J. Org. Chem. **1993,** *58,* 211-216

Ab Initio Calculations of the Stabilization Energy of Pentadienyl Radical from Rotational Barriers and from Lowering of Bond Dissociation Energies

Raymond C. Fort, Jr.,[1] David. A. Hrovat, and Weston Thatcher Borden*

Department of Chemistry, University of Washington, Seattle, Washington 98195

Received July 29, 1992

The energies of and barriers separating the *E,E*, *E,Z* and *Z,Z* geometries of pentadienyl radical have been calculated at the QCISD/6-31G*//UHF/6-31G* level, and the lowering of C–H bond dissociation energies (−ΔBDEs) by two vinyl groups and a 1,3-butadienyl group have also been computed at the QCISD/6-31G* level. The calculated barrier heights and −ΔBDEs are within about 2 kcal/mol of those that have been measured. In agreement with the results of recent experiments, the calculated rotational barriers are larger than the computed values of the comparable −ΔBDEs. The implications of this finding of a difference between these two different measures of the pentadienyl stabilization energy (SE) are discussed.

Pentadienyl radicals are important intermediates in many processes, including lipid and fatty acid autoxidation[2,3] and rearrangements of carotenoids.[4] Determination of the stabilization energy (SE) provided by resonance in pentadienyl radicals has been addressed experimentally by measurements of both the lowering of bond dissociation energies (BDEs) attendant upon the formation of pentadienyl, rather than localized radicals,[5-7] and the torsional barriers to interconversion of stereoisomeric pentadienyl radicals.[7,8]

The −ΔBDE studies prior to 1991 have been reviewed by Doering and Kitagawa in discussing their own results.[6] Doering and Kitagawa found that the presence of a conjugated butadienyl moiety lowers the energy required for breaking a C–C π bond by 16.9 kcal/mol. In another study published in 1991, Clark and co-workers[7] measured the dissociation energy of the bis-allylic C–H bond in 1,4-pentadiene by several different techniques. All of their measurements gave a value for the BDE of about 76.5 kcal/mol and a heat of formation for pentadienyl of 49.6 kcal/mol, which is exactly the same value for ΔH_f° of pentadienyl obtained by Doering and Kitagawa.[6]

However, because Clark and co-workers reported the SE provided by the two nonconjugated double bonds in 1,4-pentadiene, their value for the pentadienyl SE is larger than that of Doering and Kitagawa, who reported the SE provided by two conjugated double bonds. Using a value of 98 kcal/mol for the energy required to dissociate a secondary C–H bond in the absence of any resonance stabilization,[9] Clark and co-workers obtained a value of 21.6 kcal/mol for the pentadienyl SE,[10] which is 4.7 kcal/mol greater than the Doering and Kitagawa value of 16.9 kcal/mol.

The 4.7 kcal/mol difference between the two pentadienyl SEs reflects the energy difference between the nonconjugated π system in 1,4-pentadiene and the conjugated π system in 1,3-pentadiene. It is easy to show independently that the energy difference between the two π systems is equal to about 5 kcal/mol.[11,14]

Although there is excellent agreement between the two recent studies of the pentadienyl SE from measurements of bond dissociation energies,[6,7] measurements of the barrier to rotation in pentadienyl radical provide a somewhat higher value of the pentadienyl SE. MacInnes

---

[1] On leave at the University of Washington from the Department of Chemistry, University of Maine, Orono, ME 04469.

[2] Bascetta, E.; Gunstone, F. D.; Scrimgeour, C. M.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 110.

[3] Nelson, M. J.; Seitz, S. P.; Cowling, R. A. *Biochemistry* **1990**, *29*, 6897.

[4] (a) Burton, G. W.; Ingold, K. U. *Science* **1984**, *224*, 569. (b) Burton, G. W. *J. Nutr.* **1989**, *119*, 109.

[5] A representative group of earlier investigations: (a) Frey, H. M.; Krantz, A. *J. Chem. Soc. A* **1969**, 1159. (b) Egger, K. W.; Jola, M. *Int. J. Chem. Kinet.* **1970**, *2*, 265. (c) Dolbier, W. R., Jr.; Alonso, J. H. *J. Am. Chem.* **1972**, *94*, 2544. (d) Trenwith, A. B. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 266. (e) Trenwith, A. B. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 3131. (f) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493.

[6] Doering, W. von E.; Kitagawa, T. *J. Am. Chem. Soc.* **1991**, *113*, 4288.

