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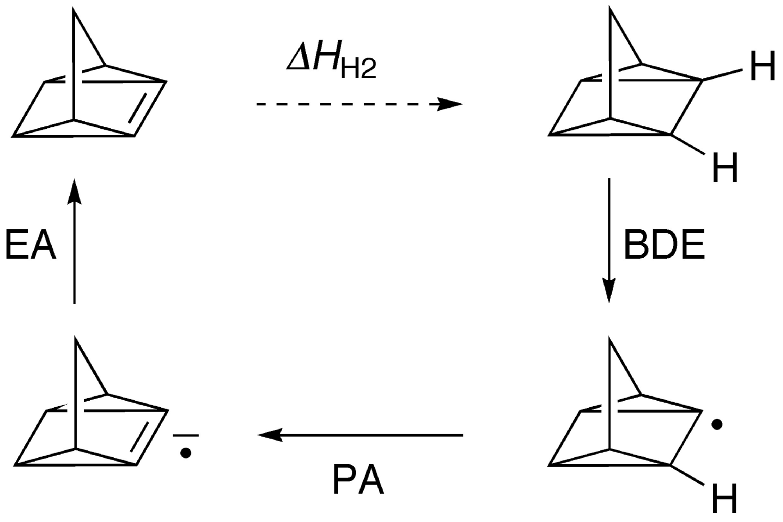

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Heat of Hydrogenation of 1,5-Dehydroquadricyclane. A Computational and Experimental Study of a Highly Pyramidalized Alkene

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Abstract: The radical anion of the highly pyramidalized alkene 1,5-dehydroquadricyclane (**1**) was generated in the gas phase from the Squires reaction of 1,5-bis(trimethylsilyl)quadricyclane with F^-/F_2. The electron binding energy and proton affinity of $\mathbf{1}^{\bullet-}$ were determined by bracketing experiments to be 0.6 ± 0.1 eV and 386 ± 5 kcal/mol, respectively. These values are in good agreement with values predicted by density functional theory (B3LYP/6-31+G*) and ab initio (CASPT2/6-31+G*) calculations. The experimental heat of hydrogenation of **1**, obtained from a thermochemical cycle, was found to be 91 ± 9 kcal/mol. This value of ΔH_{H_2} leads to values of 67 ± 9 kcal/mol for the olefin strain energy (OSE) of **1**, 172 ± 9 kcal/mol for its heat of formation, and 23 ± 9 kcal/mol for its π bond dissociation enthalpy. Since the retro-Diels−Alder reaction of neutral **1** is computed to be highly exothermic, the finding that $\mathbf{1}^{\bullet-}$ apparently does not undergo a retro-Diels−Alder reaction is of particular interest. The B3LYP/6-31+G* optimized geometry of **1** suggests that the bonding in this alkene is partially delocalized, presumably because the highly pyramidalized double bond in **1** interacts with the distal cyclopropane bonds in a manner that eventually leads to a retro-Diels−Alder reaction. The good agreement of the B3LYP and (2/2)CASPT2 values for the heat of hydrogenation and OSE of **1** with the experimentally derived values provides indirect evidence for the correctness of the B3LYP prediction that the equilibrium geometry of **1** lies part way along the reaction coordinate to the transition structure for the retro-Diels−Alder reaction.

Strained molecules have fascinated chemists for more than a century.[1] In particular, pyramidalized alkenes[2] and alkenes with twisted double bonds[3] have been the subject of many theoretical and experimental investigations. Although some pyramidalized alkenes, such as tricyclo[3.3.3.$0^{3,7}$]undec-3(7)-ene,[4] dodecahedrene,[5] and *trans*-cyclooctene,[6] are isolable, many have only a transitory existence.

For example, Szeimies and co-workers have generated and chemically trapped dehydroquadricyclane isomers **1**, **2**, and **3** in solution,[7,8] but none of these alkenes have been isolated. Nevertheless, these trapping experiments have provided some information about the relative energies of isomers **1**−**3**.[7c]

Szeimies and co-workers have computed the relative energies of these three alkenes and their singlet−triplet splittings (ΔE_{ST}) at both the two-configuration (TC)SCF/6-31G*[7a] and B3LYP/6-31G* levels of theory.[9] They also calculated the olefin strain energies (OSEs)[10] of **1**−**4** (i.e., the differences between their heats of hydrogenation and that of a relatively unstrained reference) at the TCSCF/6-31G* level of theory.[7a] However,

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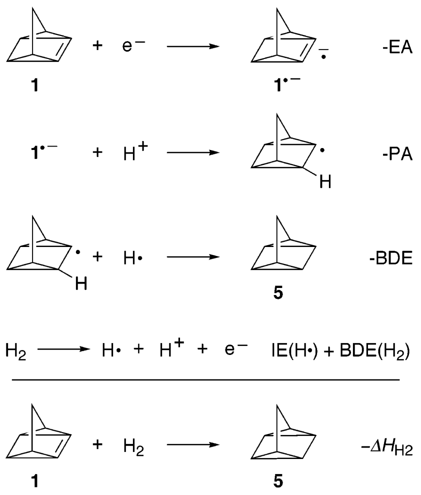
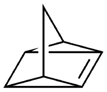
thermochemical data, such as the heat of hydrogenation (ΔH_{H_2}), have not been measured for any of these four alkenes.

