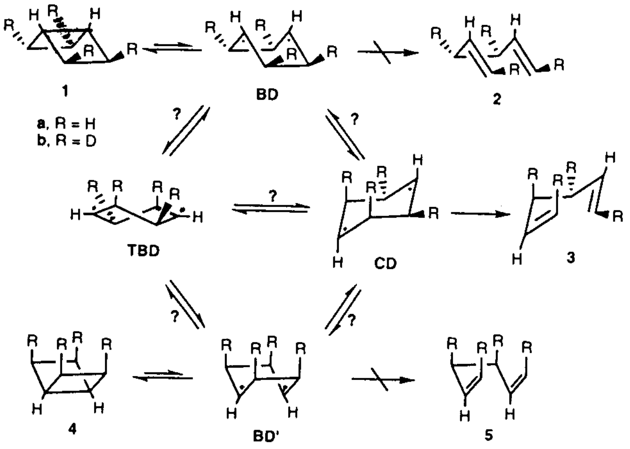
Abstract: (6/6)CASSCF and CASPT2/6-31G* calculations have been performed to understand the experimental finding of Goldstein and Benzon (*J. Am. Chem. Soc.* **1972**, *94*, 5119) that *exo*-bicyclo[2.2.0]hexane-d_4 (**1b**) undergoes ring inversion to form *endo*-bicyclo[2.2.0]hexane-d_4 (**4b**) faster than it undergoes cleavage to form *cis,trans*-1,5-hexadiene-d_4 (**3b**). Goldstein and Benzon also found that the latter reaction, which must occur via a chairlike transition structure (TS), is much faster than cleavage of **1b** to *trans,trans*-1,5-hexadiene-d_4 (**2b**) via a boatlike TS. Our calculations reveal that all three of these reactions involve ring opening of **1**, through a boat diradical TS (**BDTS**), to form a twist-boat diradical intermediate (**TBDI**). **TBDI** can reclose to **4** via a stereoisomeric boat diradical TS (**BDTS′**), or **TBDI** can cleave, either via a half-chair diradical TS (**HCDTS**) to form **3** or via a boat TS (**BTS**) to form **2**. The calculated values of $\Delta H^{\ddagger} = 34.6$ kcal/mol, $\Delta S^{\ddagger} = -1.6$ eu, and $\Delta H^{\ddagger} = 35.2$ kcal/mol, $\Delta S^{\ddagger} = 2.0$ eu for ring inversion of **1** to **4** and cleavage of **1** to **3**, respectively, are in excellent agreement with the values measured by Goldstein and Benzon. The higher value of $\Delta H^{\ddagger} = 37.6$ kcal/mol, computed for cleavage of **TBDI** to **2**, is consistent with the experimental finding that very little **2b** is formed when **1b** is pyrolyzed. The relationships between **BDTS**, **HCDTS**, and **BTS** and the chair and boat Cope rearrangement TSs (**CCTS** and **BCTS**) are discussed.

Pyrolysis of bicyclo[2.2.0]hexane (**1a**) affords 1,5-hexadiene by cleavage of two C−C σ bonds. The detailed mechanism for this apparently simple reaction has been a puzzle for over 30 years.[1]

Pyrolyses of stereochemically labeled derivatives of **1** by Paquette,[2] Roth,[3] and Goldstein[4] and their co-workers have shown that this reaction does not proceed by a least-motion pathway. Instead of **2**, the 1,5-hexadiene that would be formed by a Woodward−Hoffmann-forbidden, retrograde, $_{\sigma}2_s + {}_{\sigma}2_s$ pathway,[5] the major product in each case has been **3**, the stereoisomer expected from an allowed, retrograde, $_{\sigma}2_s + {}_{\sigma}2_a$ reaction.

However, the experiments suggest that the cleavage of **1** to **3** is not a concerted reaction.[1−4] Particularly compelling evidence for a diradical mechanism of the type shown in Scheme 1 comes from the elegant study of Goldstein and Benzon.[4a] They found that *exo*-**1**-d_4 (**1b**) undergoes cleavage almost exclusively to **3b**, with $\Delta H^{\ddagger} = 36.0 \pm 0.3$ kcal/mol; but ring inversion of **1b** to **4b** occurs slightly faster, with $\Delta H^{\ddagger} = 34.4 \pm 1.3$ kcal/mol.

