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[1,5] Sigmatropic Hydrogen Shifts in Cyclic 1,3-Dienes

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Density functional calculations have been carried out for [1,5] hydrogen shifts in 1,3-cycloalkadienes (cyclohexadiene, cycloheptadiene, and cyclooctadiene). The complexity of the potential surfaces of these reactions was found to increase with ring size. For 1,3-cyclohexadiene a single transition structure for the [1,5] hydrogen shift was located, which connects the two enantiomeric conformers. For 1,3-cycloheptadiene two enantiomeric transition structures for the [1,5] hydrogen shift were located, which interconnect three conformers of the diene, a pair of enantiomeric conformers and a third achiral conformer. Finally for 1,3-cyclooctadiene two diastereomeric transition structures were found in addition to six conformers (three pairs of enantiomeric conformers) of the diene. Calculated activation energies for the [1,5] hydrogen shifts were found to be in qualitative agreement with experiment. Variation in these energies are attributed to strain energies present in either the diene or the transition structure.

Introduction

That a conjugated diene may be converted thermally to an isomeric molecule through transfer of a hydrogen from one end of the pentadienyl system to the other was uncovered some 100 years ago.[1] These [1,5] hydrogen shift reactions received fresh scrutiny in the early 1960s, as gas chromatography and NMR spectroscopy facilitated analyses and identifications of isomers.[2] Degenerate [1,5] hydrogen shifts in cyclic conjugated dienes were demonstrated through deuterium-labeling experiments,[3] and kinetic work to define activation parameters began to appear.[4]

These thermal transformations were recognized by Woodward and Hoffmann in their seminal 1965 publication on sigmatropic reactions as orbital symmetry allowed, concerted processes involving suprafacial transfer of hydrogen across a pentadienyl π-system.[5] Most significantly, they perceived the reactions to be special cases of a general class of transformations, [*i*,*j*] sigmatropic rearrangements, each having favored stereochemical characteristics whenever mechanistically concerted.

When the present study was initiated, the literature had recorded activation energies for [1,5] hydrogen shifts in conjugated deuterium-labeled cyclopentadienes,[4] cyclohexadienes,[6] cycloheptadienes,[7] and cyclooctadienes[8] of 24, 41, 29, and 30 kcal/mol, respectively. On closer scrutiny, the experimental studies providing these values seemed less than optimal, each for different reasons.

The kinetic study for cyclopentadiene reported by Roth in 1964 involved [1,5] deuterium shifts interconverting d_5-cyclopentadiene isomers.[4] The recorded activation energy, 24.3 ± 0.5 kcal/mol, may well be somewhat higher that the E_a value one might determine through a kinetic study of the isomerizations interconverting the three monodeuteriocyclopentadienes.

The [1,5] hydrogen shifts in deuterium-labeled 1,3-cyclohexadienes were followed by de Dobbelaere; kinetic experiments at 305−330 °C led to $\Delta H^{\ddagger}$ of 40 kcal/mol, or E_a of 41 kcal/mol.[6] His clever choice of starting material, 1,4-d_2-cyclohexadiene, provided for an easy kinetic analysis over short reaction times based on the reversible equilibration of but two isomers, but when deuterium [1,5] shifts become of significance the kinetic situation is far more complicated. The details of this kinetic study have not been published.

In 1963 Mironov and co-workers followed isomerizations for monodeuterio 1,3-cycloheptadienes as the tem-

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[1] Buchner's late 19th and early 20th century investigations of [1,5] hydrogen shifts interconverting isomeric methoxycarbonylcycloheptatrienes have been summarized and in part reformulated; see (a) Grundmann, C.; Ottmann, G. *Liebigs Ann. Chem.* **1953**, *582*, 163. (b) Doering, W. von E.; Laber, G.; Vonderwahl, R.; Chamberlain, N. F.; Williams, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 5448. (c) Alder, K.; Jungen, H.; Rust, K. *Liebigs Ann. Chem.* **1957**, *602*, 94.

[2] (a) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Dokl. Akad. SSSR* **1962**, *143*, 1112. (b) Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, 2077. (c) ter Borg, A. P.; Kloosterziel, H.; Van Meurs, N. *Proc. Chem. Soc.* **1962**, 359. (d) ter Borg, A. P.; Kloosterziel, H.; Van Meurs, N. *Recl. Trav. Chim. Pays-Bas* **1963**, *82*, 717. (e) Glass, D. S.; Zirner, J.; Winstein, S. *Proc. Chem. Soc.* **1963**, 276.

[3] Mironov, V. A.; Sobolev, E. V.; Elizarova, A. N. *Tetrahedron* **1963**, *19*, 1939.

[4] Roth, W. R. *Tetrahedron Lett.* **1964**, 1009.

[5] (a) Woodward, R. B.; Hoffmann, R. *J. Am. Chem. Soc.* **1965**, *87*, 2511. (b) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, 1970.

[6] de Dobbelaere, J. R.; van Zeeventer, E. L.; de Haan, J. W.; Buck, H. M. *Theor. Chim. Acta* **1975**, *38*, 241.

[7] Mironov, V. A.; Chizhov, O. S.; Kimelfeld, Ya, M.; Akhrem, A. A. *Tetrahedron Lett.* **1969**, 499.

[8] Glass, D. S.; Boikess, R. S.; Winstein, S. *Tetrahedron Lett.* **1966**, 999.

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perature varied between 140 and 160 °C.[7] They started with the 2-*d* isomer and analyzed data for the reversible interconversion of 2-*d* and 1-*d* isomers, rather than using kinetic expressions appropriate to the four-isomer problem.[9] They estimated E_a values for the two isomerizations of 29.5 ± 1.5 and 28.6 ± 1.5 kcal/mol. Neither the primary data nor a clear explication of the data-reduction protocol employed was provided.

A 1966 kinetic study of the thermal isomerizations among the four monodeuterio 1,3-cyclooctadienes led to $E_a = 30.1$ kcal/mol.[8] Limitations posed by the experimental methods available at that time for analyzing mixtures of the four isomers—60 MHz proton NMR spectroscopy—inevitably led to relative large error limits.

There have been numerous theoretical studies of [1,5] hydrogen shifts in pentadienes. Early semiempirical calculations on this reaction predicted a C_s-symmetric, suprafacial transition structure in agreement with Woodward and Hoffmann's proposed mechanism.[10,11] The transfer is indeed suprafacial, rather than dependent on a linear C⋯H⋯C hydrogen transfer. Subsequently, STO-3G[12] and 3-21G[13] ab initio calculations on *cis*-1,3-pentadiene also predicted a suprafacial transition structure for the [1,5] hydrogen migration with C_s symmetry. Since then the results of a number of calculations of increasing sophistication have agreed at least qualitatively with the earlier calculations.[14−20]

Theoretical studies on degenerate hydrogen shifts in cyclic dienes have been less extensive. Precise refinements of calculated transition structure energies and geometries, as well as considerations of possibly important charge-transfer effects for the C_5H_6 system, have been durable concerns, while less work has been invested in the [1,5] hydrogen shifts shown by larger cyclic dienes.