Scheme 1





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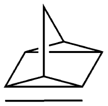

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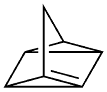

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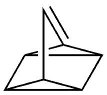

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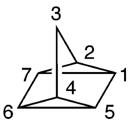

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One of the best ways to measure thermodynamic properties of reactive intermediates is to use thermochemical cycles involving the corresponding gas-phase anions.[11] For example, the electron affinity (EA)[12] of 1,5-dehydroquadricyclane (**1**) and the proton affinity (PA) of the corresponding radical anion ($\mathbf{1}^{\bullet-}$) could, at least in principle, be measured by flowing afterglow selected ion flow tube (FA-SIFT) experiments. As shown in Scheme 1, and summarized in eq 1, the PA of $\mathbf{1}^{\bullet-}$ and the EA of **1** can be combined in a thermochemical cycle with the known C5−H bond dissociation enthalpy (BDE) of quadricyclane (**5**),[13] the ionization energy (IE) of hydrogen atom, and the BDE of H_2 to yield the ΔH_{H_2} of pyramidalized alkene **1**.[14] Kass and co-workers have made use of similar thermochemical cycles to determine the ΔH_{H_2} of bicyclo[1.1.0]but-1(3)-ene[15] and cubene.[16]

$$-\Delta H_{H_2} = \mathrm{IE}(H^{\bullet}) + \mathrm{BDE}(H_2) - \mathrm{EA}(\mathbf{1}) - \mathrm{PA}(\mathbf{1}^{\bullet-}) - \mathrm{BDE}(\mathbf{5}) \quad (1)$$

A common method of generating radical anions in the gas phase is to allow $O^{\bullet-}$ to react with an organic neutral, resulting in loss of $H_2^{\bullet+}$ and formation of H_2O.[17] However, $O^{\bullet-}$ is a highly reactive and indiscriminate reagent. In fact, when $O^{\bullet-}$ was allowed to react with **5**, a mixture of dehydroquadricyclane radical anions was generated.[18]

Table 1. Calculated Electron Affinities (eV) for Dehydroquadricyclane Isomers **1**−**3**

calculation	**1**	**2**	**3**
(U)B3LYP[a]	0.75	0.65	0.75
(2/2)CASPT2[b]	0.54[c]	0.19	0.30
(U)B3LYP (corrected)[d]	0.61[e]	0.42	0.57

[a] UB3LYP/6-31+G* optimized geometries for the radical anions and B3LYP/6-31+G* optimized geometries for the alkenes. [b] TCSCF/6-31+G* optimized geometries. [c] 0.53 eV using the (U)B3LYP/6-31+G* geometries for $\mathbf{1}^{\bullet-}$ and **1**. [d] From eq 2. [e] 0.56 eV using the (2/2)CASPT2/6-31+G*//(U)B3LYP/6-31+G* value of ΔE_{ST} for **1**.

Squires and co-workers have shown that allowing a bis(trimethylsilyl) compound to react with F^-, followed by F_2, results in the regiospecific generation of a radical anion.[19] The radical anions of *o*-, *m*-, and *p*-benzyne, among others, have been generated in this way by the Squires reaction.[19,20] Herein we report the regiospecific generation of $\mathbf{1}^{\bullet-}$ from the Squires reaction of 1,5-bis(trimethylsilyl)quadricyclane (**6**).

We have measured the PA and electron binding energy of this radical anion in order to obtain values for ΔH_{H_2} and the OSE of pyramidalized alkene **1**. We present the results of calculations demonstrating that we have, indeed, measured these thermochemical quantities, rather than those of the radical anion of bicyclo[3.2.0]hepta-1,4,6-triene (**7**), which could have been formed from **1** via a retro-Diels−Alder reaction.

We also discuss the prediction by B3LYP and (2/2)CASPT2 calculations that the highly pyramidalized double bond in **1** moves the equilibrium geometry toward the transition structure for a retro-Diels−Alder reaction. This prediction is supported by the good agreement of the B3LYP and (2/2)CASPT2 values for the OSE of **1** with the value obtained from our experiments.

Results and Discussion

Ab Initio and DFT Calculations. Alkenes typically do not bind an extra electron (i.e., EA < 0).[21] However, pyramidalization of an alkene double bond has been shown to reduce the energy of the lowest unoccupied molecular orbital (LUMO).[2a,4,22] Consequently, it seemed probable that highly pyramidalized alkene **1** would bind an electron.

Unrestricted (U)B3LYP/6-31+G* calculations have been shown to provide accurate values for the EAs of many organic compounds.[23] Therefore, UB3LYP/6-31+G* calculations were performed on the radical anions and B3LYP/6-31+G* calculations were performed on the neutral alkenes in order to predict the EAs of dehydroquadricyclane isomers **1**−**3**. The results of these DFT calculations, shown in Table 1, confirm that all three dehydroquadricyclane isomers are predicted to bind an electron.

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Table 2. Calculated Values for ΔE_{ST} (kcal/mol) in Dehydroquadricyclane Isomers **1**−**3**

calculation	**1**	**2**	**3**
TCSCF[a]	14.7	26.5	23.7
(U)B3LYP[b]	20.3	18.6	24.1
(2/2)CASPT2[a]	23.5[c]	24.0	28.2

[a] TCSCF/6-31+G* optimized geometries. [b] (U)B3LYP/6-31+G* optimized geometries. [c] 24.5 kcal/mol, using (U)B3LYP/6-31+G* optimized geometries.