[7] Clark, K. B.; Culshaw, P. N.; Griller, D.; Lossing, F. P.; Martinho Simoes, J. A.; Walton, J. C. *J. Org. Chem.* **1991**, *56*, 5535.

[8] Davies, A. G.; Griller, D.; Ingold, K. U.; Lindsay, D. A.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1981**, 633. MacInnes, I.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1073.

[9] Seetula, J. A.; Russell, J. J.; Gutman, D. *J. Am. Chem. Soc.* **1990**, *112*, 1347.

[10] The value of 19.6 kcal/mol actually reported by Clark and co-workers[7] was based on a secondary C–H BDE of 96 kcal/mol, but they noted that use of the more recent value of 98 kcal/mol[9] would raise the pentadienyl SE by 2 kcal/mol.

[11] The difference of 7.1 kcal/mol between the heats of formation of 1,4- and 1,3-pentadiene[12] must be equal to the difference between the heats of hydrogenation of both isomers to pentane. Thus, 7.1 kcal/mol represents the intrinsic energy difference between the conjugated and nonconjugated double bonds in these molecules (the conjugation energy) plus the difference between the strengths of the σ bonds formed during hydrogenation. The same types of σ bonds are formed, with the exception that one more primary C–H bond is made in hydrogenating 1,4-pentadiene, in place of a secondary C–H bond that is created in hydrogenating 1,3-pentadiene. Taking 2 kcal/mol as the difference between these two C–H bond strengths[9] gives 5 kcal/mol as the conjugation energy. Moreover, in the hexadienes, where the difference between the heats of hydrogenation of the 1,4 and 1,3 isomers is exactly equal to the conjugation energy (the same number of primary and secondary C–H bonds are made in hydrogenating each isomer to hexane), the actual heats of hydrogenation of 1,4- and 1,3-hexadiene differ by 4.7 kcal/mol for the trans isomers and 4.5 kcal/mol for the cis.[13]

[12] Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, 1986.

[13] Fang, W.; Rogers, D. W. *J. Org. Chem.* **1992**, *57*, 2294.

[14] A value of 5.0 kcal/mol for *K*, the conjugation energy of 1,3-pentadiene, rather than the value of $K = 3.7$ kcal/mol used by Doering and Kitagawa,[6] brings into exact agreement their two estimates of the heat of formation of pentadienyl radical, which are derived starting from the heat of formation of each isomer of pentadiene.[12] $K = 3.7$ kcal/mol is the conjugation energy measured for 1,3-butadiene,[15] which apparently is lower than in 1,3-pentadiene or in 1,3-hexadiene[11] by about 1 kcal/mol. One might infer that an alkyl group attached to one end of a conjugated diene increases the conjugation energy over that in unsubstituted 1,3-butadiene by this amount.

[15] Kistiakowski, G. B.; Ruhoff, J. R.; Smith, H. A.; Vaughn, W. E. *J. Am. Chem. Soc.* **1936**, *58*, 146.

0022-3263/93/1958-0211$04.00/0

and Walton measured the activation energies for the interconversion of the *E,E* and *E,Z* conformers of pentadienyl radical.[7,8] At 370 K they found E_a = 11.7 kcal/mol for the conversion of *E,E* to *E,Z* and E_a = 9.3 kcal/mol for the reverse reaction. Adding to the former E_a, the value of E_a = 15.7 kcal/mol for stereomutation in the allyl radical,[16] MacInnes and Walton obtained a value of 27.4 kcal/mol for the energy necessary to destroy all the conjugation in the most stable geometry of pentadienyl.[17] This value of the pentadienyl SE, based on rotational barriers, is about 6 kcal/mol higher than the value of 21.6 kcal/mol, based on the lowering of the secondary C–H BDE by the two vinyl groups in 1,4-pentadiene.[8,10]

As first pointed out by Doering and Roth for allyl,[18] SEs based on lowerings of BDEs should, in fact, differ from SEs based on rotational barriers. The difference between the two types of SEs is equal to the change in BDE on replacing the alkyl group(s) in the reference alkane and radical with double bonds that are constrained to geometries at which they do not conjugate with the unpaired electron in the radical. In the case of allyl the experimental rotational barrier of 15.7 kcal/mol[16] is larger than the experimental −ΔBDE in propene of 13.5 kcal/mol[19] by about 2 kcal/mol.