As examples of the archetypal sigmatropic transformation, the simplest reaction of this large class, one uniformly understood to be mechanistically concerted[21] by way of a stereochemically well-defined suprafacial path, thermal [1,5] hydrogen shifts in cyclic dienes seemed well worth further, more detailed study from both experimental and theoretical sides. One could hope that variations in activation parameters could be defined and correlated with ground state and transition structure geometries and energies as geometrical constraints varied with ring size.

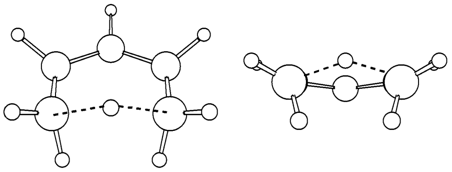
One step toward this goal has already been taken, a kinetic study of [1,5] hydrogen shifts for the four monodeutereio 1,3-cyclooctadienes.[22] The value of E_a determined, 29.0 ± 0.6 kcal/mol, was well within the error limits associated with the value reported earlier,[8] but 1.1 kcal/mol lower.

Computational Methods

Calculations were performed using GAUSSIAN 98W.[23] The density functional method was employed using B3LYP, Becke's three-parameter hybrid method[24] with the Lee−Yang−Parr correlation functional[25] and the 6-31G* basis set.[26] All stationary points were characterized by computation of second derivatives. All energies reported here include zero point energy corrections calculated with unscaled B3LYP/6-31G* frequencies obtained analytically with G98W. Internal reaction coordinate calculations[27] were used to determine reaction pathways.

Computational Results

***cis*-1,3-Pentadiene.** Two groups have recently reported DFT B3LYP/6-31G* results for the [1,5] hydrogen shift in *cis*-1,3-pentadiene.[19,20] They calculated an activation energy of 36.6 kcal/mol for the hydrogen shift via the suprafacial transition structure **PDTS**, shown in two perspectives.



PDTS

(2*E*,4*Z*)-Heptadiene. To have an estimate of the effect of alkyl substitution on the [1,5] hydrogen shift in pentadiene, calculations were performed on its dimethyl derivative, (2*E*,4*Z*)-heptadiene (**HD**). The structures of the lowest energy conformation of **HD**, the *s-trans* rotamer, and the transition structure for the [1,5] hydrogen shift (**HDTS**) were located. The activation energy (with zero point energy corrections), the difference between the energies of these two structures, was calculated to be 36.6 kcal/mol.

1,3-Cyclopentadiene. DFT B3LYP/6-31G* calculations for the degenerate rearrangement of 1,3-cyclopentadiene (**C5**) via **C5TS** were reported by Alkorta and

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(9) Baldwin, J. E.; Leber, P. A.; Lee, T. W. *J. Chem. Educ.* **2001**, *78*, 1394.

(10) Dewar, M. J. S.; Healy, E. F.; Ruiz, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 2666.

(11) Liu, Y.-P.; Lynch, G. C.; Truong, T. N.; Lu, D.-H.; Truhlar, D. G.; Garrett, B. C. *J. Am. Chem. Soc.* **1993**, *113*, 2408.

(12) Bouma, W. J.; Vincent, M. A.; Radom, L. *Int. J. Quantum Chem.* **1978**, *14*, 767.

(13) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7185.

(14) Rondan, N. G.; Houk, K. N. *Tetrahedron Lett.* **1984**, *25*, 2519.

(15) Hess, B. A., Jr.; Schaad, L. J.; Pancir, J. *J. Am. Chem. Soc.* **1985**, *107*, 149.

(16) Kahn, S. D.; Hehre, W. J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291.

(17) Carpenter, J. E.; Sosa, C. P. *THEOCHEM* **1994**, *311*, 325.

(18) Alkorta, I.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2497.

(19) Jursic, B. S. *THEOCHEM* **1998**, *423*, 189.

(20) Saettel, N. J.; Wiest, O. *J. Org. Chem.* **2000**, *65*, 2331.

(21) Doering, W. von E.; Roth, W. R.; Breuckmann, R.; Figge, L.; Lennartz, H. W.; Fessner, W. D.; Prinzbach, H. *Chem. Ber.* **1988**, *121*, 1.

(22) Baldwin, J. E.; Leber, P. A.; Lee, T. W. *J. Org. Chem.* **2001**, *66*, 5269.

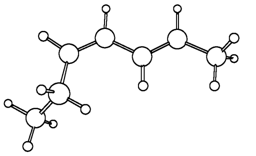
(23) *Gaussian 98W*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; 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.; 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, Inc.: Pittsburgh, PA, 1998.

(24) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

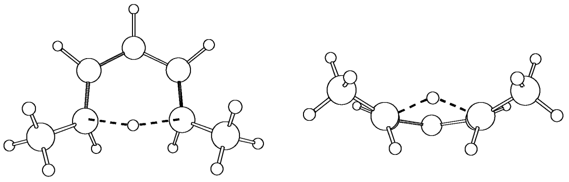
(25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(26) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(27) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154; *J. Phys. Chem.* **1990**, *94*, 5523.

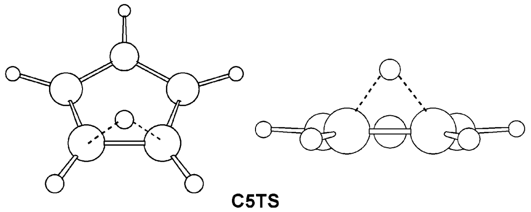


HD



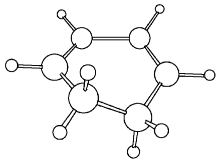
HDTS

Elguero in 1998. The activation energy for this reaction was calculated to be 27 kcal/mol.[18]

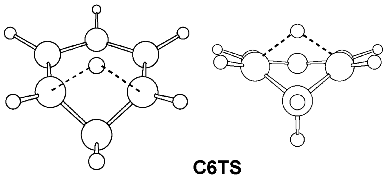


C5TS

1,3-Cyclohexadiene. A single minimum (**C6**) was located for 1,3-cyclohexadiene. It has C_2 symmetry with the C_2 axis passing through the centers of the C2−C3 and C5−C6 bonds and with a dihedral angle of the four sp^2 carbons of 13.4°. Its structure is very similar to the SCF structure reported earlier by Sygula and Rabideau.[28] The two enantiomeric forms of 1,3-cyclohexadiene (**C6** and ***ent*-C6**) are intercoverted via a planar cyclohexadiene (**C6TS**). The barrier for this inversion calculated with DFT is 1.8 kcal/mol, about one-half that obtained previously with an SCF calculation[28] and less than the most recently published experimental estimate, 3.2 kcal/mol.[29] An earlier MP2/6-31G* calculation gave a barrier of 3.6 kcal/mol.[29]



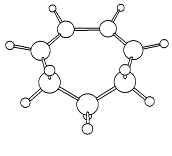
C6



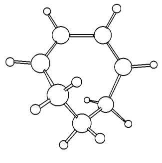
C6TS

The transition structure for the [1,5] hydrogen shift (**C6TS**) was located and found to have C_s symmetry. An IRC calculation showed that the transition structure **C6TS** connects the enantiomeric conformers of 1,3-cyclohexadiene. The calculated E_a for the [1,5] hydrogen shift is 41.9 kcal/mol.