Table 3. Calculated Relative Enthalpies (kcal/mol) at 298 K for Dehydroquadricyclane Isomers **1**−**3**

calculation	**1**	**2**	**3**
TCSCF[a]	11.6	0	4.0
B3LYP[b]	4.3	0	3.0
(2/2)CASPT2[a]	5.0[c]	0	3.4

[a] TCSCF/6-31+G* optimized geometries and thermal corrections. [b] B3LYP/6-31+G* optimized geometries and thermal corrections. [c] 2.9 kcal/mol, using the B3LYP optimized geometry and the TCSCF thermal correction for **1**.

Thus, at least in principle, it should be possible to generate $\mathbf{1}^{\bullet-}$−$\mathbf{3}^{\bullet-}$ for gas-phase experiments.

However, DFT is not the best theoretical method for predicting thermodynamic properties of pyramidalized alkenes **1**−**3**. All three of these alkenes can be expected to have some diradical character. Since B3LYP is a single-determinantal method, it is expected to perform less well than multiconfigurational methods in calculating the energies of singlet diradicals.[24]

To take account of the diradical character of the singlet alkenes, at least a two-configuration (TC) SCF wave function should be used.[24] However, TCSCF does not include dynamic electron correlation and therefore does not give accurate energies for radical anions.[25]

(2/2)CASPT2, which is based on TCSCF reference wave functions, but which also contains dynamic electron correlation,[26] is likely to give more reliable values than TCSCF for the EAs of **1**−**3**. As shown in Table 1, CASPT2 predicts that all three dehydroquadricyclane isomers will bind an electron, but (2/2)CASPT2 gives binding energies that are 0.21−0.46 eV lower than those predicted by B3LYP. Like many ab initio methods, CASPT2/6-31+G* calculations are likely to underestimate EAs.

A method for overcoming both the tendency of B3LYP to overestimate the energies of singlet diradicals and that of CASPT2 to underestimate EAs is to compute the energy difference between the radical anions and the triplets using UB3LYP, and then to subtract the energy difference between the singlet and the triplet (ΔE_{ST}) obtained from CASPT2 calculations (eq 2). This method has been used to predict the EAs of cyclopentanone-2,5-diyl[27] and acenaphthyne.[28]

$$\mathrm{EA}_{(\mathrm{corrected})} = \mathrm{EA}_{\mathrm{triplet}}(\mathrm{UB3LYP}) - \Delta E_{ST}(\mathrm{CASPT2}) \quad (2)$$

Table 2 lists the ΔE_{ST} values for **1**−**3**, computed at the (U)B3LYP/6-31+G*, TCSCF/6-31+G*,[29] and (2/2)CASPT2/6-31+G*//TCSCF/6-31+G* levels of theory. As expected, the (2/2)CASPT2 values of ΔE_{ST} are larger than the (U)B3LYP values, since B3LYP overestimates the energies of the singlet states of these pyramidalized alkenes. Consequently, as shown in Table 1, when the (U)B3LYP EAs of **1**−**3** are recomputed using eq 2, the corrected values are less than the uncorrected values by ca. 0.2 eV. Pyramidalized alkene **1** is thus calculated to have a corrected (U)B3LYP value of $\mathrm{EA}_{(\mathrm{corrected})} = 0.61$ eV.

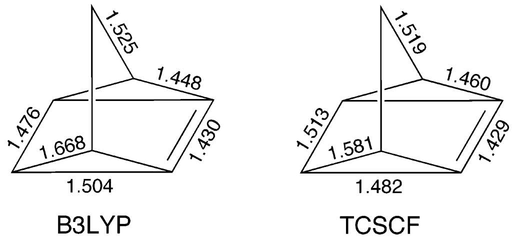
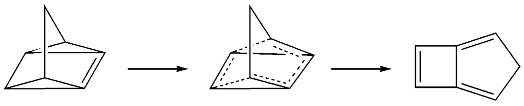


Figure 1. Comparison of the bond lengths (Å) in the B3LYP/6-31+G* and TCSCF/6-31+G* optimized geometries of **1**.

Scheme 2



1 **7**

The TCSCF value for ΔE_{ST} of **1** in Table 2 seems anomalously low, compared with both the B3LYP and (2/2)CASPT2 values. Similarly, as shown in Table 3, the TCSCF enthalpy of **1**, relative to **2**, seems about 6−7 kcal/mol too high, compared with both the B3LYP and (2/2)CASPT2 values. Both anomalies point to a problem in the TCSCF calculation of the energy of the lowest singlet state of **1**.

An important clue to the origin of the problem is evident in the comparison of the B3LYP and TCSCF optimized geometries for **1**, which are shown in Figure 1. Although the lengths of the double bond in both geometries for **1** are essentially the same, the 1.668 Å length of the C2−C7 (C4−C6) bond in the B3LYP optimized geometry is 0.087 Å longer than in the TCSCF optimized geometry. In addition, the C1−C2 (C4−C5) and C6−C7 bond lengths of, respectively, 1.448 and 1.476 Å in the B3LYP optimized geometry are both significantly shorter than the corresponding bond lengths in the TCSCF optimized geometry.