Although this difference of about 2 kcal/mol is probably not outside the error bounds in the experimental values for the two different types of allyl SEs, a difference of about this size is supported by the results of a recent ab initio study.[20] Calculations at the CISD/6-31G* level found that, if the double bond in 1-propenyl radical is prohibited from conjugating with the radical center, the primary C–H BDE in propene is 1.4 kcal/mol higher than that in ethane. As noted above, this is equal to the difference between the two types of SEs for allyl.

The experimental estimate of 27.4 kcal/mol[7,8,17] for the energy required to rotate both vinyl groups in pentadienyl out of conjugation is sufficiently larger than the experimental value of 21.6 kcal/mol for −ΔBDE for breaking a secondary C–H bond in 1,4-pentadiene[7,10] that the difference of about 6 kcal/mol appears to be outside the range of probable experimental errors. This difference between the two types of SEs measured for pentadienyl is more than twice the size of the difference in allyl, suggesting that two orthogonal vinyl groups increase the BDE for a secondary C–H by at least twice as much as one orthogonal vinyl group increases the BDE for a primary C–H.

In this paper we report the results of ab initio calculations on the pentadienyl radical. We have calculated −ΔBDE for formation of the *E,E* isomer from both 1,3- and 1,4-pentadiene, and we have also computed the barriers to twisting about the C–C bonds in various conformations of the radical. We find that the computed values of these two different types of pentadienyl SEs compare well with those obtained experimentally. The results of our calculations provide additional evidence for the existence of a difference between the two different measures of radical SEs.

Table I. UHF/6-31G* and QCISD/6-31G* Energies (Hartrees) of Conformers of Pentadienyl Radical at UHF/6-31G* Optimized Geometries and Relative QCISD/6-31G* Energies (kcal/mol)

conformer	type	*E* (UHF)	*E* (QCISD)	E_{rel} (QCISD)
1	minimum	−193.3699	−194.0195	0.0
2	ts[a]	−193.3470	−194.0034	10.1
3	minimum	−193.3662	−194.0160	2.2
4	ts[a]	−193.3467	−193.0033	10.2
5	minimum	−193.3595	−194.0106	5.6
6	mt. top[b]	−193.3172	−193.9786	25.7
7	mt. top[b]	−193.3175	−193.9788	25.5
8	ts[a]	−193.3260	−193.9867	20.6
9	mt. top[b]	−193.3170	−193.9783	25.9

[a] Transition state, one negative force constant. [b] Mountain top, two negative force constants.

Table II. RHF/6-31G*,[a] UHF/6-31G*,[b] and QCISD/6-31G* Energies (Hartrees), Calculated at Optimized[a,b] Geometries, for 1,3- and 1,4-Pentadiene, Methane, Ethane, and Propane and Methyl, Ethyl, and 2-Propyl Radicals

molecule	*E* (RHF[a]/UHF[b])	*E* (QCISD)
(*E*)-$H_2C{=}CHCH{=}CHCH_3$	−193.9592	−194.6474
(*Z*)-$H_2C{=}CHCH{=}CHCH_3$	−193.9564	−194.6450
$H_2C{=}CHCH_2CH{=}CH_2$	−193.9484	−194.6371
CH_4	−40.1952	−40.3531
$CH_3^\bullet$	−39.5590	−39.6889
C_2H_6	−79.2288	−79.5275
$C_2H_5^\bullet$	−78.5971	−78.8685
C_3H_8	−118.2637	−118.7048
$(CH_3)_2CH^\bullet$	−117.6361	−118.0505

[a] RHF/6-31G* for closed shell molecules. [b] UHF/6-31G* for radicals.

Computational Methods

Geometries were optimized with the 6-31G*[21] basis set, using UHF calculations for radicals[22] and RHF calculations for closed-shell species. Vibrational analyses were performed at the same levels of theory. The UHF energies of various geometries of pentadienyl radicals are given in Table I, and the UHF and RHF energies of the species needed to calculate −ΔBDE are contained in Table II. Zero-point vibrational energy corrections were small, in almost all cases amounting to considerably less than 1 kcal/mol; so only electronic energies are given in Tables I and II. However, the zero-point energies, as well as the optimized geometries, are available as supplementary material.[23]

The effect of electron correlation on the energies at the optimized geometries was included by performing calculations at the QCISD level, which approximates the effect of quadruple excitations, as well as single and double excitations, from the Hartree–Fock reference configuration.[24] The QCISD energies are also given in Tables I and II. A few calculations, discussed in the text, were performed at the QCISD(T) level, which includes

---

(16) Korth, H.-G.; Trill, H.; Sustmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4483.