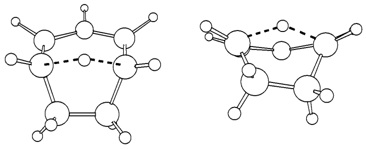
1,3-Cycloheptadiene. Computations have previously shown that there are two dominant conformers of 1,3-cycloheptadiene, one with C_s and the other with C_2 symmetry, and they are very close in energy. SCF results[30,31] predict the C_s conformer to be the more stable, whereas MP2 calculations[31] indicate that the C_2 conformer should be the more stable. However, single point calculations with MP3 reverses the MP2 ordering, finding the C_s structure is favored by 0.805 kcal/mol.[31] Experiments suggest that cycloheptadiene most likely exists in the C_s conformation in which six carbons lie in a plane with the seventh carbon out of the plane.[32,33]



C7a



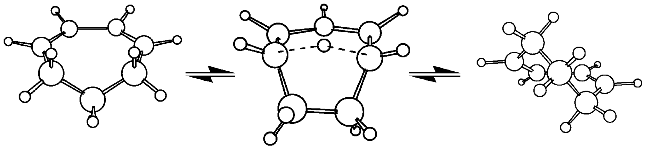
C7b



C7TS

With DFT two minima were located for 1,3-cycloheptadiene (**C7a** and **C7b**) with the lower energy conformer having C_s symmetry (**C7a**) and the higher energy conformer (**C7b**) C_2 symmetry. They differ in energy by 2.8 kcal/mol. **C7b** has an enantiomer, ***ent*-C7b**. The conformers **C7a** and **C7b** are interconverted through transition structure **C7aC7bTS**, according to IRC calculations. It lies 4.1 kcal/mol higher in energy than **C7a**. This transition structure is similar in energy and structure to that reported earlier.[31] Note that the two enantiomeric forms of **C7b** are interconverted in a two-step process via conformer **C7a**, passing through two transition structures, **C7aC7bTS** and ***ent*-C7aC7bTS** (Scheme 1).

A transition structure of C_1 symmetry for the [1,5] hydrogen shift, **C7TS**, was located and calculated to be 33.7 kcal/mol above the lower energy conformer, **C7a**. An IRC calculation indicated that the transition structure **C7TS** links the conformers **C7a** and **C7b**. Its mirror image, ***ent*-C7TS**, similarly links **C7a** and ***ent*-C7b** via a [1,5] hydrogen shift.



C7a **C7TS** **C7b**

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(28) Sygula, A.; Rabideau, P. W. *THEOCHEM* **1992**, *94*, 117.

(29) Autrey, D.; Choo, J.; Laane, J. *J. Phys. Chem. A* **2001**, *105*, 10230.

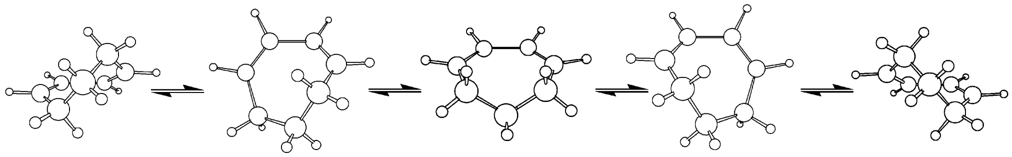
(30) Ehrendorfer, C.; Karpfen, A. *THEOCHEM* **1994**, *112*, 139.

(31) Nevins, N.; Stewart, E. L.; Allinger, N. L.; Bowen, J. P. *J. Phys. Chem.* **1994**, *98*, 2056.

(32) Haga, K.; Traetteberg, M. *Acta Chem. Scand.* **1972**, *26*, 3643.

(33) Avirah, T. K.; Malloy, T. B., Jr.; Cook, R. L. *J. Chem. Phys.* **1979**, *71*, 2194.

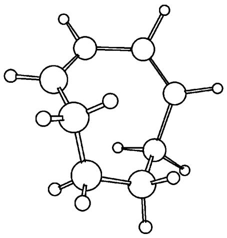
SCHEME 1



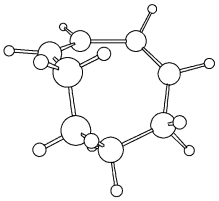
ent-C7b *ent*-C7aC7bTS C7a C7aC7bTS C7b

1,3-Cyclooctadiene. In 1976 Allinger reported that molecular mechanics calculations suggested there should be two conformers of *cis*,*cis*-1,3-cyclooctadiene very close in energy.[34] This is in agreement with an earlier ^{13}C NMR study by Anet and Yavari,[35] who concluded that there are two conformers present "as a nearly equal mixture". They assigned one conformer to a twist-boat-chair (TBC) with C_2 symmetry and the other to a twist-boat (TB) with C_1 symmetry. A more recent SCF study by La Manna and Duca reported only a single conformer with C_1 symmetry.[36]

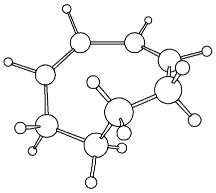
We located with the DFT method three conformers of 1,3-cyclooctadiene, **C8a**, **C8b**, and **C8c**. **C8b** and **C8c** were higher in energy than **C8a** by 0.6 and 5.5 kcal/mol, respectively. Both **C8a** and **C8c** have C_2 symmetry with the C_2 axis passing through C2−C3 and C6−C7 bonds, whereas **C8b** has C_1 symmetry. These DFT results are in very good agreement with Anet's earlier NMR study in which he found two conformers very close in energy, the former with C_2 symmetry (TBC, **C8a**) and the latter with C_1 symmetry (TB, **C8b**). Our finding a third conformer is not in conflict with Anet's results, since it is calculated to be significantly higher in energy than the other two and therefore would not have been observed in Anet's NMR study (see further discussion of this point below).



