

## Do Deviations from Bond Enthalpy Additivity Define the Thermodynamic Stabilities of Diradicals?

Daisy Y. Zhang<sup>\*,†</sup> and Weston Thatcher Borden<sup>\*,‡</sup>

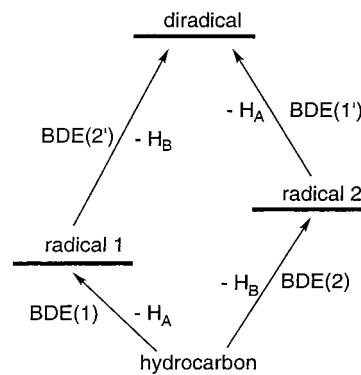
Department of Chemistry and Biochemistry, Seattle Pacific University, Seattle, Washington 98119-1997, and Department of Chemistry, Box 351700, University of Washington, Seattle, Washington 98195-1700

borden@chem.washington.edu; daisy@spu.edu

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Deviations from bond enthalpy additivity ( $\Delta$ BEA) are frequently used to assess the thermodynamic stabilities of diradicals. (U)B3LYP/6-31G\* calculations have been performed in order to determine how well  $\Delta$ BEA values actually do reflect the thermodynamic stabilities of the triplet states of diradicals in which one or both nonbonding electrons occupy a delocalized  $\pi$  orbital. The calculations find that different pathways for forming  $\sigma,\pi$ -diradicals, such as  $\alpha,2$ - and  $\alpha,4$ -dehydrotoluene (**4** and **6**), give  $\Delta$ BEA values that differ by ca. 1 kcal/mol. The path dependency of the  $\Delta$ BEA values is computed to be one order of magnitude larger for non-Kekulé hydrocarbon diradicals, such as *m*-benzoquinodimethane (**12**) and 1,3-dimethylenecyclobutane-2,4-diyl (**15**), than for  $\sigma,\pi$ -diradicals. Since the  $\Delta$ BEA values for forming **4**, **6**, **12**, and **15** are all path dependent, we conclude that  $\Delta$ BEA values for diradicals with one or two delocalized, nonbonding  $\pi$  electrons do not, in general, uniquely define the thermodynamic stabilities of the diradicals. Hence,  $\Delta$ BEA values should not be used for this purpose, especially for non-Kekulé hydrocarbon diradicals.

The thermodynamic stability of a diradical, relative to a hypothetical diradical in which the presence of the first radical center has no effect on the energy required to create the second, is often assessed by the difference between the heat of formation of the diradical and the heat of formation computed for it from bond enthalpy additivity (BEA).<sup>1–10</sup> BEA holds when the overall enthalpy change for breaking two bonds in a closed-shell molecule, to form a diradical, is equal to the sum of bond dissociation enthalpies (BDEs) for breaking the same two bonds to form two monoradicals.



**Figure 1.** Bond dissociation enthalpies (BDEs) for forming two monoradicals from a hydrocarbon, by breaking bonds to  $H_A$  and  $H_B$ , and for forming a diradical from each of the monoradicals by breaking the bonds to the same two hydrogens.

Deviations from BEA have usually been used to assess the thermodynamic stabilities of diradicals formed from hydrocarbons. As shown in Figure 1, the overall enthalpy change for forming a diradical by breaking two C–H bonds in a hydrocarbon is  $BDE(1) + BDE(2') = BDE(1') + BDE(2)$ . For breaking the same pair of bonds to form two monoradicals, the sum of the BDEs is  $BDE(1) + BDE(2)$ . Thus, BEA holds in diradicals for which  $BDE(1) = BDE(1')$  and  $BDE(2) = BDE(2')$ ; i.e., diradicals in which the presence of one radical center does not affect the enthalpy for creation of the second radical center.

Deviations from BEA ( $\Delta$ BEA) occur when, for breaking a given bond, the dissociation enthalpy for forming a monoradical differs from that for forming a diradical. As shown graphically in Figure 1, the first law of thermodynamics requires that  $\Delta$ BEA =  $BDE(1') - BDE(1) = BDE(2') - BDE(2)$ . Thus, the size of  $\Delta$ BEA is indepen-

<sup>†</sup> Seattle Pacific University.

<sup>‡</sup> University of Washington.

(1) For some examples involving propane-1,3-diyls and cyclohexane-1,4-diyls, see: (a) Doering, W. von E. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 5279. (b) Getty, S. J.; Hrovat, D. A.; Xu, J. D.; Barker, S. A.; Borden, W. T. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1689. (c) Skancke, A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1998**, *120*, 7079; and (d) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, H.-Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529.

(2) Deviations from BEA have also been used to assess the thermodynamic stabilities of silylenes and carbenes. See, for example: (a) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246. (b) Carter, E. A.; Goddard, W. A., *J. Phys. Chem.* **1986**, *90*, 998. (c) Clauberg, H.; Minsek, D. W.; Chen, P. *J. Am. Chem. Soc.* **1992**, *114*, 99.

(3) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976; (a) pp 63–65; (b) pp 118–120.

(4) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279.

(5) Wenthold, P. G.; Wierschke, S. G.; Nash, J. J.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 7378.

(6) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475.

(7) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Soc. Mass Spectrom.* **1999**, *10*, 800.

(8) (a) Hammad, L. A.; Wenthold, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 11203. (b) For a closely related study of  $\Delta$ BEA for forming 1,3,5-trimethylenebenzene, see: Hammad, L. A.; Wenthold, P. G. *J. Am. Chem. Soc.* **2001**, *123*, 12311.