Scheme 1



The formation of **4b** does not completely exclude a concerted, retrograde, $_{\sigma}2_s + {}_{\sigma}2_a$ mechanism for cleavage of **1b** to **3b**, which, fortuitously, has a slightly higher activation enthalpy than ring inversion to give **4b**. However, Occam's razor favors the more economical interpretation of the experimental results, shown in Scheme 1, in which diradicals are involved in the formation of both **3b** and **4b**. In this mechanistic scheme the measured value of $\Delta\Delta H^{\ddagger} = 1.6 \pm 1.0$ kcal/mol between the two pathways in the pyrolysis of **1b** is equal to the difference in enthalpy between the transition structure (TS) that leads to cleavage of the initially formed boat diradical (**BD**) to **3b** and the TS that leads to closure of **BD** to **4b**.

The diradical mechanism, shown in Scheme 1, raises more questions than it answers. For example, is the rate-determining step in the formation of **4** from **1** ring opening of **1** to form **BD** or conformational isomerization of **BD** to the inverted boat diradical (**BD′**)? Is a chair diradical (**CD**) on the reaction path

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[1] For a brief review see: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; pp 163−65.

[2] Paquette, L. A.; Schwartz, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3215.

[3] (a) Roth, W. R., personal communication to Bergman, R. G., cited by Bergman, R. G. in *Free Radicals*; Kochi, J. K., Ed.; Wiley-Interscience: New York, 1973; Vol. 1, p 191. (b) See also: Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 3865.

[4] (a) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 5119. (b) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7147.

[5] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

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in the **BD** → **BD′** conformational change; or, as Alder has suggested,[6] does the conversion of **BD** to **BD′** proceed via a twist boat diradical (**TBD**)?[7] If **TBD** does lie on the reaction path for ring inversion of **1**, is **TBD** an intermediate or a TS?

A pathway that involves **TBD** would allow the interconversion of **1** and **4** to bypass **CD**. However, it is much more difficult to imagine how the cleavage of **BD** to **3** could avoid formation of **CD**. Moreover, if **CD** is the TS for cleavage of **BD** to **3**, **CD** cannot be on the reaction path for ring inversion of **1** to **4**.[8]

As noted by Goldstein and Benzon,[4b] the heat of formation of the TS for the cleavage of **1** to **3** is ca. 12 kcal/mol above that[9] of the chair TS for the Cope rearrangement.[10,11] On the other hand, the heat of formation of the TS that leads from **1** to **3** is very close to the current estimate of the heat of formation[12] of a chair diradical in which there is no through-bond or through-space interaction between the radical centers at C-1 and C-4.[10] If **CD** is the TS leading to **3**, what type of geometry does it have that precludes both types of stabilizing interactions between these radical centers?

Even though small amounts of products, corresponding to **2**, were observed in the pyrolyses of bicyclo[2.2.0]hexanes, substituted with ester[2] or alkyl groups,[3] Goldstein and Benzon found very little **2b**, when **1b** was pyrolyzed.[4a] How much higher in enthalpy is the TS for formation of **2** than the TS for formation of **4**? Does the TS for formation of **2**, like the TS for the boat Cope rearrangement of 1,5-hexadiene,[11] have C_{2v} symmetry?

To answer these questions we have undertaken ab initio calculations of the potential energy surface (PES) for ring inversion and cleavage of **1**. Herein we report the results of our calculations and the conclusions to which they lead, regarding the topography of this portion of the C_6H_{10} PES and the relationship of the TSs on it to the TSs for the chair and boat Cope rearrangements of 1,5-hexadiene.