C8a



C8b

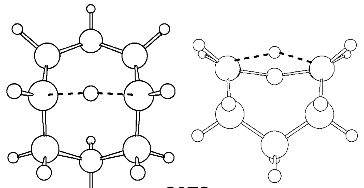


C8c

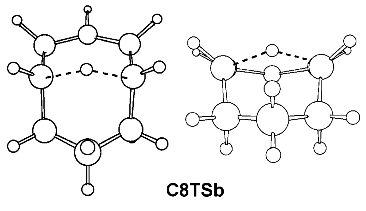
The question then arises how these three conformers are interconverted. A search of the potential surface yielded three transition structures (**C8aC8cTS**, **C8cC8bTS**, and **C8bC8bTS**), which were shown by IRCs to link the three conformers (**C8a**, **C8b**, and **C8c**) and provide a pathway for the three conformers to reach an equilibrium mixture (Figure 1). Ten of the eleven stationary-point structures are chiral; the exception is **C8bC8bTS**, which has C_s symmetry. **C8bC8bTS** links **C8b** and its enantiomer, ***ent*-C8b**, and as a result "connects" the enantiomeric set of conformers and transitions structures. For example, for **C8a** to racemize it must go through an elaborate pathway involving a sequence of conversions, to conformers **C8c**, **C8b**, ***ent*-C8b**, ***ent*-C8c,** and finally to ***ent*-C8a** in turn, passing through five transition structures along the pathway.

This pathway differs in two respects from the one obtained with force field calculations[37] by Anet.[35] First, he reported that **C8a** and **C8b** were linked by a transition structure with C_2 symmetry, while our results predict that these two minima are connected via a C_2-symmetric *intermediate*, **C8c**. There are two intervening transition structures of C_1 symmetry (see Figure 1). While of course it is not certain that our pathway is the correct one for connecting these two minima of nearly equal energy, the pathway proposed by Anet cannot be correct. His pathway connecting these two minima (one of C_1, the other of C_2 symmetry) has a C_2 transition structure that violates the symmetry rules of Pechukas for transition structures.[38,39] Second, Anet found two pathways with transition structures of different energy for the "racemization" of **C8b**, whereas we located only one pathway with the DFT method. Anet obtained from his NMR studies a free energy of activation of 9.1 kcal/mol for the interconversion of **C8a** and **C8b**; this value is in fine qualitative agreement with our computed activation energies for the two reactions, 7.8 kcal/mol for **C8a** to **C8b** and 7.3 kcal/mol for **C8b** to **C8a**.

Given that three conformers of 1,3-cyclooctadiene were found, it was not surprising that two different transition structures for the [1,5] hydrogen shift were located, **C8TSa** and **C8TSb**. The former was calculated to be 3.2



C8TSa



C8TSb

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(34) Allinger, N. L.; Viskocil, J. F., Jr.; Burkert, U.; Yuh, Y. *Tetrahedron* **1976**, *32*, 33.

(35) Anet, F. A. L.; Yavari, I. *Tetrahedron Lett.* **1975**, *19*, 1567; *J. Am. Chem. Soc.* **1978**, *100*, 7814.

(36) La Manna, G.; Duca, D. *J. Mol. Struct.* **1996**, *111*, 109.

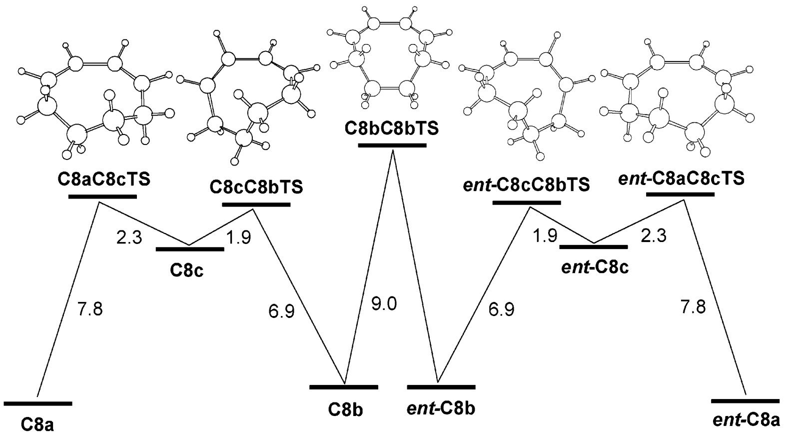

FIGURE 1. Conformers of 1,3-cyclooctadiene and the transition structures linking them. Energies are in kcal/mol.

kcal/mol lower in energy than the latter. Both transition structures have C_s symmetry, which suggests that they each link a pair of enantiomeric conformers. IRC calculations confirmed this, with **C8TSa** connecting **C8b** and ***ent*-C8b** with an activation energy of 31.4 kcal/mol and **C8TSb** connecting the lower energy conformers of the ground state **C8a** and ***ent*-C8a** with an activation energy of 35.2 kcal/mol. The computation of the activation energy of the [1,5] hydrogen shift in 1,3-cyclooctadiene to be compared with that from experiment is considered below.

Discussion

We have chosen the [1,5] hydrogen shift in *cis*-1,3-pentadiene (**PD**) as the "model" reaction to facilitate comparisons with the [1,5] shifts in the cycloalkadienes studied here. There are two conformations of *cis*-1,3-pentadiene, *s-cis* and *s-trans*; the latter is calculated with DFT to be 3.7 kcal/mol more stable than the former.[20] The DFT geometry of the transition structure for the [1,5] hydrogen shift, **PDTS**, is shown in Figure 2.[19,20] As pointed out by Saettel and Wiest,[20] the energy difference between the *s-trans* conformer and the transition structure gives the activation energy for this reaction, and with DFT it was found[20] to be 36.6 kcal/mol, in excellent agreement with the experimental[40] value of 36.3 ± 0.5 kcal/mol.

Since the cycloalkadienes studied here all have carbons substituted at the 1 and 5 positions of the parent pentadienyl π-system, we carried out DFT calculations on (2*E*,4*Z*)-heptadiene (**HD**). It gives rise to a transition structure (**HDTS**) very similar in structure to that of the parent system (Figure 2).