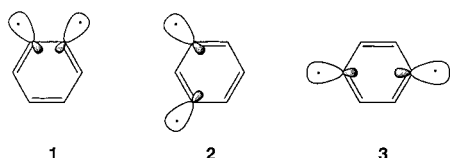
(9) Wenthold, P. G.; Kim, J. B.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 1354.

(10) Hill, B. T.; Squires, R. R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1027.

dent of which of the two possible monoradicals serves as the immediate precursor of a diradical.

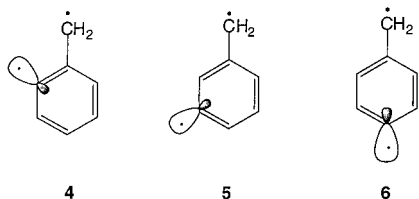
With the definition,  $\Delta\text{BEA} = \text{BDE}(1') - \text{BDE}(1)$ , a positive  $\Delta\text{BEA}$  means that the dissociation enthalpy for the bond to  $\text{H}_\text{A}$  is larger in forming a diradical than a monoradical. Therefore, a positive  $\Delta\text{BEA}$  is usually taken to mean that the interaction between the pair of nonbonding electrons in a diradical is thermodynamically destabilizing, and a negative  $\Delta\text{BEA}$  value is similarly interpreted as meaning that the interaction between the pair of nonbonding electrons in a diradical provides net stabilization.

Negative  $\Delta\text{BEA}$  values are expected to be found in singlet diradicals, such as the dehydrobenzenes (**1–3**), in which through-space or through-bond interactions between the two radical centers stabilize the diradical.<sup>11</sup> When the interaction is through space, the magnitude of the negative  $\Delta\text{BEA}$  value is equal to the strength of the bond formed by this interaction.<sup>3a</sup>



Experiments by Wenthold, Squires, and Lineberger did, in fact, find negative  $\Delta\text{BEA}$  values for forming the lowest singlet state of *o*-, *m*-, and *p*-dehydrobenzene.<sup>4</sup> In contrast, these authors found the lowest triplet state of each dehydrobenzene to have  $\Delta\text{BEA} \approx 0$ . Hence, the interactions between the nonbonding electrons in each of the three triplet dehydrobenzenes are apparently quite small.

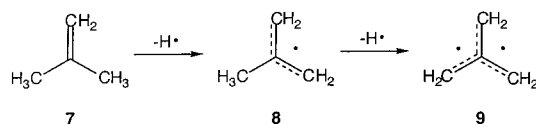
In contrast to the case in the triplet dehydrobenzenes, Squires and co-workers found that the triplet states of  $\alpha$ ,2- and  $\alpha$ ,4-dehydrotoluene diradicals (respectively, **4** and **6**) do show negative  $\Delta\text{BEA}$  values of a few kcal/mol.<sup>5</sup> This finding is due to the fact that the probability of electrons of the same spin occupying the  $\sigma$  and the  $2p-\pi$  AOs of the dehydro ring carbon is higher in each of these two triplet diradicals than in either of the possible monoradicals from which it might be formed. The lower Coulomb repulsion that results from correlation between electrons of the same spin stabilizes each of the triplet diradicals, relative to benzyl and  $\sigma$ -tolyl monoradicals.



In  $\alpha$ ,3-dehydrotoluene diradical (**5**), the unpaired  $\pi$  electron does not appear in the  $2p-\pi$  AO of the  $\sigma$ -dehydro ring carbon, but dynamic spin polarization results in the appearance of spin in this  $2p-\pi$  AO that is of opposite sign to the spin in the  $2p-\pi$  AOs of the ortho and para carbons. Therefore, unlike the case in **4** and **6**, in **5** it

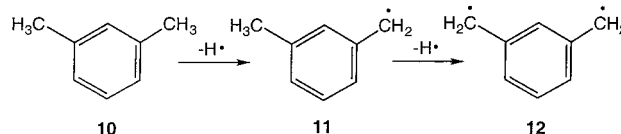
was the singlet state, rather than the triplet, that was found to have a negative  $\Delta\text{BEA}$  by Squires and co-workers.<sup>5</sup>

In non-Kekulé hydrocarbon diradicals, both of the nonbonding electrons occupy  $\pi$  orbitals. For forming triplet trimethylenemethane (**9**), the prototypical diradical of this class, a small positive value of  $\Delta\text{BEA}$  is predicted by Hückel theory. The change in the Hückel energy of  $\alpha + 2(\sqrt{3} - \sqrt{2})|\beta|$  on forming **9** from 2-methylallyl radical (**8**) is ca.  $0.2|\beta|$  smaller than the change in the Hückel energy of  $\alpha + 2(\sqrt{2} - 1)|\beta|$  on forming **8** from isobutylene (**7**).



On the other hand, the negative spin density at C-2 in 2-methylallyl radical (**8**) should lower the methyl C–H BDE for forming triplet **9** from **8**, relative to that for forming **8** from **7**. Apparently, these two types of effects nearly cancel, since *ab initio* calculations predict and experiments have found  $\Delta\text{BEA}$  values near zero for forming the triplet ground state of **9** from **7**.<sup>6,7</sup>

Similar types of effects on  $\Delta\text{BEA}$ , which work in opposite directions, are also present in the formation of triplet *m*-benzoquinodimethane (**12**) from *m*-xylene (**10**). Apparently, these effects again almost cancel, for, as in the formation of triplet **9**, calculations predict and experiments have found values of  $\Delta\text{BEA} \approx 0$  for forming triplet **12** from **10**.<sup>8,9</sup>



Because the nonbonding molecular orbitals (NBMOs) of both **9** and **12** have atoms in common, the lowest singlet state in each of these planar diradicals is predicted, by qualitative theory,<sup>12</sup> as well as by quantitative calculations,<sup>13</sup> to be well above the triplet state in energy. These predictions have been confirmed experimentally for both **9** ( $\Delta E_{\text{ST}} = 16.1 \pm 0.1$  kcal/mol)<sup>6,7</sup> and **12** ( $\Delta E_{\text{ST}} = 9.6 \pm 0.2$  kcal/mol).<sup>9</sup> Since the triplet states of these diradicals have  $\Delta\text{BEA} \approx 0$ , the lowest planar singlet state of each diradical has a positive  $\Delta\text{BEA}$  that is about the same size as  $\Delta E_{\text{ST}}$ .