(17) MacInnes and Walton report a SE of 25.0 kcal/mol[7,8] because from the sum of the observed barriers to rotation in pentadienyl and allyl they subtract an estimate of the correction for the hypothetical barrier to rotation about a single bond between trigonal carbons in the absence of any conjugation.

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

(19) Roth, W. R.; Bauer, F.; Beitat, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453. Doering, W. von E.; Roth, W. R.; Bauer, F.; Boenke, M.; Breuckmann, R.; Ruhkamp, J.; Wortmann, O. *Chem. Ber.* **1991**, *124*, 1461.

(20) Coolidge, M. B.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 2354.

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

(22) Because, unlike ROHF wave functions for radicals, UHF wave functions contain some correlation between electrons of opposite spin, UHF wave functions do not exhibit artifactual symmetry breaking and localization. Thus, despite the contamination from higher spin rates that is present in UHF wave functions (e.g., S^2 = 1.23 in the UHF wave functions for planar pentadienyl radicals), UHF calculations are preferred to ROHF for optimizing the geometries of radicals. Reviews: Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737; Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(23) This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the article, and can be ordered from the ACS. See any current masthead page for ordering information.

(24) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

corrections for the effects of triple excitations.[24] However, these QCISD(T) calculations gave almost exactly the same relative energies as those performed at the QCISD level. All calculations were carried out using the Gaussian 90 package of ab initio programs.[25]

Results and Discussion

Barriers to Rotation. A planar geometry with C_{2v} symmetry and C–C bond lengths of R_{12} = 1.374 Å and R_{23} = 1.415 Å was found to be an energy minimum for (*E*,*E*)-pentadienyl radical (1). As shown in Table I, 1 is calculated to be 2.2 kcal/mol lower in energy than (*E*,*Z*)-pentadienyl (3), which our UHF/6-31G* calculations also find to have a planar equilibrium geometry. Our calculated energy difference between 1 and 3 is very close to the value of 2.4 kcal/mol, measured by MacInnes and Walton.[7,8]

1 2 3

The transition state 2, connecting 1 and 3, was located, and as shown in Table I, its QCISD energy was found to be 10.1 kcal/mol higher than that of 1. This calculated value for the barrier height is somewhat smaller than the value of E_a = 11.7 ± 0.5 kcal/mol, obtained by MacInnes and Walton from EPR line-shape analysis.[7,8] Recalculation of the barrier height at the QCISD(T) level increased the computed value but by only 0.1 kcal/mol.[26]

The UHF-optimized geometry of (*Z*,*Z*)-pentadienyl (5) was found to be nonplanar with a dihedral angle of 25.9° between the plane containing C_1–C_2–C_3 and that containing C_3–C_4–C_5. However, the UHF energy of this C_2 geometry was computed to be only 0.3 kcal/mol lower than that of the optimized, planar, C_{2v} geometry for 5. The QCISD energy of 5 is 5.6 kcal/mol greater than that of 1. With an energy difference of this size between 5 and 1, it is not surprising that the EPR experiments, in which the equilibration of 1 with 3 was studied, failed to detect the presence of 5.[7,8]

3 4 5

Despite the fact that 5 is significantly higher in energy than 1, transition state 4, which connects 5 with 3, is calculated to have nearly the same energy as transition state 2, which connects 1 with 3. The two transition states differ in that the vinyl group, which is twisted out of conjugation with the allylic radical in both, is attached in an *E* fashion in 2 and in a *Z* fashion in 4. Clearly, this stereochemical difference has almost no effect on the relative energies of the two transition states.

In contrast, comparison of the energies of 1, 3, and 5 in Table I shows that, when the vinyl group lies in, or nearly in, the same plane as the allylic moiety, *E* attachment is calculated to be 2–3 kcal/mol lower than *Z*. Presumably, the absence of a corresponding energetic advantage of the *E* stereochemistry of 2 over the *Z* stereochemistry of 4 reflects the fact that the vinyl group, when twisted out of the plane of the remaining three carbons, is much less sterically demanding than when it lies in this plane.

(*E*,*E*)-Pentadienyl (1) and (*Z*,*Z*)-pentadienyl (5) can be directly connected by pathways that involve synchronous rotation of both vinyl groups. We located the energy maxima, 6 and 7, along both con- and disrotatory pathways. The former pathway preserves a C_2 symmetry axis, the latter a C_s symmetry plane.