Perhaps more importantly, the activation energy for the hydrogen migration is computed to be identical (36.6 kcal/mol) to that calculated for the parent pentadiene system. Peripheral methyl substitution at C1 and C5 of the pentadienyl core affects neither the transition state geometry greatly (see Figure 2) nor the energy of activation. Hence, the choice of 1,3-pentadiene as a model system for comparison with the cycloalkadienes is a reasonable one: in cyclic dienes changes from system to system may be considered related to variations in geom-

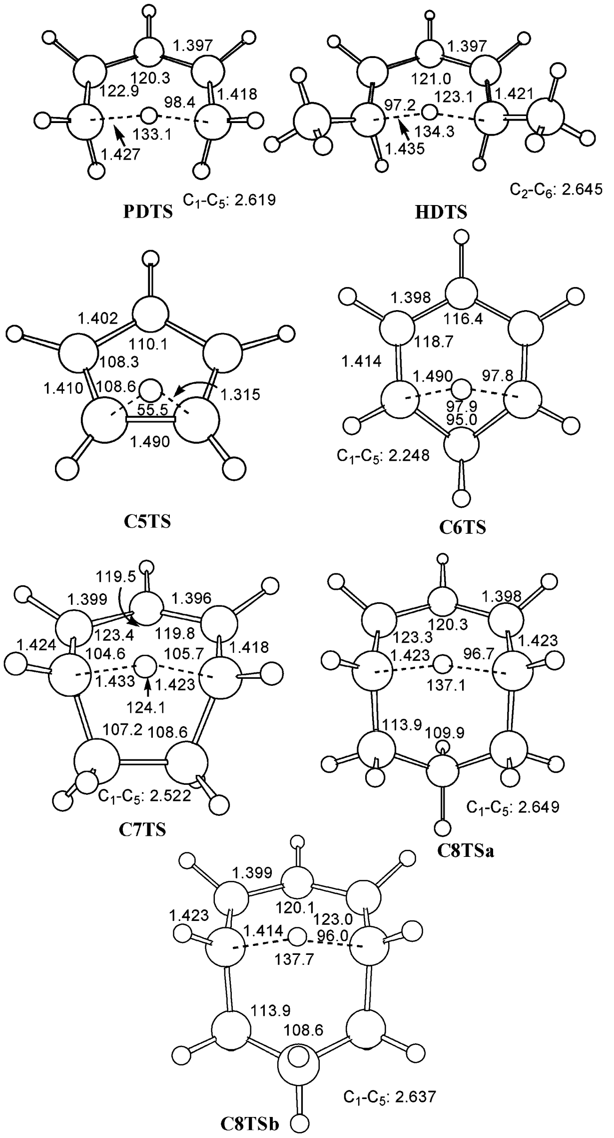

FIGURE 2. Partial geometries of transition structures. **PDTS**[15,17] and **C5TS**[18] results are from previous calculations.

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(37) Boyd, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 5353; *J. Chem. Phys.* **1968**, *49*, 2574.

(38) Pechukas, P. *J. Chem. Phys.* **1976**, *64*, 1516.

(39) Schaad, L. J.; Hu, J. *J. Am. Chem. Soc.* **1998**, *120*, 1571.

(40) Roth, W. R.; König, J. *Justus Liebigs Ann. Chem.* **1966**, *699*, 24.

etry and but little perturbed by simple electronic effects associated with $-(CH_2)_n-$ tethers.

The smallest cyclic 1,3-diene that can undergo a [1,5] hydrogen shift is cyclopentadiene. The nature of the transition structure of the hydrogen shift has received wide coverage in the literature beginning with a paper in 1963 by Mironov, Sobolev, and Elizarova,[3] a paper that has been regrettably slighted in recent papers on [1,5] shifts. Based on their finding that methylcyclopentadienes undergo facile isomerization, they stated, "...the relatively low potential barriers of such transformations, attests to the aromatic stabilization in the transitional (*sic*) state." Although their paper predates Woodward and Hoffmann's considerations of sigmatropic rearrangements, they depict reaction pathways that in effect involve [1,5] hydrogen sigmatropic shifts. Semiempirical calculations reported in the 1970s also suggested that the transition structure for the hydrogen shift in cyclopentadiene is stabilized by contributions from the cyclopentadiene anion.[6,41] Subsequently the results of ab initio calculations were similarly interpreted.[14,42−44] Alkorta and Elguero reported DFT B3LYP/6-31G* calculations for this reaction and obtained the transition structure (**C5TS)** whose geometry is shown in Figure 2.[18] They computed its activation energy to be 27 kcal/mol, some 2.7 kcal/mol higher than the experimental value. Both the experimental and calculated activation energies for the hydrogen shift in 1,3-cyclopentadiene are significantly lower than those for 1,3-pentadiene. which may be taken as some support for the suggestion that the transition structure has some aromatic stabilization from the cyclopentadiene anion. An explanation for the relatively low E_a value based on a more significant strain energy contribution from ground-state cyclopentadiene than from **C5TS** cannot, in our view, be justified.

The overall potential surface of the cyclohexadiene system is summarized in Figure 3. It is seen that the two enantiomeric conformers (**C6** and ***ent*-C6**) are linked by the two transition structures, **C6C6TS** and **C6TS**. They both have the C_s symmetry required to bring about "racemization" of the two enantiomeric conformers. The DFT geometry of the transition structure (**C6TS**) for the [1,5] hydrogen shift in 1,3-cyclohexadiene is shown in Figure 2. It has the same point-group, C_s, as was found for the transition structures **PDTS** and **C5TS**. However, the calculated activation energy for the [1,5] hydrogen shift in 1,3-cyclohexadiene (41.9 kcal/mol) is significantly higher than that of the chosen model system, **PD**, (36.6 kcal/mol) in contrast to the smaller activation energy found for the 1,3-cyclopentadiene system. To account for this increase in the activation energy of **C6** over the model system, one must examine the geometry of the hydrogen shift transition structure for the presence of strain. The geometry of the reacting diene system must be scrutinized for strain as well, since the activation energy depends on the energy difference between the diene and the transition structure. There are distinct differences between the geometry of **PDTS** and that of **C6TS**. The C···H···C angle in **C6TS** is 97.9° compared with 133.1° in **PDTS**. Furthermore the distance between terminal carbons C1 and C5 is much smaller in **C6TS** than in **PDTS** (2.248 vs 2.619 Å) and yet much larger than in **C5TS** (1.490 Å). This "pinching together" of these two carbons (C−C−C angle = 95.0°) in **C6TS** is of course due to the bridging methylene group. Hence one can conclude, qualitatively, that there is significant strain energy in transition structure **C6TS** relative to that in **PDTS**. This alone might account for the increased activation energy for **C6**. However, one must also examine the geometry of ground-state diene **C6**. If it contains significant strain energy relative to the model system diene (**PD**), this would have the effect of decreasing the activation energy for the [1,5] hydrogen shift. From Figure 4 it is apparent that 1,3- cyclohexadiene very likely has little strain energy, compared to the acyclic diene **PD**. It adopts a "half-chair" conformation that relieves the strain due to eclipsing of hydrogens in the planar form, and all C−C−C angles are close to what one expects for a strain-free system. Hence the increased activation energy for the hydrogen shift in 1,3-cyclohexadiene compared with E_a for the reaction in 1,3-pentadiene may be attributed to the strain present in the transition structure for the suprafacial rearrangement. We note that there is agreement between the calculated (41.9 kcal/mol) and experimentally estimated (41 kcal/mol)[6] E_a values.