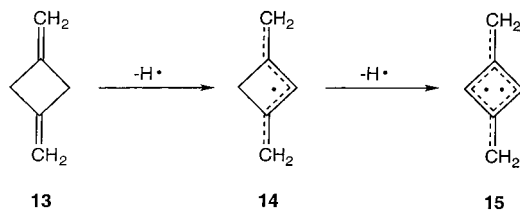
Like **9** and **12**, 1,3-dimethylenecyclobutane-2,4-diyl (**15**) is a non-Kekulé hydrocarbon diradical in which the lowest singlet state is predicted to be well above the triplet state in energy.<sup>12,13</sup> However, unlike the case in **9** and **12**, both calculations and experiments have found a large, positive value of  $\Delta\text{BEA}$  for forming the triplet state of **15** from 1,3-dimethylenecyclobutane (**13**).<sup>10</sup> The B3LYP/6-31+G\* calculations of Hill and Squires predicted  $\Delta\text{BEA} = 13.2$  kcal/mol (13.4 kcal/mol without diffuse functions in the basis set), and their experiments found  $\Delta\text{BEA} =$

(12) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(13) Review: Borden, W. T. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999; pp 61–102.

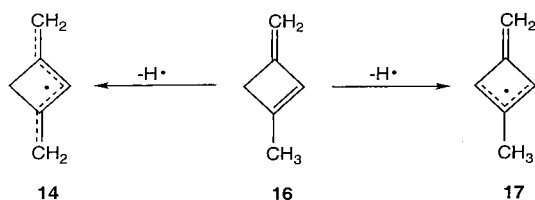
(11) See, for example: Hoffmann, R.; Imamura, A. *J. Am. Chem. Soc.* **1968**, *90*, 1499.

$16.6 \pm 3.6$  kcal/mol. Hill and Squires attributed the large, positive  $\Delta\text{BEA}$  to partial antiaromaticity in **15**.



We have refined the explanation of Hill and Squires.<sup>14</sup> We showed that, because one of the NBMOs of **15** is confined to just two of the ring carbons, not all of the resonance structures that can be drawn for this diradical actually contribute to its electronic structure. Consequently, on breaking a second ring C–H bond in penta-dienylic radical **14** to form triplet **15**, the additional resonance stabilization is allylic, rather than pentadienylic. Calculations on derivatives of **13–15** with heteroatoms in place of the exocyclic  $\text{CH}_2$  groups have confirmed this conclusion.<sup>15</sup>

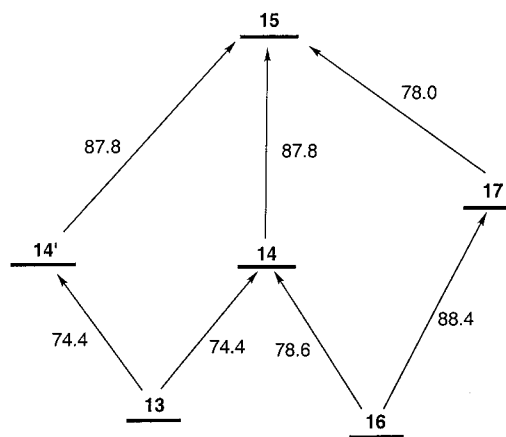
A smaller contributor to the large value of  $\Delta\text{BEA}$  on forming triplet **15** from **13** is the fact that the double bonds in **13** are not conjugated. Our B3LYP/6-31G\* calculations found that 1-methyl-3-methylenecyclobutene (**16**) is 4.2 kcal/mol lower in energy than **13**.<sup>14</sup> Thus, in forming radical **14**, a methyl C–H bond in **16** has a BDE that is 4.2 kcal/mol larger than a ring C–H bond in **13**.



However, our calculations also found that a ring C–H bond in **16** has a BDE that is 14.0 kcal/mol larger than a ring C–H bond in **13**. The reason is that the NBMO in radical **17**, like one of the NBMOs in diradical **15**, is confined to just two of the ring carbons. Therefore, only two of the three resonance structures that can be drawn for radical **17** actually contribute to its structure. Consequently, because breaking a ring C–H bond in both **14** and **16** generates an unpaired electron in an allylic NBMO, radical **14** and hydrocarbon **16** have ring C–H BDEs that are almost identical. In fact, we computed the  $\Delta\text{BEA}$  for forming triplet **15** from hydrocarbon **16** to be only  $-0.6$  kcal/mol.

The  $\Delta\text{BEAs}$  for forming triplet **15** from hydrocarbons **13** and **16** thus differ by  $13.4 - (-0.6) = 14.0$  kcal/mol. As already noted, 4.2 kcal/mol of this difference is due to the difference between the enthalpies of the two hydrocarbons. However, more than twice this amount is due to the 9.8 kcal/mol higher enthalpy of radical **17**, compared to radical **14**.