Computational Methodology

Geometries of stationary points were located with (6/6)CASSCF calculations. The six-orbital active space was comprised of the bonding and antibonding orbitals between the bridgehead atoms, C(1) and C(4) in **1**, and between C(2) and C(3), and C(5) and C(6). The vibrational analyses, necessary to characterize stationary points and to convert the electronic energies into relative enthalpies at 400 K, were also performed at the (6/6)CASSCF level of theory. These CASSCF calculations were carried oue with the Gaussian 98 suite of programs.[13]

The effects of dynamic electron correlation[14] were included by performing (6/6)CASPT2 calculations[15] at the CASSCF geometries, using MOLCAS.[16] The CASSCF wave function had a nearly constant weight of 80.0 ± 0.3% in all of the CASPT2 calculations. The 6-31G* basis set[17] was employed for both types of calculations.

Results and Discussion

The (6/6)CASPT2/6-31G* relative enthalpies of the stationary points are given in Figure 1, along with pictorial representations of their CASSCF geometries. Complete descriptions of the geometries of all the stationary points, their computed vibrational frequencies, their CASSCF and CASPT2 energies, and the zero-point and thermal corrections to these energies are available as Supporting Information.

At both the CASSCF and CASPT2 levels, **1** is calculated to prefer an enantiomeric pair of C_2 equilibrium geometries; but the C_{2v} TS which connects them is computed to be less than 0.1 kcal/mol higher in energy. Cleavage of the C(1)−C(4) bond in **1** is predicted to occur via a C_2 TS, which leads to a D_2 twist-boat diradical intermediate (**TBDI**).[18]

As shown in Figure 1, the two radical centers in **TBDI** are planar and nearly orthogonal to the C(2)−C(3) and C(5)−C(6) bonds; so there is very little interaction between the radical centers, either through space or through these bonds. Consequently, **TBDI** is truly a diradical. This assessment is confirmed by the nearly equal weights ($c_1^2/c_2^2 = 1.28$) of the two most important configurations in the CASSCF wave function, $\Psi = c_1|...b_1^2\rangle - c_2|...b_2^2\rangle + ...$, for **TBDI**. The 28% larger contribution of the configuration in which the b_1 NBMO is doubly occupied shows that the through-space interaction between the nonbonding 2p AOs at C(1) and C(4) is slightly stronger in **TBDI** than the interaction of these AOs through the C(2)−C(3) and C(5)−C(6) bonds.[10]

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[6] Alder, R. W., personal communication to Gajewski, J. J., cited in ref 1.

[7] The possible involvement of a **TBD** was also discussed by Paquette and Schwartz in ref 2.

[8] If **CD** is the TS in the formation of **3**, **CD** must have one and only one imaginary frequency, which corresponds to a vibrational mode that cleaves either the C(2)−C(3) or the C(5)−C(6) bond. However, if **CD** were also an intermediate in the ring inversion of **1** to **4**, **CD** would have no imaginary frequencies; and if it were a TS in both reactions, **CD** would have two imaginary frequencies.

[9] Doering, W. von E.; Toscano, V. G.; Beasley, G. H. *Tetrahedron* **1971**, *27*, 5299.

[10] For reviews of the Cope rearrangement see: (a) Reference 1, pp 166−176. (b) Borden, W. T.; Loncharich, R. J.; Houk, K. N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 213. (c) Houk, K. N.; Li, Y.; Evanseck, J. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 682. (d) Houk, K. N.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81. (e) Wiest, O.; Montiel, D. C.; Houk, K. N. *J. Phys. Chem. A* **1997**, *101*, 8378.

[11] For ab initio calculations on the chair and boat Cope TSs see: (a) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072. (b) Kozlowski, P. M.; Dupuis, M.; Davidson, E. R. *J. Am. Chem. Soc.* **1995**, *117*, 774. For density functional calculations see: (c) Wiest, O.; Black, K. A.; Houk, K. N. *J. Am. Chem Soc.* **1994**, *116*, 10336. (d) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334.

[12] Using the 1981 value for the C−H BDE in forming the isopropyl radical from propane, a heat of formation for a noninteracting chair diradical, 7 kcal/mol above the chair Cope TS, was obtained: Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279. However, a heat of formation for a noninteracting chair diradical, 11 kcal/mol higher than the chair Cope TS, is obtained with the 2 kcal/mol higher secondary C−H BDE measured by Russell et al.: Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.

[13] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

[14] Review: Borden, W. T.; Davidson, E. R. *Acc. Chem. Res.* **1996**, *29*, 87.