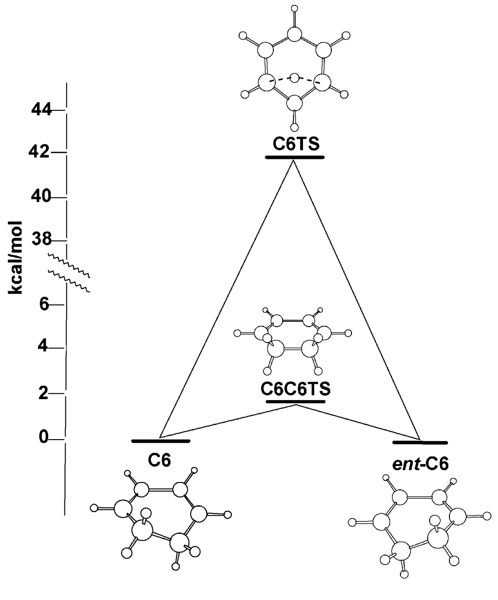

FIGURE 3. Potential surface of 1,3-cyclohexadiene.

The potential surface for 1,3-cycloheptadiene has seven stationary points (Figure 5). All are chiral with the exception of **C7a**, which has C_s symmetry. The **C7a** conformer is linked to the enantiomeric conformers of **C7b** by both the conformational and the [1,5] hydrogen shift pathways. As seen from Figure 5, both conformers of 1,3-cycloheptadiene (**C7a** and **C7b**) may undergo the [1,5] hydrogen shift. One therefore might consider using the Winstein−Holness equation[45] to obtain the experimentally observed activation energy. The calculated

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[41] de Dobbelaere, J. R.; de Haan, J. W.; Buck, H. M.; Visser, G. J. *Theor. Chim. Acta* **1973**, *31*, 95.

[42] Replogle, K. S.; Carpenter, B. K. *J. Am. Chem. Soc.* **1984**, *106*, 5751.

[43] Kahn, S. D.; Heher, W. J.; Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 8291.

[44] Bachrach, S. M. *J. Org. Chem.* **1993**, *58*, 5414.

[45] Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 5562.

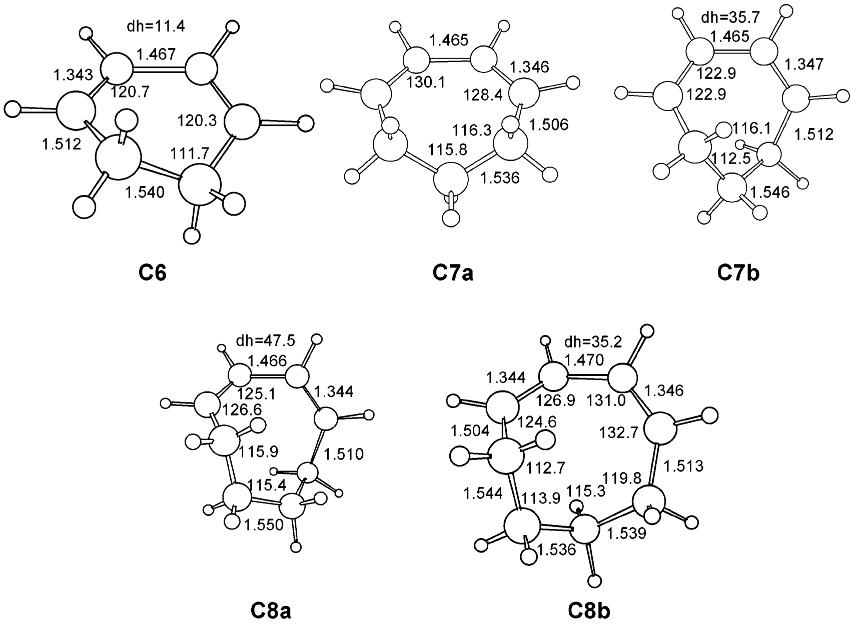

FIGURE 4. Partial geometries of the dienes. Geometry of **C6** taken from ref 21.

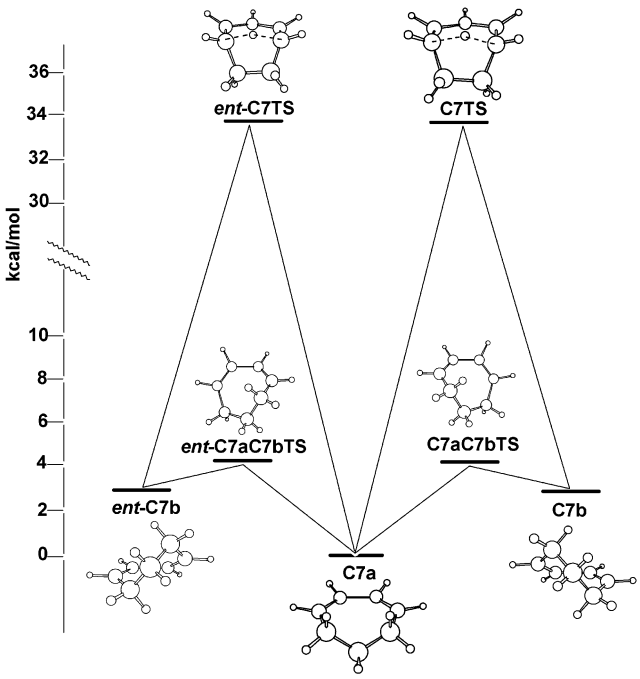

FIGURE 5. Potential surface of 1,3-cycloheptadiene.

equilibrium constant for **C7a** and **C7b**, however, is only 0.002, which means that conformer **C7b** is present to such a minute extent at equilibrium that direct reactions from it to the transition structure will make no significant contribution to the reaction overall. Hence the computed activation energy for **C7a** to **C7TS**, 33.7 kcal/mol, should correspond with the E_a value experimentally observed.