The origin of the difference between the  $\Delta\text{BEA}$  values for the pathways from **13** and **16** to triplet **15** can be easily analyzed by comparing the pair of thermocycles that are shown in Figure 2. Monoradical **14** is common



**Figure 2.** B3LYP/6-31G\* BDEs (kcal/mol)<sup>14</sup> for forming triplet 1,3-dimethylenecyclobutane-2,4-diyl (**15**) from 1,3-dimethylenecyclobutane (**13**) and from 1-methyl-3-methylenecyclobutene (**16**).<sup>16</sup>

to both thermocycles. However, the enthalpies of hydrocarbons **13** and **16** differ, as do the enthalpies of radicals **14'**<sup>16</sup> and **17**.

The BDE for forming a monoradical by breaking a ring C–H bond is 14.0 kcal/mol larger for **16**  $\rightarrow$  **17** than for **13**  $\rightarrow$  **14'**. Since the ring C–H BDE for forming triplet **15** from **14** is common to both of the thermocycles, the difference between the ring C–H BDEs in hydrocarbons **13** and **16** is responsible for the 14.0 kcal/mol difference between the  $\Delta\text{BEA}$  values for forming triplet **15** from these two hydrocarbons.

If a diradical can be formed from only one hydrocarbon, then, unlike the case for **15**, the diradical has a unique  $\Delta\text{BEA}$  value. For example, diradicals such as **1–3**, which have both of their nonbonding electrons localized in  $\sigma$  orbitals, can be formed by breaking a pair of C–H bonds in just one hydrocarbon. Therefore, the  $\Delta\text{BEA}$  value for each of the dehydrobenzenes (**1–3**) is unique, and this value can be used to define the thermodynamic stability of each of these diradicals.

In contrast, diradicals that have one or both nonbonding electrons in a delocalized  $\pi$  orbital can, in general, be formed from more than one isomeric hydrocarbon. Therefore,  $\sigma,\pi$ -diradicals, such as the  $\alpha,n$ -dehydrotoluenes (**4–6**), and non-Kekulé hydrocarbon diradicals, such as *m*-benzoquinodimethane (**12**) and 1,3-dimethylenecyclobutane-2,4-diyl (**15**) have more than one  $\Delta\text{BEA}$  value. If the sizes of the different  $\Delta\text{BEA}$  values are highly dependent on the path by which the diradical is formed, then none of them provides an unambiguous definition of the thermodynamic stability of the diradical.

To address the question of whether, as in the case of **15**, the  $\Delta\text{BEA}$  values for formation of **4**, **6**, and **12** are highly path-dependent, we have carried out electronic structure calculations. Herein we report the results of those calculations. They show the  $\Delta\text{BEA}$  values for these diradicals are sufficiently path-dependent that the  $\Delta\text{BEA}$  values fail to provide unambiguous definitions of the thermodynamic stabilities of these diradicals.

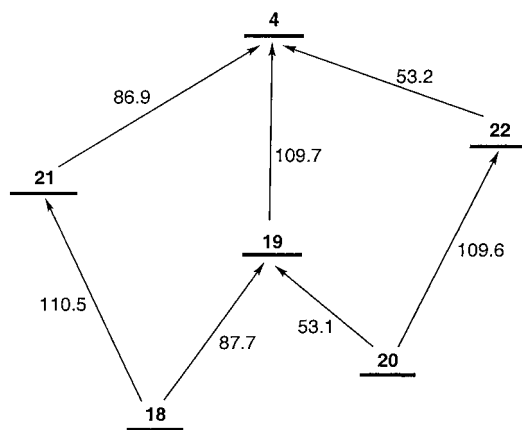
**Computational Methodology.** As in our previous studies of  $\Delta\text{BEAs}$  for formation of **5**,<sup>14,15</sup> DFT calculations on  $\Delta\text{BEAs}$  for formation of **4**, **6**, and **12** were carried out

(14) (a) Zhang, D. Y.; Borden, W. T. *J. Mol. Struct.* **2000**, 556, 151. (b) Because corrections for differences in heat capacities were not made, the enthalpy differences in that paper differ by a few tenths of a kcal/mol from the  $\Delta\Delta H_{298}$  values cited here.

(15) Zhang, D. Y. *J. Phys. Org. Chem.* **2001**, 14, 295.

(16) Radical **14'** differs from radical **14** only by the equivalent ring carbon of **13** at which a C–H bond is broken.





**Figure 3.** B3LYP/6-31G\* BDEs (kcal/mol) for forming triplet  $\alpha$ ,2-dehydrotoluene (**4**) from toluene (**18**) and from 5-methylene-1,3-cyclohexadiene (**20**).

with the 6-31G\* basis set,<sup>17</sup> utilizing Becke's, three-parameter, hybrid, functional<sup>18</sup> and the nonlocal correlation functional of Lee, Yang, and Parr.<sup>19</sup> All of the calculations were performed using the Gaussian 98 suite of programs.<sup>20</sup>

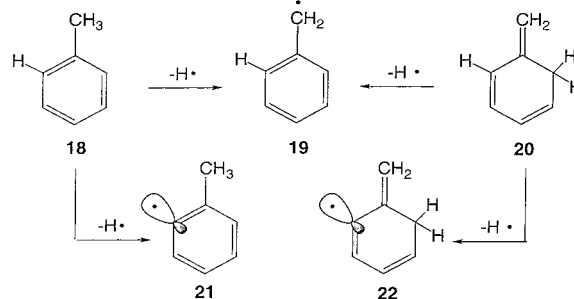
A vibrational analysis was carried out at each stationary point, to confirm its identity as an energy minimum. The harmonic frequencies were used, without scaling, to calculate the zero-point energies and thermal corrections necessary to compute the bond dissociation enthalpies (BDEs) at 298 K. The B3LYP/6-31G\* optimized geometries, electronic energies, and zero-point and thermal corrections are available as Supporting Information.