[15] Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218.

[16] Andersson, K.; Blomberg, M. R. A.; Fülscher, M. P.; Karlström, G.; Lindh, R.; Malmqvist, P.-Å.; Neogrády, P.; Olsen, J.; Roos, B. O.; Sadlej, A. J.; Schütz, M.; Seijo, L.; Serrano-Andrés, L.; Siegbahn, P. E. M.; Widmark, P.-O., *MOLCAS*, Version 4: University of Lund: Lund, Sweden, 1997.

[17] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[18] At the CASSCF level the D_2 structure is 0.2 kcal/mol higher in energy than a C_2 geometry for this diradical. However, because the D_2 structure has two imaginary frequencies, its enthalpy is computed to be 1.8 kcal/mol lower than that of the C_2 intermediate. At the CASPT2 level the D_2 structure is 0.7 kcal/mol lower in energy than the C_2 structure, and the two negative CASSCF force constants are both positive at the CASPT2 level. In computing the CASPT2 enthalpy of the D_2 diradical intermediate, it makes no sense to use the CASSCF zero-point energy and thermal corrections for the D_2 mountain top. Therefore, for estimating the zero-point energy and thermal corrections to the CASPT2 energy of D_2 **TBDI**, we used the CASSCF values for the C_2 intermediate.

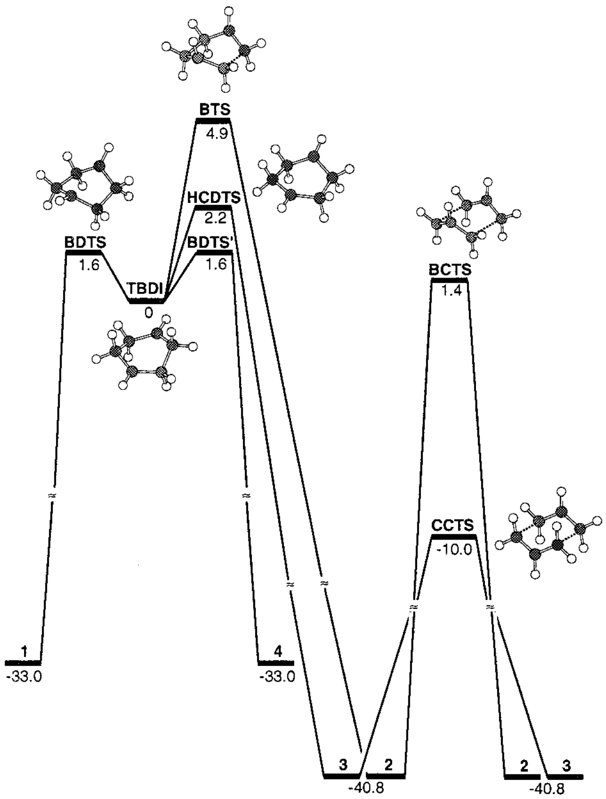
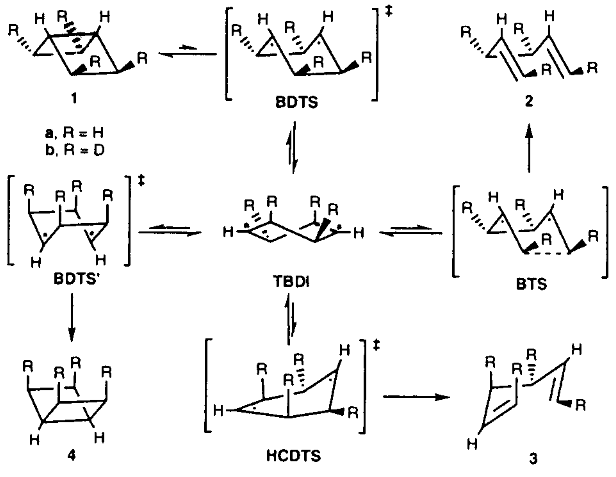


Figure 1. Schematic depiction of the (6/6)CASPT2/6-31G* PES (ΔH in kcal/mol) for inversion of bicyclo[2.2.0]hexane (**1**) to form **4** and for cleavage of **1** to form the stereoisomeric 1,5-hexadienes **2** and **3**. Enthalpies are relative to that of the twist-boat diradical intermediate (**TBDI**). Also shown are the enthalpies of the chair Cope TS (**CCTS**) and the boat Cope TS (**BCTS**), relative to that of **TBDI**.