The bond lengths in the B3LYP/6-31+G* optimized geometry for **1** suggest that the bonding in this pyramidalized alkene is partially delocalized, presumably because the double bond in **1** interacts with the distal cyclopropane bonds in a manner that would eventually lead to the retro-Diels−Alder reaction, shown in Scheme 2. At the B3LYP/6-31+G* level of theory, this retro-Diels−Alder reaction of **1** to form **7** is predicted to be highly exothermic ($\Delta H = -73.1$ kcal/mol), with an activation enthalpy of only $\Delta H^{\ddagger} = 10.0$ kcal/mol.

Because TCSCF correlates only the pair of π electrons in the highly pyramidalized double bond of **1**, TCSCF does not describe as well as B3LYP the partially delocalized bonding in

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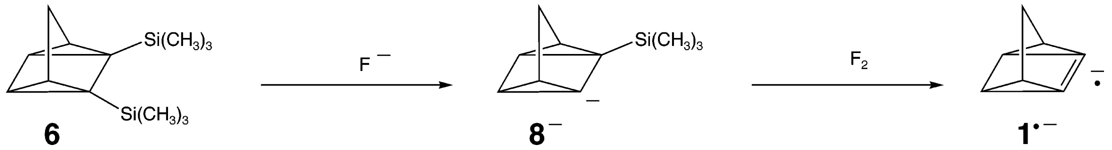
(29) Szeimies and co-workers have previously reported TCSCF/6-31G* values of ΔE_{ST} for **1**−**4**.[7a] However, our calculations revealed that the triplet energies in ref 7a were obtained with UHF wave functions. Using ROHF energies for the triplets, the relative sizes of the ΔE_{ST} values for **2** and **3** in Table 2 are reversed from those given in ref 7a.

Scheme 3



1. Since (2/2)CASPT2 does provide correlation for all electrons in **1**, if the geometry of **1** could be optimized at this level of theory, this geometry would presumably be closer to that optimized at B3LYP rather than at the TCSCF level of theory. Indeed, when the (2/2)CASPT2 enthalpy of **1** was recomputed at the B3LYP optimized geometry, the (2/2)CASPT2 energy was found to be 2.1 kcal/mol lower than at the TCSCF optimized geometry.[30]

Using the (2/2)CASPT2/6-31+G*//(U)B3LYP/6-31+G* value of ΔE_{ST} for **1**, the corrected (U)B3LYP EA for the alkene is predicted to be 0.56 eV. In contrast, **7**, the product of a retro-Diels−Alder reaction of **1**, is not predicted to bind an electron. In fact, at the (U)B3LYP/6-31+G* level of theory, $\mathbf{7}^{\bullet-}$ is actually computed to be higher in energy than **7** by 0.15 eV. Therefore, a retro-Diels−Alder reaction of $\mathbf{1}^{\bullet-}$ should lead to electron loss.

The reaction, $\mathbf{1}^{\bullet-} \rightarrow \mathbf{7} + e^-$, would be very exothermic, because $\Delta H = -73.1$ kcal/mol for $\mathbf{1} \rightarrow \mathbf{7}$ is far in excess of $\mathrm{EA}_{(\mathrm{corrected})} = 13.0$ kcal/mol for $\mathbf{1}^{\bullet-} \rightarrow \mathbf{1} + e^-$. An upper limit to the enthalpy of activation for this reaction should be $\Delta H^{\ddagger}(\mathbf{1}^{\bullet-} \rightarrow \mathbf{7} + e^-) = \mathrm{EA}(\mathbf{1}) + \Delta H^{\ddagger}(\mathbf{1} \rightarrow \mathbf{7}) = 23.0$ kcal/mol. $\Delta H^{\ddagger}(\mathbf{1} \rightarrow \mathbf{7}) = 10.0$ kcal/mol for the retro-Diels−Alder reaction of neutral **1** should provide a very conservative lower limit. Consequently, it seemed reasonable to expect that, if generated in a FA-SIFT apparatus, $\mathbf{1}^{\bullet-}$ would survive long enough to be detected, despite the possibility of its undergoing a very exothermic retro-Diels−Alder reaction to form **7**, with concomitant loss of an electron.

FA-SIFT Experiments. In our FA-SIFT apparatus, the Squires reaction of **6** (Scheme 3) did generate a $C_7H_6^{\bullet-}$ ion, albeit in low abundance. The abundance of anion $\mathbf{8}^-$ was also low. The low intensity of these ions was due, at least in part, to the low vapor pressure of bis(trimethylsilane) **6**.