6

7

Although 6 and 7 are the transition states along these two pathways, vibrational analyses showed that they are mountain tops on the global energy surface for pentadienyl radical, since both 6 and 7 were found to have two negative force constants. The vibration corresponding to one of these force constants preserves the symmetry of the reaction pathway, C_2 for 6 and C_s for 7. However, the second negative force constant for 6 and for 7 corresponds to a vibration that breaks the symmetry of the reaction pathway. In the case of 6 this vibration involves disrotation of the two vinyl groups and in 7 it involves conrotation.

From both 6 and 7 the symmetry-breaking mode connects two equivalent geometries of 3, *E*,*Z* and *Z*,*E*. If the two vinyl groups in 3 are constrained to rotate synchronously, 6 and 7 are each the transition state for one of the two possible modes of rotation. This is the second type of pathway, involving synchronous vinyl group rotation, along which 6 and 7 are each a transition state. Because 6 and 7 are each the transition state along two pathways, 6 and 7 each have two negative force constants.

Passage between 1 and 5 and between the two equivalent forms of 2 can circumvent the mountain tops, corresponding to 6 and 7, by asynchronous rotation of the vinyl groups. Thus, the lowest energy pathway leading from 1 to 5 involves rotating just one vinyl group to form 3, via transition state 2, and then rotating the second vinyl group to form 5, via transition state 4. There are two such pathways, differentiated only by which vinyl group rotates first. The two equivalent forms of 3 can also be interconverted by two pathways, but the pathways are nonequivalent. One involves 1 as an intermediate and passes over two equivalent forms of transition state 2; the other involves 5 and passes over two equivalent forms of transition state 4.

Comparison of the energies of transition states 2 and 4 with those of mountain tops 6 and 7 shows the energetic advantage of rotating the vinyl groups in pentadienyl radical sequentially, rather than synchronously, to be about 15.5 kcal/mol. This comparison also gives the energy required to rotate the second vinyl group out of conjugation, thus destroying the allylic resonance that remains in 2 and 4 after rotation of the first vinyl group. The calculated value of about 15.5 kcal/mol is close to that computed[20,27] and found experimentally[16] for the rotational barrier in the parent allyl radical.

The average energy of 6 and 7, relative to 1, is 25.6 kcal/

---

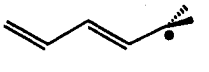
[25] Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1990.

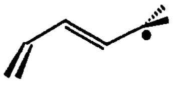
[26] The QCISD(T) energies of 1 and 2 were, respectively, −194.0427 and −194.0264 hartrees.

[27] The QCISD/6-31G* value of 15.3 kcal/mol for the barrier to rotation in allyl is exactly the same as the CISD/6-31G* value[20] when both sets of calculations are performed at the UHF/6-31G* optimized geometries. The QCISD/6-31G* value of 14.2 kcal/mol for −ΔBDE in forming allyl, rather than ethyl radical, is 0.3 kcal/mol higher than the CISD/6-31G* value.[20]

mol.[28] This is slightly smaller than the 27.4 kcal/mol that McInnes and Walton estimate to be necessary to rotate both vinyl groups out of conjugation in pentadienyl radical.[7,8] The difference of 1.8 kcal/mol between the two estimates of the energy necessary to destroy all the conjugation in pentadienyl is due almost entirely to the difference between the experimental value of 11.6 kcal/mol for the activation energy for converting 1 to 3[7,8] and the calculated energy difference of 10.1 kcal/mol between 1 and transition state 2.

A different mode of localizing the radical center in pentadienyl is to rotate the bond between C_1 and C_2 in 1. The C_s structure (8) that results is the transition state for interchanging the two hydrogens at C_1. As expected, either from the bond lengths in 1 or from the more delocalized structure of 2, compared to 8, rotation about C_1–C_2 in 1 is calculated to require more energy than rotation about C_2–C_3. As shown in Table I, transition state 8 is computed to have a QCISD energy that is 20.6 kcal/mol above that of 1 and 10.5 kcal/mol higher than that of 2.