Scheme 2



Ring inversion of **1** to form **4** is predicted to require passage over two identical TSs, each of which connects directly to **TBDI**. These boat diradical TSs are labeled **BDTS** and **BDTS′** in Scheme 2, which depicts how they interconvert through the intermediacy of **TBDI**.

As shown in Figure 1, the geometry of **BDTS** allows more through-space interaction between the radical centers at C(1) and C(4) than the geometry of **TBDI** does. Consequently, the ratio of $c_1{}^2/c_2{}^2 = 2.73$ in **BDTS** is larger than that in **TBDI**. Nevertheless, the greater H−H eclipsing in **BDTS** than in **TBDI** results in the CASPT2 energy of **BDTS** being 1.6 kcal/mol above that of **TBDI**. Starting from **1**, ring inversion via **1** → **BDTS** → **TBDI** → **BDTS′** → **4** is computed to have $\Delta H^{\ddagger} =$ 34.6 kcal/mol, which is almost exactly the value measured by Goldstein and Benzon.[4a]

Cleavage of **1** to **3** is also predicted to involve the intermediacy of **TBDI**. The TS for this reaction is shown in Figure 1. Since this TS is a half chair diradical, it is labeled **HCDTS** in Figure 1 and Scheme 2.

Like the twist-boat geometry of **TBDI**, the geometry of **HCDTS** precludes either strong through-space or through-bond interactions between the radical centers at C(1) and C(4). Therefore, like **TBDI**, **HCDTS** has slightly less bonding between C(1) and C(4) than **BDTS**, as shown by the fact that the CASSCF wave function for **HCDTS** has $c_1{}^2/c_2{}^2 = 1.50$. Presumably, it is for this reason that the CASSCF and CASPT2 energies and enthalpies of **HCDTS** are all computed to be 0.6−0.8 kcal/mol higher than those of **BDTS**. However, like **BDTS**, **HCDTS** has more H−H eclipsing than **TBDI**; consequently, the CASPT2 enthalpy of **HCDTS** is 2.2 kcal/mol greater than that of **TBDI**.

Passage over **HCDTS** converts the D_2 geometry of **TBDI** into a C_{2h} chair geometry, from which cleavage to **3** can occur without any additional barrier.[19] The CASPT2 enthalpy difference of 0.6 kcal/mol between **HCDTS** for cleavage of **1** to **3** and **BDTS** for ring inversion in **1** to form **4** is slightly smaller than, but just within experimental error of Goldstein and Benzon's value of $\Delta\Delta H^{\ddagger} = 1.6 \pm 1.0$ kcal/mol.

As noted in the introduction, the experimental heat of formation of the TS (**HCDTS**) that leads from **1** to **3** is ca. 12 kcal/mol higher than that of the chair Cope TS (**CCTS**) for the degenerate rearrangement of **3**. However, as also noted, the experimental heat of formation of **HCDTS** is very close to the current estimate[12] of the heat of formation of a chair cyclohexane-1,4-diyl in which there is no through-bond or through-space interaction between the radical centers.

As shown in Figure 1, the CASPT2/6-31G* difference between the heats of formation of **HCDTS** and **CCTS** is, in fact, $\Delta\Delta H^{\ddagger} = 12.2$ kcal/mol. The value of $c_1{}^2/c_2{}^2 = 1.50$ in **HCDTS** makes it easy to understand why, experimentally, the TS for cleavage of **1** to **3** has about the same heat of formation as that expected for a chair cyclohexane-1,4-diyl in which the radical centers do not interact, either through space or through the C(2)−C(3) and C(5)−C(6) bonds.[12]

In addition to reclosing to **1** (via **BDTS**), or closing to **4** (via **BDTS′**), or cleaving to form **3** (via **HCDTS**), **TBDI** can also undergo cleavage to **2** via a boat TS (**BTS**). To compute the enthalpy difference between **BTS** for cleavage of **TBDI** to **2** and **HCDTS** for cleavage of **TBDI** to **3**, we attempted to locate **BTS**.