To characterize the $C_7H_6^{\bullet-}$ ion generated from the Squires reaction of **6**, EA and PA bracketing experiments were performed, along with semiquantitative determinations of the rate constants (see Experimental Section). Only a small depletion of the $C_7H_6^{\bullet-}$ signal was observed with added H_2O ($k \approx 8 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}). In contrast, the ion reacts with more acidic reagents much more rapidly, with rate constants ranging from $k \approx 5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for MeOH to $k \approx 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} for CHF_2CH_2OH. There is a clear gap in reactivity observed between MeOH and H_2O. The PA of $C_7H_6^{\bullet-}$ was thus bracketed to be between those of MeOH ($\Delta H_{\mathrm{acid}} = 382 \pm 1$ kcal/mol)[31] and H_2O ($\Delta H_{\mathrm{acid}} = 390.3$ kcal/mol), giving $\mathrm{PA}(\mathbf{1}^{\bullet-}) = 386 \pm 5$ kcal/mol. This experimental value for $C_7H_6^{\bullet-}$ is in good agreement with the B3LYP/6-31+G* predicted value of PA = 388.1 kcal/mol for $\mathbf{1}^{\bullet-}$.[32]

The PA of $\mathbf{1}^{\bullet-}$, both measured and calculated, is similar to the experimental PA of the radical anion of bicyclo[1.1.0]but-1(3)-ene (PA = 386 ± 5 kcal/mol)[15] but smaller than the PA of the radical anion of cubene (PA = 392 ± 3 kcal/mol).[16] B3LYP/6-31+G* predicts PA = 391.3 kcal/mol for cubene, in excellent agreement with the experimental value.

Rapid electron transfer ($k \approx 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) was observed when $C_7H_6^{\bullet-}$ was allowed to react with SO_2 (EA = 1.107 ± 0.008 eV). Slower depletion of the $C_7H_6^{\bullet-}$ signal ($k \approx 1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $\approx 5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) and formation of CS_2^- and O_2^- were observed upon reactions with CS_2 (EA = 0.51 ± 0.10 eV) and O_2 (EA = 0.451 ± 0.007 eV), respectively. The results of the EA bracketing experiments suggest that the latter two electron-transfer reactions are slightly endothermic processes of $\mathbf{1}^{\bullet-}$. Given the uncertainty in the EA of CS_2, the observed slow electron transfer to this compound places upper and lower bounds of 0.7 and 0.5 eV, respectively, for the electron binding energy of $\mathbf{1}^{\bullet-}$. This leads to an experimental electron binding energy of 0.6 ± 0.1 eV for $\mathbf{1}^{\bullet-}$, which is consistent with the apparently endothermic electron transfer to O_2. This EA value is within experimental error of both the corrected B3LYP/6-31+G* EA of 0.61 (0.56) eV and the (2/2)CASPT2/6-31+G* EA of 0.54 (0.53) eV for **1** (Table 1).

Using $\mathrm{PA}(\mathbf{1}^{\bullet-}) = 386 \pm 5$ kcal/mol and $\mathrm{EA}(\mathbf{1}) = 0.6 \pm 0.1$ eV, combined with the known value of BDE = 109.4 ± 1.3 kcal/mol for the C5−H bond of **5**,[13] eq 1 gives a value of $\Delta H_{H_2} = 91 \pm 9$ kcal/mol[33] for **1**. This experimental value for the heat of hydrogenation of **1** is, within experimental error, the same as both the (2/2)CASPT2 value of $\Delta H_{H_2} = 89.9$ kcal/mol and the B3LYP value of $\Delta H_{H_2} = 94.0$ kcal/mol. Within experimental error, $\Delta H_{H_2} = 91 \pm 9$ kcal/mol for **1** is also the same as the experimental value of $\Delta H_{H_2} = 88 \pm 5$ kcal/mol for cubene.[16]

The heat of formation of **1** can be derived by adding the experimental heat of hydrogenation of **1** to the heat of formation of **5** ($\Delta H_f = 81.05 \pm 0.55$ kcal/mol).[31] The value thus obtained is $\Delta H_f(\mathbf{1}) = 172 \pm 9$ kcal/mol.

The π BDE of **1** can be determined by combining the experimental value for the heat of hydrogenation of **1** with the BDEs of the C−H bonds formed in **5**[13] and the BDE of H_2. The π BDE of **1** is thus found to be 23 ± 9 kcal/mol.[34] This π BDE is 11 kcal/mol larger than the experimental value of 12 ± 9 kcal/mol for the π BDE in cubene,[16] but the uncertainties in

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[30] The effects of recalculating the (2/2)CASPT2 values of EA, ΔE_{ST}, and the relative enthalpy of **1** at (U)B3LYP, rather than TCSCF optimized geometries are given in footnotes to Tables 1−3. The (2/2)CASPT2/6-31+G*//UB3LYP/6-31+G* energies of the radical anion and the triplet state of **1** are, respectively, 0.9 and 0.8 kcal/mol lower than the (2/2)-CASPT2/6-31+G*//TCSCF/6-31+G* values. That the (2/2)CASPT2 energy of the singlet is lowered by more than twice as much as those of the radical anion and triplet is not surprising, given the large differences, shown in Figure 2, between the B3LYP and TCSCF optimized singlet geometries.

[31] Unless otherwise noted, all thermochemical data are taken from: Linstrom, P. J., Mallard, W. G., Eds. *NIST Chemistry WebBook*; NIST Standard Reference Database No. 69, March 2003; National Institute of Standards and Technology: Gaithersburg, MD (http://webbook.nist.gov).

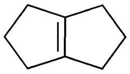
[32] In principle, rearrangements could have formed the radical anion of norbornenyne ($C_7H_6^{\bullet-}$). However, our independent studies of this radical anion find that it shows very different reactivity than that ascribed to $\mathbf{1}^{\bullet-}$. Hoenigman, R. L., Ph.D. Dissertation, University of Washington, 2002.

[33] The error distribution in a bracketing experiment is not gaussian and cannot be treated with the conventional root mean error evaluation. A conservative limit for the error is a sum of the errors of the corresponding reference values.

these experimental values are too large to draw any firm conclusions about what their relative sizes actually are.