8


9

The energy required to remove the conjugation within the butadiene moiety of 8, by rotating 90° about the C_3–C_4 bond to form 9, is calculated to amount to 5.3 kcal/mol. Not surprisingly, this is essentially the same as the QCISD energy (5.4 kcal/mol) that we compute for the same type of rotation in going from *transoid*-1,3-pentadiene to the transition state that connects it with *cisoid*-1,3-pentadiene.[29] Alternatively, 9 could be formed from 2 by rotating about the C_1–C_2 bond, resulting in loss of the allylic resonance in 2. This rotation is computed to require 15.8 kcal/mol at the QCISD level, which again compares well with both the calculated[20,27] and experimental[16] values for the barrier to rotation in the parent allyl radical.

It might appear surprising that the energy of 9 is so close to that of 6 and 7, since 9 has the odd electron localized at a primary carbon, whereas in both 6 and 7 the radical center is a secondary carbon. On the basis of the difference between the C–H BDEs for formation of primary and secondary alkyl radicals,[9] one might have expected 9 to be about 2 kcal/mol higher in energy than 6 or 7, but the energy difference is an order of magnitude smaller than this. Presumably, the fact that one double bond in 9 is disubstituted, whereas both double bonds are monosubstituted in 6 and 7, provides a compensating factor.

$-\Delta$BDEs. We obtain $-\Delta$BDE provided by the two vinyl groups in 1,4-pentadiene, relative to the BDE of the secondary C–H in propane, from the energy of the isodesmic reaction[20,30]

$$(CH_3)_2CH_2 + 1 \rightarrow (CH_3)_2CH\bullet + H_2C{=}CHCH_2CH{=}CH_2 \quad (1)$$

Using the QCISD energies in Tables I and II, we calculate a value of 23.0 kcal/mol for the energy change in this reaction. This compares reasonably well with the value, obtained for pentadienyl by Clark and co-workers,[7] of $-\Delta$BDE = 21.6 kcal/mol, relative to a value of 98 kcal/mol for the BDE of a secondary C–H bond.[9,10]

For comparison with the experimental value of Doering and Kitagawa[6] for the $-\Delta$BDE provided by the conjugated double bonds in a 1,3-butadienyl group, we compute the energy change for the isodesmic reaction

$$H_3CCH_3 + 1 \rightarrow H_3CCH_2\bullet + (E)\text{-}H_2C{=}CHCH{=}CHCH_3 \quad (2)$$

Our calculated QCISD value of $-\Delta$BDE = 19.5 kcal/mol for the effect of 1,3-butadienyl on the primary C–H BDE in ethane is 2.6 kcal/mol larger than their value of $-\Delta$BDE = 16.9 kcal/mol.

Doering and co-workers have also found that the $-\Delta$BDE that is provided by a conjugated (*E,Z*)-diene in forming an (*E,Z*)-pentadienyl radical is about 1 kcal/mol less than the $-\Delta$BDE provided by a conjugated (*E,E*)-diene in forming an (*E,E*)-pentadienyl radical.[31] Consistent with this experimental result is our computational finding that, although the QCISD energy of (*Z*)-1,3-pentadiene is 1.5 kcal/mol higher than that of the *E* stereoisomer, the QCISD energy of (*E,Z*)-pentadienyl radical (3) is 2.2 kcal/mol higher than that of the *E,E* stereoisomer 1. The 0.7 kcal/mol difference between these two numbers represents the greater energetic difficulty in forming 3 from (*Z*)-1,3-pentadiene.[32]

As a check on the accuracy of the relative energies computed for the species, other than 1, that appear in eqs 1 and 2, some additional comparisons with experiment can be made. We compute that (*E*)-1,3-pentadiene is 6.5 kcal/mol more stable than its 1,4-isomer. The actual difference in their measured heats of formation is 7.1 ± 0.4 kcal/mol.[12] Our computed QCISD value for the energy change in the isodesmic reaction

$$H_3CCH_3 + (CH_3)_2CH\bullet \rightarrow H_3CCH_2\bullet + (CH_3)_2CH_2 \quad (3)$$

is 2.9 kcal/mol, which can be compared with a recent experimental estimate of the difference between primary and secondary C–H BDEs of about 2 kcal/mol.[9]

These two comparisons with experiment indicate that our computed value for the energy change in the reaction

$$H_3CCH_3 + (CH_3)_2CH\bullet + H_2C{=}CHCH_2CH{=}CH_2 \rightarrow H_3CCH_2\bullet + (CH_3)_2CH_2 + (E)\text{-}H_2C{=}CHCH{=}CHCH_3 \quad (4)$$

will be too large by 1–2 kcal/mol. Since eq 4 is just the difference between eq 2 and eq 1, an error of 1–2 kcal/mol in the energy computed for eq 4 predicts that the error in the computed value for the energy change in eq 2 will be larger by 1–2 kcal/mol than that in eq 1. This is, presumably, why our computed value for the energy change in eq 2 differs from the experimental value of Doering and

---

[28] The QCISD(T) energy difference between 1 and 7 is the same as the QCISD energy difference of 25.5 kcal/mol that is given in Table I.