At the CASSCF level we found two C_{2v} stationary points[20] along a path connecting **TBDI** to the TS for the boat Cope

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[19] At the CASSCF level there is a chair diradical intermediate, which is 5.7 kcal/mol lower in enthalpy than **TBDI**, and to which **TBDI** is connected by **HCDTS**. Cleavage of this C_{2h} diradical intermediate to **3** requires passage over a C_2 TS, but with an enthalpic barrier of only 0.2 kcal/mol. However, the existence of this intermediate is an artifact of the absence of dynamic electron correlation from the (6/6)CASSCF wave function.[14] At the CASPT2 level this intermediate disappears, leaving the TS for the chair Cope rearrangement as the only C_{2h} stationary point on the CASPT2 potential surface.[11]

[20] (a) One of these stationary points is a minimum in C_{2v} symmetry, with CASSCF and CASPT2 energies that are respectively 5.4 and 7.3 kcal/mol higher than that of **TBDI**. However, on the global CASSCF PES this C_{2v} minimum is the TS for interconverting enantiomeric D_2 conformations of **TBDI**. (b) We also located a C_{2v} CASSCF energy maximum, with C(3)−C(4) and C(5)−C(6) bond lengths of 1.837 Å and CASSCF and CASPT2 energies that are, respectively, 8.6 and 5.3 kcal/mol above that of **TBDI**. However, a vibrational analysis showed that this C_{2v} stationary point has large imaginary frequencies for two vibrations; hence, it is a mountain top on the global CASSCF PES.

rearrangement (**BCTS**).[11] However, neither of these stationary points proved to be the CASSCF TS for cleavage of **TBDI** to **2**, and neither is even a stationary point on the CASPT2 PES. Previous CASPT2 calculations have found that, other than **1**, the only C_{2v} stationary point is the boat Cope TS (**BCTS**).[11a]

We were able to locate a true CASSCF TS for the direct cleavage of **TBDI** to **2**, which does not involve passage through **BCTS**.[21] Starting from the CASSCF C_{2v} mountain top that we found,[20b] we searched along displacements that were equal combinations of the two vibrations with imaginary frequencies. One of these vibrations corresponds to in-phase and the other to out-of-phase stretching of the C(2)−C(3) and C(5)−C(6) bonds. Displacements that are equal combinations of these two vibrational modes leave the length of one of these C−C bonds the same as at the C_{2v} mountain top but shorten or lengthen the other C−C bond. Searching in this manner led to a true CASSCF TS, with C_s symmetry and with one unique C−C bond length of 1.846 Å and the other 1.692 Å. The geometry of the boat TS (**BTS**) for cleavage of **TBDI** to **2** is depicted in Figure 1.

BTS has $c_1^2/c_2^2 = (3.29)^{-1}$; hence, it has less diradical character than **BDTS**, **BDTS′**, and **HCDTS**—the TSs which connect **TBDI** to respectively **1**, **4**, and **3**. Nevertheless, as shown in Figure 1, the CASPT2 enthalpy of **BTS** for formation of **2** is 3.3 kcal/mol above that for **BDTS** and **BDTS′** and 2.7 kcal/mol above that for **HCDTS**. Major contributors to the higher energy of **BTS** are its boat geometry and the relatively short bonds between C(2)−C(3) and C(5)−C(6), which allow significant through-space interaction betweeen the nonbonding AOs at C(1) and C(4). Because the ratio $c_1^2/c_2^2 < 1$ in **BTS**, through-bond coupling is dominant in this TS. Therefore, the interaction between the AOs at C(1) and C(4) is antibonding and, hence, destabilizes **BTS**.[10]

On the basis of the calculated enthalpy difference of 2.7 kcal/mol between **BTS** and **HCDTS**,[22] at most a few percent of **2b** would have been present in the **3b** that Goldstein and Benzon found to be, by far, the major product in the pyrolysis of **1b**. However, the rather long C(2)−C(3) bond in **BTS** should result in its energy being lowered by radical-stabilizing substituents at these two carbons, relative to the energy of **HCDTS**. Thus, the larger amounts of products, analogous to **2**, that were observed in the pyrolyses of derivatives of **1** with radical stabilizing substituents at C(2) and C(3)[2,3a] can easily be rationalized.