## Results

Figure 2 suggests a general method for determining whether two pathways to the same diradical have different  $\Delta$ BEA values. Choose two isomeric hydrocarbons that can form the same monoradical by breaking one C–H bond in each hydrocarbon and different monoradicals by breaking another C–H bond in each hydrocarbon. Both sets of monoradicals must, of course, lead to the same diradical. The difference between the  $\Delta$ BEA values for forming the same diradical from the two isomeric hydrocarbons will then be equal to the difference between the C–H BDEs for forming the two different monoradicals from the two hydrocarbon isomers.

**Triplet  $\alpha$ , $n$ -Dehydrotoluenes **4** and **6**.** Figure 3 shows how this type of analysis can be applied to evaluating the difference between the  $\Delta$ BEA values for formation of triplet  $\alpha$ ,2-dehydrotoluene (**4**). This diradical can be formed starting from either toluene (**18**) or

5-methylene-1,3-cyclohexadiene (**20**). Breaking a C–H bond at the tetrahedral carbon in either **18** or **20** leads to the benzyl radical **19**. However, breaking the C–H bond at C-2 in the two different hydrocarbons leads to two different  $\sigma$  radicals, respectively **21** and **22**.



The results displayed in Figure 3 reveal that formation of triplet **4** from **18** has  $\Delta$ BEA =  $-0.8$  kcal/mol. This B3LYP value is smaller in magnitude but has the same sign as the values measured by Squires et al. and also obtained by them from wave-function-based calculations.<sup>5</sup> In contrast, forming triplet **4** from **20** is computed to have a positive value of  $\Delta$ BEA =  $0.1$  kcal/mol. As shown in Figure 3, the difference of  $0.9$  kcal/mol between the two  $\Delta$ BEA values is due to the difference between the C–H BDEs in forming  $\sigma$  radicals **21** and **22** from, respectively, toluene (**18**) and triene **20**.<sup>21</sup>

The energetics for formation of triplet  $\alpha$ ,4-dehydrotoluene (**6**) are nearly the same as those depicted in Figure 3 for formation of triplet  $\alpha$ ,2-dehydrotoluene (**4**). As found by Squires et al.,<sup>5</sup>  $\Delta$ BEA for formation of triplet **6** from toluene (**18**) is negative, and again, the B3LYP value of  $\Delta$ BEA =  $-1.1$  kcal/mol is smaller in magnitude than the values both calculated and measured by Squires. In contrast, formation of **6** from 5-methylene-1,3-cyclohexadiene (**20**) has a positive  $\Delta$ BEA of  $0.1$  kcal/mol. The difference of  $1.2$  kcal/mol between these  $\Delta$ BDE values is due to the difference between the C–H BDEs at C-4 in **18** and **20**, and it is again **20** that has the lower C–H BDE.<sup>22</sup>

The differences between the  $\Delta$ BEA values for forming  $\alpha$ ,2- and  $\alpha$ ,4-dehydrotoluene (**4** and **6**) from toluene (**18**) and from 5-methylene-1,3-cyclohexadiene (**20**) are small, amounting to  $0.9$  kcal/mol for formation of **4** and  $1.2$  kcal/mol for formation of **6**. These differences are small enough almost certainly to fall well within the error limits of any experiments designed to measure the  $\Delta$ BEA values for these two diradicals.

However, the calculated energy differences of ca.  $1$  kcal/mol between the two  $\Delta$ BEA values for each of these diradicals do have theoretical importance. Because the  $\Delta$ BEA values are themselves small, whether **4** and **6** are formed from **18** or from **20** determines whether the  $\Delta$ BEA values are positive or negative. Hence, whether triplet diradicals **4** and **6** are calculated to be thermodynamically stabilized, by having electrons of the same spin in the

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

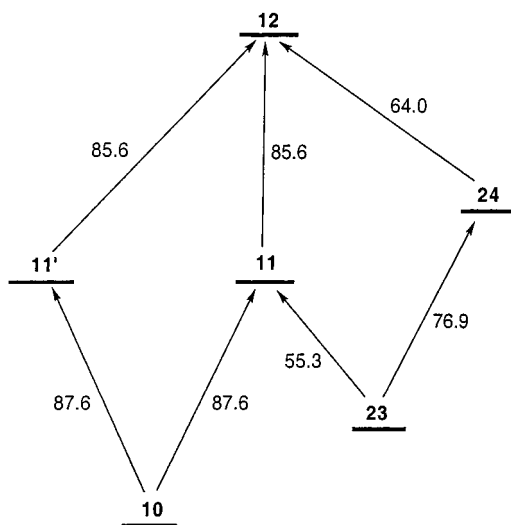
(18) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(19) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

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

(21) Diradical **4** can also be formed from 3-methylene-1,4-cyclohexadiene, for which the BDE of the C–H bond at C-2 is essentially the same as that for the C–H bond at C-2 in **20**. Therefore, both methylenecyclohexadienes give  $\Delta$ BEA =  $0.1$  kcal/mol.

(22) We conjecture that spin polarization of the  $\pi$  electrons is more effective at stabilizing the unpaired  $\sigma$  electron in radical **22**, formed from the conjugated triene (**20**), than in radical **21**, formed from the aromatic hydrocarbon (**18**).