Not only is this activation energy significantly lower than that for 1,3-cyclohexadiene, it is also about 3 kcal/mol smaller than that for the model system, 1,3-pentadiene. It is comparable with the observed value of about 29 kcal/mol estimated for methyl-substituted cycloheptadienes.[7] This observed value is also smaller than that for the hydrogen shift in 1,3-pentadiene. Comparison of the geometry of the transition structure (**C7TS**) in Figure 2 with that of **PDTS** indicates that, unlike **C6TS**, **C7TS** would appear to be a relatively strain-free transition structure. All C−C−C angles in the diene part of the molecule are very similar to those in the pentadiene transition structure. Furthermore the C−C−C angles of the bridging $CH_2-CH_2-CH_2$ group are very close to being tetrahedral. The C_1 symmetry of **C7TS** is most likely due to the relief of the eclipsing of its hydrogens. We note that the C···H···C angle is 9° smaller than in the parent system, which indicates that there might be some, but probably not much, strain in this transition structure. On the other hand one sees from Figure 4 that there is likely to be significant strain in 1,3-cycloheptadiene (**C7a**), since all C−C−C angles are larger than what one would expect for a strain-free diene. For example the C1−C2−C3 angle is 130.1°, well above the "desired" 120° in such a diene, and the C−C−C angles present about the sp^3 carbons are also larger than that expected for tetrahedral carbons. Hence we propose that the lower calculated activation energy for the [1,5] hydrogen shift in 1,3-cycloheptadiene compared to the parent diene, **PD**, is a result of the increased strain in the diene rather than any type of special stabilization of the transition structure.

Of the three conformers located for 1,3-cyclooctadiene, only two would seem likely to undergo the [1,5] hydrogen shift (**C8a** and **C8b**). The reason for this is apparent when one examines the structures of the dienes (see Figures 4 and 6). Each of the conformational isomers which undergo the shift contains a hydrogen orientated (shown by dotted lines in the figure) favorably for the hydrogen shift to occur. In fact these two conformers differ primarily in the positions of C6, C7, and C8. The differing positions of these three carbons are reflected in the two transition structures to which they lead (**C8TSa** and **C8TSb**) as seen in Figure 6. The two transition structures are in fact very similar, differing

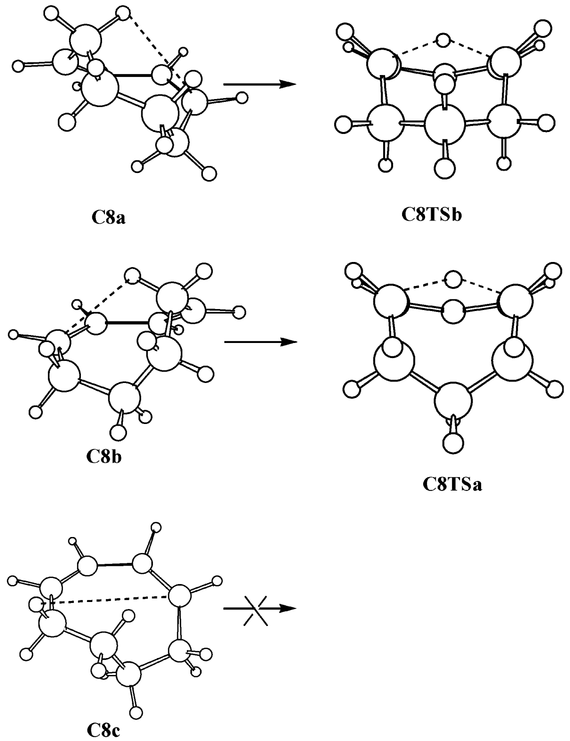

FIGURE 6. Conformers and [1,5] hydrogen shift transition structures of 1,3-cyclooctadiene.

mainly in the three-carbon bridge: they are conformationally isomeric transition structures. The structure of the third conformer (**C8c**) is such that neither hydrogen at C5 is oriented favorably for the hydrogen shift to occur. Hence it is not surprising that no transition structure linking this conformer to a product through a hydrogen shift was found.

When one combines the results of the IRCs of the hydrogen shifts connecting ground state and transition structure conformers an overall "reaction pathway map" for [1,5] hydrogen shifts in 1,3-cyclooctadiene is obtained (shown in Figure 7). The overall pathway has a "mirror plane" of symmetry perpendicular to the plane of the page passing through the two achiral transition structures, **C8TSa** and **C8bC8bTS**. All other stationary point structures shown in Figure 7 besides these two are mirror-image related to another; ten of these, five pairs of enantiomers, are chiral, and **C8TSb** is achiral.

Since there are two conformers of comparable energy leading to two different transition structures for the [1,5] hydrogen shift, the calculation of the activation energy to be compared with experiment is potentially more complicated than for the smaller cycloalkadienes discussed above. To calculate the experimentally observed activation energy, one now has to take into account two transition structures arising from two different conformers that are in equilibrium and of similar energy; they differ by only 0.6 kcal/mol.

This situation is covered by the Winstein−Holness equation (eq 1), which relates the empirical rate constant,

$$k = N_a k_a + N_b k_b \tag{1}$$

k, which would be "ordinarily evaluated without regard to conformational questions," to two rate constants, k_a and k_b, for two reactions from two conformers leading to two different transition structures, as well as to the mole fractions N_a and N_b of the two conformers at equilibrium.[45,46] It is possible to restate the Winstein−Holness equation in terms of activation energies using the Arrhenius equation (eq 2) to give the relationship of the

$$k = A\,e^{-E_a/RT} \tag{2}$$

activation energies of the two reactions, E_a(a) and E_a(b), in terms of an "empirical activation energy", E_a(emp), the activation energy that would be measured experimentally (eq 3). If one assumes that the Arrhenius pre-exponential

$$e^{-E_a^{emp}/RT} = N_a\,e^{-E_a^{a}/RT} + N_b\,e^{-E_a^{b}/RT} \tag{3}$$

factors are the same for the two reactions, a reasonable assumption in the case treated here since the two transition structures are very similar to one another and the two conformers leading to the transition structures are very similar, then the empirical or observed activation energy for this system may be derived from the activation energies for the two reactions and the equilibrium constant for the two conformers, all of which can be computed. The reactions described here for 1,3-cyclooctadiene can be treated by the Winstein−Holness equation as re-expressed above in terms of activation energies (eq 3), since the third conformer (**C8c**) apparently does not undergo the hydrogen shift reaction but simply is involved in the equilibrium of the two conformers **C8b** and **C8a**. Also the equilibrium between the enantiomeric conformers of **C8b** would not affect this treatment, since it only interconverts the two enantiomers of **C8b** via transition structure **C8bC8bTS**.

Using the calculated equilibrium constant of 0.36 for **C8b** and **C8a** and the two activation energies of 35.2 and 31.4 kcal/mol, one obtains from eq 3 an "observed" activation energy of 32.2 kcal/mol at 298 K. This is in fair agreement with our recently reported experimental activation energy for the hydrogen shifts of monodeuterio 1,3-cyclooctadienes of 29.0 ± 0.6 kcal/mol.[22] Both the experimental and calculated activation energies are lower than for the model system, 1,3-pentadiene. Examination of the geometry of the two transition structures, **C8TSa** and **C8TSb** (see Figure 2), indicates that they should be relatively strain-free. On the other hand, it is seen from Figure 4 that the two conformers, **C8a** and **C8b**, involved in the calculation of the observed energy of activation indicates that they are certainly not strain-free. For example they both have significant twisting about the single bond of the diene system (the dihedral angle of the H−C−C−H of this single bond is 47.5° and 35.2°, respectively). This, as in the case of the 1,3-cycloheptadiene system, should result in a lowered activation energy relative to the 1,3-pentadiene system as is found both experimentally and computationally.