[29] For a computational study of the barrier height for this process in 1,3-butadiene and leading references to other computational and experimental studies, see: Wiberg, K. B.; Rosenberg, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 1509.

[30] This allows cancellation of errors that would occur if the absolute BDEs were computed: Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 271–324.

[31] Doering, W. von E.; Birladeanu, L.; Cheng, X.-H.; Kitagawa, T.; Sarma, K. *J. Am. Chem. Soc.* **1991**, *113*, 4558.

[32] In contrast, because we calculate the QCISD energy of cisoid-(*E*)-1,3-pentadiene to be 2.5 kcal/mol (3.4 kcal/mol, if planarity is enforced on the diene)[29] higher than that of the transoid stereoisomer, the formation of 1 from the latter stereoisomer is computed to require 0.3 (1.2) kcal/mol more energy than formation of 3 from the former. In this case the destabilizing interactions between C-1 and C-4 are larger in the cisoid diene than in 3, as would be predicted from simple Hückel theory by comparing the π bond orders between these two carbons in 1,3-butadiene and 1,3-pentadienyl radical.

Kitagawa[6] by 2.6 kcal/mol, whereas our computed value for the energy change in eq 1 differs from the experimental value of Clark and co-workers[7] by only 1.6 kcal/mol. As noted in the introduction, both experimental studies obtained exactly the same heat of formation for the pentadienyl radical.

Comparison of −ΔBDEs with Rotation Barriers. The energy that we compute is required to twist two vinyl groups in **1** out of conjugation to form **6**, **7**, or **9** is 25.5–25.9 kcal/mol. The average of these energies is higher by 2.2 kcal/mol than the −ΔBDE = 23.5 kcal/mol that we compute for the effect of two vinyl groups on the BDE for a secondary C–H bond. The QCISD energy of 20.6 kcal/mol, required to reach the transition state **8** for rotating a terminal methylene group in **1** out of conjugation, is 1.1 kcal/mol higher than the −ΔBDE that we compute for the effect of 1,3-butadienyl on the BDE for a primary C–H bond. The latter difference is half as large as the former and exactly the same as the difference between the QCISD rotational barrier of 15.3 kcal/mol in allyl and the QCISD value of 14.2 kcal/mol for the effect of a vinyl group on the BDE of a primary C–H bond.[27]

As discussed in the introduction, the differences between SEs measured by rotational barriers and those obtained from −ΔBDEs are due to the fact that an unsaturated group or groups, when they are rotated out of conjugation with the radical center, have a smaller effect on lowering the C–H BDE than the same number of alkyl groups.[18,20] This is easily seen by subtracting eq 1 from the expression **1** → **6** (or **7** or **9**). The resulting isodesmic reaction is

$$(CH_3)_2CH\bullet + H_2C{=}CHCH_2CH{=}CH_2 \rightarrow (CH_3)_2CH_2 + \mathbf{6}\ (\mathbf{7}\text{ or }\mathbf{9}) \quad (5)$$

which we compute to be endothermic by 2.0–2.4 kcal/mol.[33] Similarly, subtracting eq 2 from the expression **1** → **8** yields

$$H_3CCH_2\bullet + (E)\text{-}H_2C{=}CHCH{=}CHCH_3 \rightarrow H_3CCH_3 + \mathbf{8} \quad (6)$$

which we calculate to be endothermic by 1.1 kcal/mol. Apparently, replacing the two methyl groups in propane and propyl radical by two vinyl groups that cannot conjugate with the radical center raises the C–H BDE twice as much as replacing a methyl group in ethane and ethyl radical by either a butadienyl or a vinyl group[27] that cannot conjugate with the radical center.

Two explanations have previously been suggested to explain the effect on BDEs of unsaturated groups that are prevented from conjugating with a radical center.[20] Both the greater electronegativity[34] of an unsaturated, compared to a saturated group, and the inability of bonds to sp^2 carbons to hyperconjugate as well as the weaker bonds to sp^3 carbons[35] could be responsible for this effect.