Nevertheless, it is noteworthy that, although the experimental value of the π BDE in **1** is 11 kcal/mol larger than that in cubene, **1** is found to have a 3 kcal/mol larger heat of hydrogenation. The reason is straightforward: each of the pair of cyclopropyl C−H bonds formed in the hydrogenation of **1** (BDE = 109.4 ± 1.3 kcal/mol)[13] is 7 kcal/mol stronger than each of the pair of cyclobutyl C−H bonds formed in the hydrogenation of cubene (BDE = 102 ± 4 kcal/mol).[16]

The OSE of **1** is the difference between the heat of hydrogenation of **1** and that of an unstrained reference alkene.[10] Szeimies and co-workers used bicyclo[3.3.0]oct-1(5)-ene (**9**) as the reference alkene to compute the OSE of **1**.[7a] If ΔH_{H_2} = 24.5 kcal/mol is used for **9**,[35] the experimental value of ΔH_{H_2} = 91 ± 9 kcal/mol for **1** gives OSE = 67 ± 9 kcal/mol. B3LYP/6-31+G* calculations predict the OSE of **1** to be 69.5 kcal/mol, and (2/2)CASPT2 predicts OSE = 65.3 kcal/mol. These values are in excellent agreement with the OSE obtained from the experimental value of the heat of hydrogenation of **1**.



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In contrast, the TCSCF/6-31G* value of OSE = 79.0 kcal/mol for **1**[7a] is considerably larger than both the experimentally derived value and the (2/2)CASPT2 and B3LYP/6-31+G* calculated values. The main reason TCSCF/6-31G* overestimates the OSE of **1** is that, as discussed above, the TCSCF level of theory provides a poor description of the partially delocalized bonding in **1**.

Conclusions

The radical anion of 1,5-dehydroquadricyclane ($\mathbf{1}^{\bullet-}$) has been generated independently of the three other isomeric dehydroquadricyclane radical anions ($\mathbf{2}^{\bullet-}$−$\mathbf{4}^{\bullet-}$) via the Squires reaction of **6**. Although the retro-Diels−Alder reaction of $\mathbf{1}^{\bullet-}$ to give **7**, with concomitant electron loss, is computed to be very favorable thermodynamically, $\mathbf{1}^{\bullet-}$ has sufficient kinetic stability to be detected in our FA-SIFT apparatus.

The $C_7H_6^{\bullet-}$ ion formed from the Squires reaction of **6** was found to have an electron binding energy of 0.6 ± 0.1 eV and a proton affinity of 386 ± 5 kcal/mol. These experimental values are in good agreement with the values predicted for $\mathbf{1}^{\bullet-}$ by B3LYP/6-31+G* and (2/2)CASPT2/6-31+G* calculations.

Using these experimental values, the heat of hydrogenation of pyramidalized alkene **1** was found to be ΔH_{H_2} = 91 ± 9 kcal/mol. This value is in excellent agreement with the value of ΔH_{H_2} = 94.0 kcal/mol predicted by B3LYP/6-31+G* calculations and the value of ΔH_{H_2} = 89.9 kcal/mol predicted by (2/2)CASPT2 calculations. From the heat of hydrogenation, the heat of formation of **1** was determined to be ΔH_f = 172 ± 9 kcal/mol, the π BDE to be 23 ± 9 kcal/mol, and the olefin strain energy to be OSE = 67 ± 9 kcal/mol for this highly pyramidalized alkene.

The experimentally derived value of OSE = 67 ± 9 kcal/mol is in much better agreement with the B3LYP/6-31+G* and (2/2)CASPT2/6-31+G* values of 69.5 and 65.3 kcal/mol, respectively, than with the TCSCF/6-31G* value of OSE = 79 kcal/mol.[7a] This finding suggests that the bonding in **1** is partially delocalized, as predicted by B3LYP and (2/2)CASPT2, rather than localized, as predicted by TCSCF. Thus, our experiments provide indirect support for the B3LYP prediction that the highly pyramidalized double bond in **1** results in the equilibrium geometry lying part way along the reaction coordinate from the localized TCSCF structure to the completely delocalized transition structure for a retro-Diels−Alder reaction.

Computational Methods

DFT geometry optimizations were performed with Becke's hybrid three-parameter functional[36] and the correlation functional of Lee, Yang, and Parr[37] (B3LYP). A B3LYP vibrational analysis was performed at each stationary point to confirm its identity as an energy minimum or as a transition state and to provide the zero-point and thermal energy corrections necessary to convert the B3LYP electronic energies to enthalpies at 298 K. For this purpose the B3LYP vibrational frequencies were used without scaling.

Ab initio geometry optimizations were carried out with (2/2)CASSCF (i.e., TCSCF) for neutral structures and (3/2)CASSCF (i.e., ROHF) for radical anions. The active electrons were distributed among the π- or π-like molecular orbitals. CASSCF vibrational analyses were performed in order to establish the nature of each stationary point found and to obtain zero-point and thermal corrections to its energy. The CASSCF vibrational frequencies were used without scaling. To include the effects of dynamic electron correlation,[25] (2/2)CASPT2[26] single-point calculations were performed at CASSCF geometries. The CASSCF zero-point and thermal corrections were used to convert the CASPT2 electronic energies to enthalpies.