Conclusions

Calculations for the ground states of *cis*-1,3-pentadiene, (2*E*,4*Z*)-heptadiene, cyclopentadiene, 1,3-cyclohexadiene,

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(46) Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994; pp 647−655.

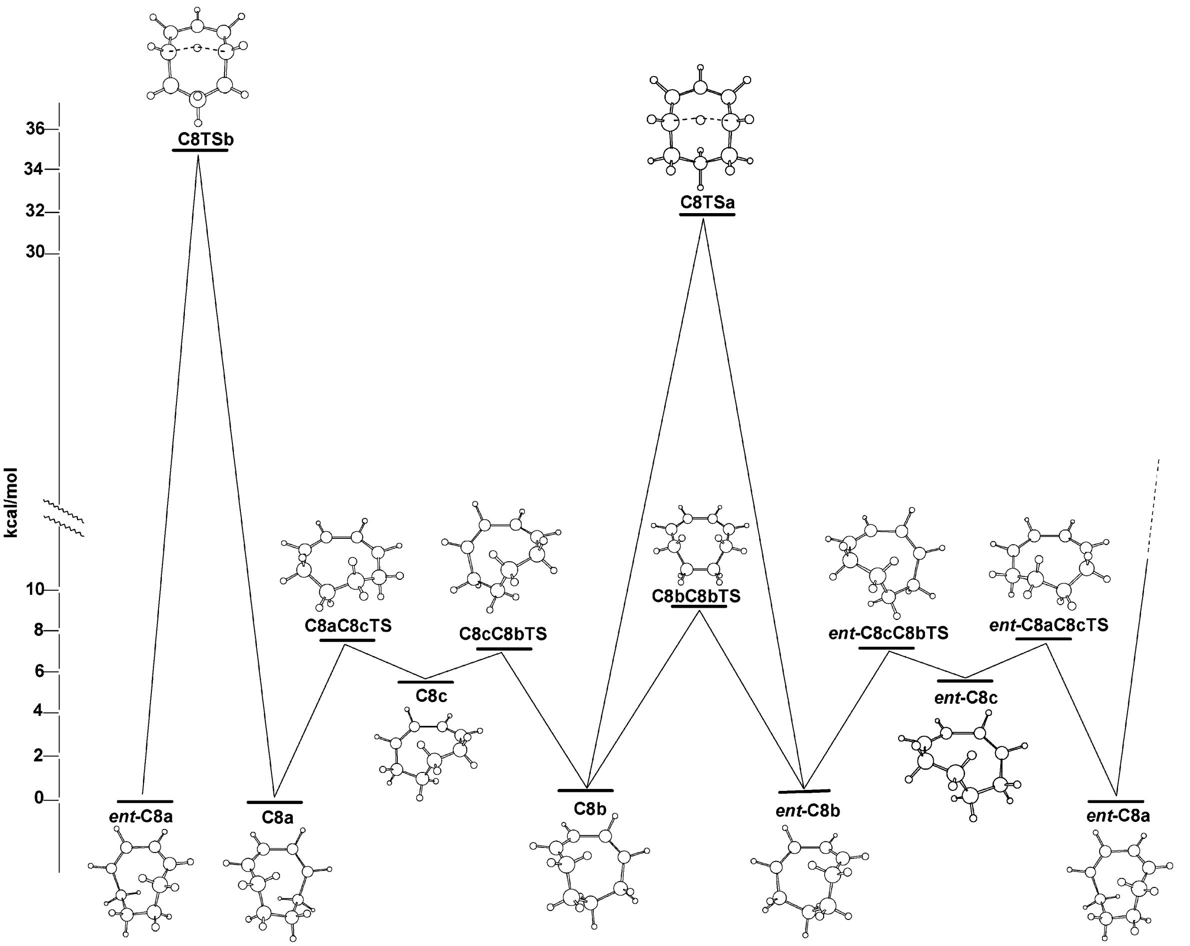

FIGURE 7. Schematic plot of the stationary points found for the 1,3-cyclooctadiene system.

1,3-cycloheptadiene, and 1,3-cyclooctadiene and for the related transition structures for thermal [1,5] hydrogen shifts have been carried out using the density functional theoretical method. They have provided calculated geometries and energies for all stationary points. Internal reaction coordinate calculations have been employed to identify reaction pathways.

The calculated E_a values are close to but somewhat larger than the experimental estimates. While the agreement between E_a(cal) of 36.6 and E_a(exp) of 36.3 ± 0.5 kcal/mol for the [1,5] hydrogen shift in *cis*-1,3-pentadiene is excellent, for the **C5** to **C8** 1,3-cycloalkadienes the gaps are 3, 0.9, 4.7, and 3 kcal/mol, respectively, the calculated value in each case being the larger. That there is some "positive" bias in the calculated values seems clear, but one must remember that the experimental E_a values are not all known with sure accuracy. We also note that solvation effects have not been studied here, though they would be expected to be minimal for these reactions.

In 1,3-cyclohexadiene E_a(cal) for a [1,5] hydrogen shift is 5.3 kcal/mol higher than for the acyclic model diene, a consequence of enhanced transition structure strain energy dictated by geometrical constraints.

The [1,5] hydrogen shifts in both 1,3-cycloheptadiene and 1,3-cyclooctadiene have lower E_a(cal) values than seen for *cis*-1,3-pentadiene, by some 2.9 and 4.6 kcal/mol, respectively. These differences are considered here to be associated with contributions to ground-state strain energy present in the cycloalkadienes but not in *s-trans-cis*-1,3-pentadiene.

The complexity of reaction paths, or "reaction pathway maps", for [1,5] hydrogen shifts in the **C5** to **C8** 1,3-cycloalkadienes increases with ring size. The [1,5] hydrogen shifts in cycloheptadiene are mediated by two enantiomerically related C_1-symmetric transition structures, while in cyclooctadiene two diastereomerically related C_s-symmetric transition structures are involved. Conformationally isomeric transition structures for [1,5] hydrogen shifts, as well as for various isomerizations among ground-state conformationally isomeric structures, may be essential parts of a reaction pathway map for degenerate [1,5] hydrogen shifts in cycloalkadienes and, no doubt, in some other sigmatropic rearrangements.

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Supporting Information Available: Cartesian coordinates, total electronic energies, and computed thermodynamic data for all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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