Summary and Conclusions

The results of our calculations provide the answers to the questions posed in the introduction. As depicted in Figure 1 and Scheme 2, ring opening of **1** leads to a twist boat diradical intermediate (**TBDI**). It is computed to have a barrier of only 1.6 kcal/mol to closure to **4** or reclosure to **1** via boat diradical TSs **BDTS′** and **BDTS**, respectively. The computed enthalpy of activation for ring inversion (**1** → **4**) of $\Delta H^{\ddagger} = 34.6$ kcal/mol is essentially the same as the value of $\Delta H^{\ddagger} = 34.4 \pm 1.3$ kcal/mol measured by Goldstein and Benzon for **1b** → **4b**.[4]

Also in excellent agreement with their experimental results on the pyrolysis of **1b** is our finding that cleavage of **1** to **3**, via a half chair diradical TS (**HCDTS**), has a slightly higher enthalpy of activation than ring inversion. At the CASPT2 level we calculate $\Delta\Delta H^{\ddagger} = 0.6$ kcal/mol, which is slightly smaller than, but within experimental error of Goldstein and Benzon's value of $\Delta\Delta H^{\ddagger} = 1.6 \pm 1.0$ kcal/mol.[4]

HCDTS really is a diradical, as shown by the value of $c_1^2/c_2^2 = 1.50$ in **HCDTS** being close to unity. Thus, it is understandable that the experimental heat of formation of the TS for cleavage of **1** to **3**[4] is approximately the same as that estimated for a chair diradical in which the radical centers do not interact.[12]

The boat TS (**BTS**) for cleavage of **TBDI** to **2** has $c_1^2/c_2^2 = (3.29)^{-1}$, so it has significantly less diradical character than **HCDTS**. Nevertheless, **BTS** is computed to be 2.7 kcal/mol higher in enthalpy than **HCDTS**. Since through-bond interactions are dominant in **BTS**, it is presumably destabilized by antibonding between the radical centers at C(1) and C(4).

The CASSCF values of $\Delta S^{\ddagger} = -1.6$ and 2.0 eu for **1** → **BDTS** and **HCDTS**,[23] respectively, agree very well with the experimental values of $\Delta S^{\ddagger} = -0.7 \pm 1.6$ eu for ring inversion of **1b** to **4b** and $\Delta S^{\ddagger} = 1.5 \pm 0.6$ eu for cleavage of **1b** to **3b**.[4] Therefore, not only our calculated enthalpies of activation, but also our computed entropies of activation for these two reactions are in very good agreement with those measured by Goldstein and Benzon.[4] In addition to suggesting that the TSs that we have found are quite good approximations to the actual TSs for ring inversion and cleavage of **1**, this agreement provides additional evidence[11a] of the ability of (6/6)CASPT2 calculations to reproduce with high accuracy that portion of the C_6H_{10} PES on which **1**−**4** and the TSs that connect them lie.

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Supporting Information Available: Optimized geometries and energies for all the stationary points discussed in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) **BCTS** cannot simultaneously be the TS for the boat Cope rearrangement and the TS for cleavage of **TBDI**; otherwise **BCTS** would have more than one imaginary frequency. Therefore, cleavage of **TBDI** to **2** via **BCTS** would have to pass over a TS, higher in energy than **BCTS**, whose imaginary frequency would be for a vibration that connected **TBDI** with **BCTS**. However, repeated searches failed to find such a TS.

(22) Since these TSs were located at the CASSCF level, they are probably close to but not exactly at the geometries of the true TSs on the CASPT2 PES. Unfortunately, analytical gradients are not available for CASPT2 wave functions; so locating the CASPT2 TSs precisely would be a daunting task.

(23) The calculated value of $\Delta S^{\ddagger} = 3.4$ eu for passage over **BTS** is 1.5 eu larger than that for passage over **HCDTS**.