**Figure 4.** B3LYP/6-31G\* C-H BDEs (kcal/mol) for forming triplet *m*-benzoquinodimethane (**12**) from *m*-xylene (**10**) and from 1-methyl-5-methylene-1,3-cyclohexadiene (**23**).<sup>23</sup>

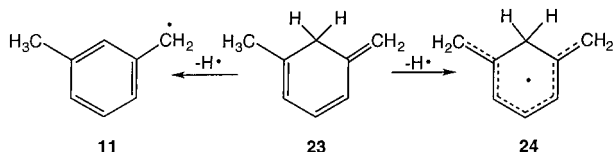
nonbonding  $\sigma$  and  $\pi$  MOs, is dependent on the arbitrary choice of the path to the each of these diradicals.

As discussed in the Introduction, the  $\Delta$ BEA values for triplet 1,3-dimethylenecyclobutane-2,4-diyl (**15**) are also path-dependent. However, the difference between the  $\Delta$ BEA values is more than one order of magnitude larger for non-Kekulé hydrocarbon diradical **15** (14.0 kcal/mol) than for  $\sigma,\pi$ -diradicals **4** (0.9 kcal/mol) and **6** (1.2 kcal/mol). Our calculations on triplet *m*-benzoquinodimethane (**12**) reveal that, for this non-Kekulé hydrocarbon diradical too, the  $\Delta$ BEA values are much more path-dependent than are the  $\Delta$ BEA values for **4** and **6**.

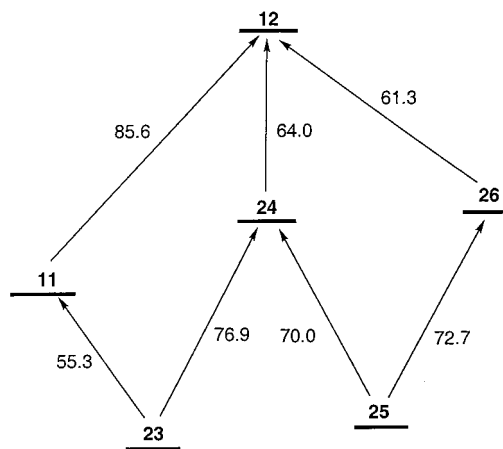
**Triplet *m*-Benzoquinodimethane (**12**).** As shown in Figure 4, our calculations find that formation of triplet **12** from *m*-xylene (**10**) involves methyl C-H BDEs of, respectively, 87.6 and 85.6 kcal/mol for forming *m*-methylbenzyl radical (**11**) from **10** and triplet **12** from **11**. Our calculations thus predict  $\Delta$ BEA = -2.0 kcal/mol for formation of triplet **12** from **10**.

Our computational results are in reasonable agreement with the experimental data of Hammad and Wenthold,<sup>8</sup> who found first and second C-H BDEs of  $90.1 \pm 1.7$  and  $90.7 \pm 2.9$  kcal/mol in forming triplet **12** from **10**. The experimental BDEs are both slightly higher than those we compute, but the uncertainties in the experimental values are large enough to make our computed value of  $\Delta$ BEA = -2.0 kcal/mol fall within experimental error of Hammad and Wenthold's value of  $\Delta$ BEA =  $0.6 \pm 3.4$  kcal/mol.

Benzylic radical **11** can also be formed by breaking a ring C-H bond in conjugated triene **23**. Breaking a methyl C-H bond in **23** leads to heptatrienylic radical **24**, and breaking a C-H bond at C-6 of the ring in **24** leads to diradical **12**.



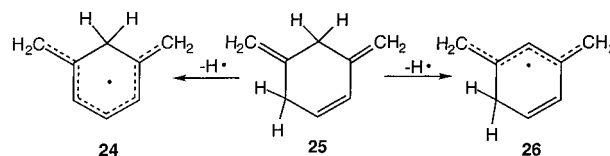
The BDEs calculated for forming triplet **12** from both **10** and **23** are shown in Figure 4. The  $\Delta$ BEA for forming



**Figure 5.** B3LYP/6-31G\* C-H BDEs (kcal/mol) for forming triplet *m*-benzoquinodimethane (**12**) from 1-methyl-5-methylene-1,3-cyclohexadiene (**23**) and from 3,5-dimethylenecyclohexene (**25**).

**12** from **23** is 8.7 kcal/mol, which is 10.7 kcal/mol greater than  $\Delta$ BEA = -2.0 kcal/mol for forming **12** from **10**. Analysis of the two pathways to **12** in terms of the thermocycles in Figure 4 shows that this increase is attributable to the  $87.6 - 76.9 = 10.7$  kcal/mol lower BDE for breaking a methyl C-H bond in triene **23**, to form heptatrienylic radical **24**, than for breaking a methyl C-H bond in *m*-xylene (**10**), to form benzylic radical **11**.<sup>23</sup> Since a methyl C-H bond is broken in forming both radicals, 10.7 kcal/mol represents the B3LYP/6-31G\* difference between the heptatrienylic resonance energy in forming **24** from **23** and the benzylic resonance energy in forming **11** from **10**.

A third  $\Delta$ BEA value for **12** can be obtained if heptatrienylic radical **24**, rather than benzylic radical **11**, is considered to be the monoradical that is common to two pathways. Radical **24** can be formed from **25**, as well as from **23**. Triene **25** can break a ring C-H bond to form not only linearly conjugated heptatrienylic radical **24** but also cross-conjugated vinylpentadienylic radical **26**.



Hydrocarbon **23** is a conjugated triene, whereas, hydrocarbon **25** has only two of its three double bonds in conjugation. In addition, **23** has one more endocyclic double bond than **25** does. As shown in Figure 5, these differences result in **23** being computed to be lower in enthalpy than **25** by 6.9 kcal/mol.