All calculations were performed using the 6-31+G* basis set.[38] The B3LYP and CASSCF calculations were carried out using the Gaussian 98 suite of programs,[39] while the CASPT2 calculations were performed using the MOLCAS package of programs.[40]

Experimental Section

Gas-phase Experiments. Gas-phase ion chemistry experiments were performed at 298 K using a tandem flowing afterglow selected ion flow tube (FA-SIFT) instrument that has been described previously.[41] The reactant ion, F^-, was generated in the source flow tube by electron impact on NF_3. The F^- ions were mass selected by the SIFT quadrupole mass filter and injected into the second flow tube containing helium (∼0.5 Torr), where they encountered **6**, which was added through a fixed inlet near the upstream end of the flow tube. The $\mathbf{8}^-$ ion thus generated was allowed to react with F_2 (5% in He, ∼0.5 mTorr), which was added downstream, forming an anion at *m*/*z* 90 ($C_7H_6^{\bullet-}$) via the

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(34) Using Benson's definition (Benson, S. E., Ed. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; pp 63−65) of the π BDE of **1** as the negative of the enthalpy of the disproportionation reaction of two molecules of 1-quadricyclyl radical to form **1** and **5**, the CASPT2 value for the π BDE of **1** is 24.7 kcal/mol. This value is very similar to the CASPT2 values of ΔE_{ST} = 23.5 and 24.5 kcal/mol in Table 2, as well as to the experimental value of 23 ± 9 kcal/mol for the π BDE of **1**.

(35) There apparently has been no measurement of the heat of hydrogenation of **9**. Therefore, we have used calculated values. (2/2)CASPT2/6-31+G*//TCSCF/6-31+G* and B3LYP/6-31+G* both predict ΔH_{H_2} = 24.5 kcal/mol for **9**; therefore, we believe that this value is reliable.

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

(38) (a) Harihan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Clark T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(39) Frisch, M. J.; et al. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(40) Andersson, K.; et al. *MOLCAS*, version 4.1; Department of Theoretical Chemistry, Chemical Centre: University of Lund, Lund, Sweden, 1999.

(41) (a) Van Doren, J. M.; Barlow, S. E.; DePuy, C. H.; Bierbaum, V. M. *Int. J. Mass Spectrom. Ion Processes* **1987**, *81*, 85. (b) Bierbaum, V. M. In *The Encyclopedia of Mass Spectrometry: Volume 1, Theory and Ion Chemistry*; Gross, M. L., Caprioli, R., Armentrout, P. B., Eds.; Elsevier: San Diego, 2003.

Squires reaction. For reactivity studies of $C_7H_6^{\bullet-}$ (e.g., PA and EA bracketing experiments), neutral reagents were added farther downstream. All ionic species were mass analyzed and detected using the quadrupole mass filter/electron multiplier at the end of the flow tube.

Due to the low vapor pressure of reagent **6**, intensities of $\mathbf{8}^-$ and $C_7H_6^{\bullet-}$ anions were rather low, while unreacted F^- ions (PA = 371.3 kcal/mol, EA($F^\bullet$) = 3.4012 eV)[31] were present in large excess in the reaction flow tube. In addition, impurity ions at *m*/*z* 89 and 91 were more abundant than $C_7H_6^{\bullet-}$. The heavier of these two anions is presumably quadricyclanide anion ($C_7H_7^-$, PA = 402.9 kcal/mol),[31] formed from the reaction of F^- with 1-(trimethylsilyl)quadricyclane, which was present as an impurity (∼2%) in the sample. The lighter anion is presumably trimethylsiloxide $(CH_3)_3SiO^-$, formed from the reaction of F^- with an impurity (∼2%), $(CH_3)_3SiOSi(CH_3)_3$. The first isotopomer of the trimethylsiloxide anion (with either ^{29}Si or ^{13}C) provided a small background (typically ∼20%) at *m*/*z* 90 for $C_7H_6^{\bullet-}$. In fact, prior to addition of F_2, the observed *m*/*z* 90:*m*/*z* 89 ratio was approximately 0.1, in agreement with the natural isotopic abundance ratio for $(CH_3)_3SiO^-$ of 0.083.

Since $(CH_3)_3SiO^-$ is weakly basic (reported PAs of 358.9 and 362.9 kcal/mol)[31] and strongly bound (EA = 2.80 eV at B3LYP/6-31+G*), this anion did not significantly interfere with the EA and PA determinations in the present study. The signals for $(CH_3)_3SiO^-$ ions with either ^{29}Si or ^{13}C were subtracted from the *m*/*z* 90 signal as a constant background. After the background subtraction, the reactivity of the *m*/*z* 90 signal was examined with fixed flow rates of proton-transfer reagents H_2O ($\Delta H_{acid} = 390.3$ kcal/mol), MeOH ($\Delta H_{acid} =$ 382 kcal/mol), EtOH ($\Delta H_{acid} = 378.3$ kcal/mol), *t*-BuOH ($\Delta H_{acid} =$ 374.7 kcal/mol), and CHF_2CH_2OH ($\Delta H_{acid} = 366.4$ kcal/mol) and electron-transfer reagents SO_2 (EA = 1.107 eV), CS_2 (0.51 eV), and O_2 (0.451 eV).[31] Semilogarithmic depletions of the *m*/*z* 90 signal were compared with that for a known reaction, and approximate reaction rate constants were obtained.