It should be noted, however, that replacement of hydrogen(s) in methane by unsaturated group or groups, even when they are prohibited from conjugating with the radical center in methyl, lowers the methane BDE. Substituting $CH_3\bullet$ for the radicals in the left hand side of eqs 5 and 6 and CH_4 for the alkanes in the right hand side gives reactions that are calculated at the QCISD level to be exothermic by, respectively, 6.2 and 3.2 kcal/mol. Thus, it appears that unsaturated groups can provide hyperconjugative, as well as conjugative, stabilization for radical centers, but they do not provide as much hyperconjugative stabilization as the same number of alkyl groups.

Conclusions

Our calculations predict that (*Z*,*Z*)-pentadienyl radical (**5**) is 5.6 kcal/mol less stable than the *E*,*E* isomer **1**, which explains why **5** has not been detected by EPR studies of pentadienyl.[7,8] Our calculated value of 2.2 kcal/mol for the energy difference between (*E*,*Z*)-pentadienyl (**3**) and **1** is in very good agreement with the experimental value of 2.4 kcal/mol. However, despite the much lower energy of **1** than **5**, the transition states **2** and **4** connecting each of them to **3** are computed to be nearly isoenergetic.

We calculate that the barrier to interchanging the two types of terminal hydrogens in **1** by rotating a terminal methylene group out of conjugation with the butadienyl moiety (transition state **8**) requires 20.6 kcal/mol. This prediction remains to be tested experimentally. Our calculations find that the lowering of the C–H BDE that results from replacing a methyl group in ethane by 1,3-butadienyl is 19.5 kcal/mol, which is 1.1 kcal/mol lower than the calculated barrier to hydrogen interchange via **8**, but 2.6 kcal/mol higher than the experimental pentadienyl SE of 16.9 kcal/mol, obtained by Doering and Kitagawa.[6]

The results of our calculations support the proposition that the difference between the energy required to twist two vinyl groups out of conjugation in pentadienyl radical and the effect of the two vinyl groups in 1,4-pentadiene on the secondary C–H BDE really is larger than the difference between the rotational barrier in allyl and the effect of the vinyl group on the C–H BDE of propene. Our results for pentadienyl and allyl indicate that the differences between the rotational barriers and the corresponding −ΔBDEs increase approximately linearly with the number of unsaturated groups attached to the radical center.

However, the energy of 25.5–25.9 kcal/mol that we calculate is necessary to convert **1** to **6**, **7**, or **9** is smaller than the value of 27.4 kcal/mol, obtained from the experiments of MacInnes and Walton.[7,8] In contrast, the calculated lowering by 23.5 kcal/mol of the secondary C–H BDE in propane by the two vinyl groups in 1,4-pentadiene is larger than the experimental value of 21.6 kcal/mol, obtained by Clark and co-workers.[7] Consequently, the difference of 2.0–2.4 kcal/mol between these two energies that we have computed is significantly smaller than the 5.8 kcal/mol found by these experiments.

Acknowledgment. We thank the National Science Foundation for support of this research and for a grant that made possible the purchase of the Convex C-2 computer on which many of these calculations were performed. We thank also the San Diego Supercomputer Center for a generous grant of time on the Cray Y-MP on

---

[33] Using the QCISD(T) energies (hartrees) for 1,4-pentadiene (E = −194.6607), **7** (E = −194.0021), propane (E = −118.7156), and isopropyl radical (E = −118.0606), this reaction is computed to be endothermic by 2.3 kcal/mol.

[34] Coolidge, M. B.; Borden, W. T. *J. Am. Chem. Soc.* **1988**, *110*, 2298.

[35] For example, the C–H BDE of ethene[36] exceeds that of ethane[37] by about 10 kcal/mol.

[36] Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

[37] (a) Parmar, S. S.; Benson, S. *J. Am. Chem. Soc.* **1989**, *111*, 57 and references cited therein. (b) Ruscic, B.; Berkowitz, J.; Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 114.

which some of the calculations were effected. R.C.F. thanks the Board of Trustees of the University of Maine System for a sabbatical leave during the course of which this research was accomplished.

Supplementary Material Available: UHF/6-31G*-optimized geometries and zero-point energies of pentadienyl radical conformations **1**–**9**, whose electronic energies are given in Table I, and RHF(UHF)/6-31G*-optimized geometries and zero-point energies of the molecules and radicals whose electronic energies are given in Table II (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the article, and can be ordered from the ACS. See any current masthead page for ordering information.