However, this enthalpy difference between hydrocarbons **23** and **25** is much smaller than the enthalpy difference between radicals **11** and **26**. *m*-Methylbenzyl radical (**11**) contains an aromatic ring; whereas, the vinylpentadienylic radical (**26**) does not. As a result, **11** is computed to be lower in enthalpy than **26** by fully 24.3 kcal/mol. Consequently, the C-H BDE for forming **11**

(23) Radical **11'** differs from radical **11** only by the equivalent methyl group of **10** at which a C-H bond is broken.

from **23** is  $24.3 - 6.9 = 17.4$  kcal/mol less than the C–H BDE for forming **26** from **25**.

As shown in Figure 5, this 17.4 kcal/mol difference between C–H BDEs in **23** and **25** is equal to the difference between the  $\Delta$ BEAs for forming triplet **12** from **23** and from **25**. Coincidentally,  $\Delta$ BEA =  $-8.7$  kcal/mol for forming triplet **12** from triene **25** has exactly the same size but opposite sign as the  $\Delta$ BEA value for forming this diradical from triene **23**.

### Discussion

The difference of 17.4 kcal/mol between the  $\Delta$ BEAs for forming diradical **12** from trienes **23** and **25** is even larger than the difference of 14.0 kcal/mol between the  $\Delta$ BEAs for forming diradical **15** from hydrocarbons **13** and **16**. The very large path dependence of the  $\Delta$ BEA values for forming **12** and **15** means that the thermodynamic stability of neither of these two non-Kekulé hydrocarbon diradicals is uniquely defined by a  $\Delta$ BEA value.

The path dependence of the  $\Delta$ BEA values for these non-Kekulé diradicals might not be such a problem, if it were largely due just to differences between the heats of formation of the various hydrocarbons from which each diradical can be formed. If this were the case, knowing the  $\Delta$ BEA for the pathway from one hydrocarbon to a diradical, the  $\Delta$ BEA for the pathway from a second hydrocarbon to the same diradical could be obtained from the difference between the heats of formation of the two hydrocarbons. For example, from  $\Delta$ BEA =  $-2.0$  kcal/mol for formation of *m*-benzoquinodimethane (**12**) from *m*-xylene (**10**) and the 32.3 kcal/mol difference between the heat of formation 1-methyl-5-methylenecyclohexane (**23**) and **10**, one would then be able to predict  $\Delta$ BEA = 30.3 kcal/mol for formation of **12** from **23**.

However, the enthalpies of the radicals that lie along different pathways to the same diradical play a very important role in determining the  $\Delta$ BEA value for each pathway. For example, the  $\Delta$ BEA for formation of **12** from **23** is actually calculated to be only 8.7 kcal/mol. As shown in Figure 4, the 21.6 kcal/mol higher enthalpy of heptatrienylic radical **24**, compared to benzylic radical **11'**, offsets all but 10.7 kcal/mol of the higher enthalpy of **23**, relative to **10**.

Similarly, the heat of formation of triene **25** is computed to be 6.9 kcal/mol higher than that of triene **23** and 39.2 kcal/mol higher than that of **10**. Nevertheless, the value of  $\Delta$ BEA =  $-8.7$  kcal/mol for **25**  $\rightarrow$  **12** is 17.4 kcal/mol lower than the  $\Delta$ BEA value for **23**  $\rightarrow$  **12** and 6.7 kcal/mol lower than the  $\Delta$ BEA value for **10**  $\rightarrow$  **12**. Figure 5 shows the reason for the low  $\Delta$ BEA value for **25**  $\rightarrow$  **12** is that the enthalpy of radical **26** is 24.3 kcal/mol higher than that of radical **11**.

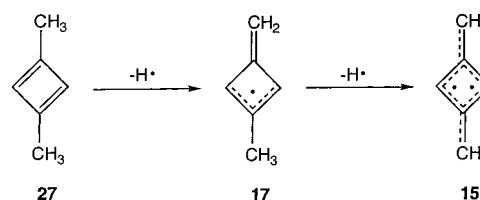
Since different pathways to the same diradical will, in general, have different  $\Delta$ BEA values, an important question to address is whether there is some criterion by which the pathway that "best" characterizes the thermodynamic stability of the diradical might be chosen. For example, since the interaction energies between nonbonding electrons of the same spin are usually small, it seems reasonable that  $\Delta$ BEA for formation of a triplet non-Kekulé hydrocarbon diradical should, in general, be close to zero [as indeed it is for formation of triplet trimethylenemethane (**9**)]. Then, if there are several different pathways to a diradical, knowing that  $\Delta$ BEA  $\approx 0$  would enable one to choose the pathway that "best"

defines the thermodynamic stability of the diradical. Using this criterion, **10**  $\rightarrow$  **12** and **16**  $\rightarrow$  **15** are then obviously the "best" pathways for defining the thermodynamic stabilities of these two diradicals.<sup>24</sup>

Of course, this procedure is patently circular. If one begins by assuming that  $\Delta$ BEA  $\approx 0$  is the correct value for formation of a triplet non-Kekulé hydrocarbon diradical, then one has already decided that the heat of formation of the diradical is essentially that predicted by  $\Delta$ BEA. Calculating or measuring  $\Delta$ BEA for different pathways to a diradical would show which of the pathways gave the  $\Delta$ BEA value that was closest to zero. However, neither the calculations nor the measurements would provide information, regarding the thermodynamic stability of the diradical, which was not already implicit in the assumption that the diradical has  $\Delta$ BEA  $\approx 0$ .