Syntheses. The synthesis of 1,5-bis(trimethylsilyl)quadricyclane (**6**) was modeled after the synthesis of 1,5-dibromoquadricyclane, described by Szeimies and co-workers.[7b] Ether solvents were dried over and distilled from Na/benzophenone. All other reagents were used as received, unless otherwise noted. Alkoxides were handled and stored in a glovebox. Column chromatography was performed using silica gel 60 (230−410 mesh, 0.04−0.063 mm). Photolysis was carried out with a 200-W high-pressure quartz mercury vapor lamp in a water bath. Glassware was flame dried under vacuum, and all reactions were carried out under argon, unless otherwise noted.

2-Bromo-3-(trimethylsilyl)norbornadiene(10). A solution of potassium *tert*-butoxide (14.4 g, 0.128 mol) in 114 mL of THF was added to a cooled solution (−78 °C) of norbornadiene (18.5 mL, 0.171 mol) in 36 mL of THF under an atmosphere of argon. *n*-Butyllithium (47 mL, 0.118 mol, 2.5 M in hexanes) was added dropwise over 20 min. The solution was stirred for 30 min at −78 °C, and a solution of 1,2-dibromoethane (4.6 mL, 0.053 mol) in 20 mL of THF was added dropwise over 20 min. The solution was warmed to −40 °C and stirred for 1 h. Chlorotrimethylsilane (30 mL, 0.236 mol) was added, and the reaction mixture was warmed to room temperature over 1 h. Saturated NH_4Cl (100 mL) and water (100 mL) were added, and the layers were separated. The water layer was extracted with ether, and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by vacuum fractional distillation with an 8-in. Vigreux column (81−87 °C, water aspirator) gave 9.0 g (0.037 mol, 69.8% yield) of clear liquid (98.2% pure by GC): ^1H NMR ($CDCl_3$, 300 MHz) δ 0.13 (s, 9H), 1.92 (dt, *J* = 1.6 Hz, 6.2 Hz, 1H), 2.11 (dt, *J* = 1.6 Hz, 6.2 Hz, 1H), 3.51 (m, 1H), 3.17 (m, 1H), 6.69 (ddd, *J* = 2.0 Hz, 5.2 Hz, 0.8 Hz, 1H), 6.81 (ddd, *J* = 3.0 Hz, 5.2 Hz, 0.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ −1.4, 56.1, 61.8, 72.7, 141.5, 143.2, 147.7, 148.2; MS (EI) 244, 242 (M^+), 199, 197, 163, 147, 97, 73 (100%).

2,3-Bis(trimethylsilyl)norbornadiene (11). *tert*-Butyllithium (50 mL, 0.085 mol, 1.7 M in pentane) was added slowly over 10 min to a cooled (−78 °C) solution of **10** (9.0 g, 0.037 mol) in 40 mL of ether under an argon atmosphere. The reaction mixture was stirred for 1 h at −78 °C, after which chlorotrimethylsilane (28 mL, 0.221 mol) was added. The solution was warmed to room temperature over 3.5 h, saturated NH_4Cl (50 mL) and water (50 mL) were added, and the layers were separated. The water layer was extracted with ether, and the organic layers were combined and dried over $MgSO_4$. The solvent was removed by rotary evaporation. Purification by column chromatography (silica, 19.5 cm × 2 cm, hexanes) gave 7.1 g (0.03 mol, 81.3% yield) of clear liquid (96.2% pure by GC): ^1H NMR ($CDCl_3$, 400 MHz) δ 0.15 (s, 18H), 1.64 (m, *J* = 1.6 Hz, 6.0 Hz, 2H), 3.92 (m, *J* = 1.6 Hz, 2H), 6.60 (app t, *J* = 2.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 0.3, 58.2, 71.7, 142.1, 165.2; MS (EI) 236 (M^+), 221, 162 (100%), 155, 133, 97, 73.

1,5-Bis(trimethylsilyl)quadricyclane (6). A solution of **11** (2.23 g, 9.45 mmol) and acetophenone (0.049 mL, 0.43 mmol) in 25 mL of ether was degassed for 5 min under argon and then irradiated for 18 h. The solvent was removed by rotary evaporation to yield 2.03 g (8.6 mmol, 91.0% yield) of clear liquid: ^1H NMR ($CDCl_3$, 400 MHz) δ −0.02 (s, 18H), 1.27 (dt, *J* = 1.2 Hz, 4.0 Hz, 2H), 1.48 (d, *J* = 4.0 Hz, 2H), 2.01 (dt, *J* = 1.2 Hz, 10.8 Hz, 1H), 2.16 (dt, *J* = 1.2 Hz, 10.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ −1.0, 13.2, 19.3, 27.9, 32.9; MS (EI) 236 (M^+), 221, 162, 155, 133, 73, 66 (100%). Exact mass: calcd for $C_{13}Si_2H_{24}$, 236.1411; found, 236.1402.

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Supporting Information Available: Optimized geometries and energies, including zero-point energy and thermal corrections, for calculated structures, ^1H and ^{13}C NMR spectra for compounds **6** and **11**, and complete refs 39 and 40. This information is available free of charge via the Internet at http://pubs.acs.org.

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