Another possible justification for choosing **10**  $\rightarrow$  **12** as the "best" pathway for defining the thermodynamic stability of **12** is that this pathway involves breaking two C–H bonds that are equivalent by symmetry in **10**. Consequently, the  $\Delta$ BEA value for **12** that is associated with this pathway at least has the virtue of involving only one monoradical (**11**), rather than the pair of monoradicals that are required for obtaining  $\Delta$ BEA for **12** from pathways that start from **23** or from **25**. However, neither this pathway, nor any other, has a fundamental claim to providing the "best"  $\Delta$ BEA value for defining the thermodynamic stability of a diradical, just because the pathway involves breaking two equivalent C–H bonds in a hydrocarbon.

This can easily be demonstrated by consideration of possible pathways to 1,3-dimethylenecyclobutane-2,4-diyl (**15**). This diradical can be formed by breaking two equivalent C–H bonds in not only 1,3-dimethylenecyclobutane (**13**), but also in 1,3-dimethylcyclobutadiene (**27**), and these two pathways give very different values of  $\Delta$ BEA for **15**.



The enthalpy of **27** is calculated to be 31.9 kcal/mol higher than that of **13** and 36.1 kcal/mol higher than that of **16**. Figure 2 shows that the BDE for forming **17** from **27** is therefore  $88.4 - 36.1 = 52.3$  kcal/mol, compared to BDE = 78.0 for forming **15** from **17**. Consequently,  $\Delta$ BEA =  $78.0 - 52.3 = 25.7$  kcal/mol for forming **15** by breaking two equivalent C–H bonds in **27**, which is 12.3 kcal/mol higher than the value of  $\Delta$ BEA = 13.4 kcal/mol for forming **15** by breaking two equivalent C–H bonds in **13**.

The large difference of 12.3 kcal/mol between these two  $\Delta$ BEA values for diradical **15** shows that the  $\Delta$ BEA

(24) An ad hoc justification for choosing **10** and **16** as the hydrocarbons that give the "best" definition of  $\Delta$ BEA for, respectively, diradicals **12** and **15**, might be that **10** has a lower enthalpy than either **23** or **24** and that **16** has a lower enthalpy than **13**. However, there is no reason to suppose that the hydrocarbon isomer of lowest enthalpy will always give  $\Delta$ BEA  $\approx 0$  for triplet diradical formation. For example, substituting vinyl groups for both hydrogens at the exocyclic carbons in **13** and making the corresponding substitutions in **16** reverses the relative enthalpies of these tetravinyl derivative of **13** and **16** from those of the unsubstituted hydrocarbons.



value for forming a diradical by a pathway that involves breaking equivalent pairs of C–H bonds in a hydrocarbon does not necessarily provide an unambiguous assessment of the thermodynamic stability of a diradical. Indeed, why should one choose either the pathway from **13** or **27** as being fundamentally superior for defining the  $\Delta\text{BEA}$  for **15** than the pathway from **16**, which involves breaking two different types of C–H bonds?

One chemist might argue that the pathway from **27** is better than the other two for defining the  $\Delta\text{BEA}$  for forming **15** because, like **15**, **27** has a fully conjugated four-membered ring. However, another chemist might assert that the pathway from **13** is better than the pathway from **27**, because not only would the methyl C–H BDE in 1,3-dimethylcyclobutadiene (**27**) be difficult to measure; but also, **27** is a very high energy molecule, with a heat of formation calculated to be 31.9 kcal/mol higher than that of **13**. A third chemist might counter this argument by pointing out that, if the enthalpy of the hydrocarbon is used as a criterion for choosing the “best” pathway to define the  $\Delta\text{BEA}$  value for forming **15**, then the pathway from **16** is obviously superior to the other two, since the heat of formation of **16** is lower than those of both **13** and **27**.<sup>24</sup>

It is not our purpose in this paper to argue which of these pathways provides the “best”  $\Delta\text{BEA}$  value for defining the thermodynamic stability of diradical **15**. Rather, we simply point out that there are three pathways to **15**, and each gives a very different  $\Delta\text{BEA}$  value, ranging from  $\Delta\text{BEA} = 25.7$  kcal/mol for **27**  $\rightarrow$  **15**, to  $\Delta\text{BEA} = 13.4$  kcal/mol for **13**  $\rightarrow$  **15**, to  $\Delta\text{BEA} = -0.6$  kcal/mol for **16**  $\rightarrow$  **15**. This path dependence means that, in general, one cannot associate a unique  $\Delta\text{BEA}$  value with a non-Kekulé hydrocarbon diradical, such as **15**, but only with a particular path to the diradical.

## Conclusions

Our B3LYP/6-31G\* calculations on triplet  $\sigma,\pi$  and non-Kekulé hydrocarbon diradicals show that for each diradical, a different  $\Delta\text{BEA}$  value is obtained for each of the isomeric hydrocarbons from which the diradical can be formed. The path dependence of the  $\Delta\text{BEA}$  values is one order of magnitude larger for formation of the non-Kekulé hydrocarbon diradicals on which we have performed calculations than for formation of the  $\sigma,\pi$ -diradicals.

$\Delta\text{BEA}$  values do provide thermodynamic information about different *pathways* to the same diradical. The  $\Delta\text{BEA}$  value that is associated with each pathway defines how a particular C–H BDE in a hydrocarbon is altered in one of the radicals that lies on the pathway from the hydrocarbon to the diradical. However, when a diradical can be formed from more than one hydrocarbon, the path dependence of the  $\Delta\text{BEA}$  values means that none of them provides a unique assessment of the thermodynamic stability of the diradical.

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**Supporting Information Available:** Table of B3LYP/6-31G\* electronic energies and zero-point and thermal corrections for **4**, **6**, and **10–27** and detailed descriptions of the B3LYP/6-31G\*-optimized geometry for each of these molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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