

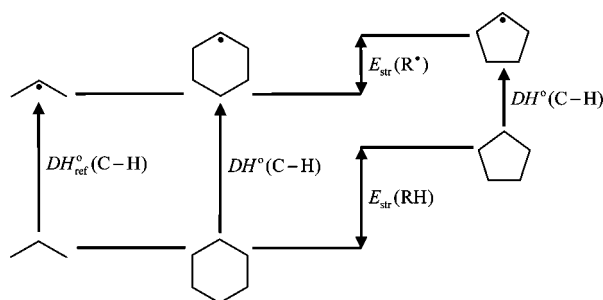
Energetic Differences between the Five- and Six-Membered Ring Hydrocarbons: Strain Energies in the Parent and Radical Molecules

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The C–H bond dissociation enthalpies (BDEs) for the five- and six-membered ring alkanes, alkenes, and dienes were investigated and discussed in terms of conventional strain energies (SEs). New determinations are reported for cyclopentane and cyclohexane by time-resolved photoacoustic calorimetry and quantum chemistry methods. The C–H BDEs for the alkenes yielding the alkyl radicals cyclopenten-4-yl and cyclohexen-4-yl and the α -C–H BDE in cyclopentene were also calculated. The *s*-homodesmotic model was used to determine SEs for both the parent molecules and the radicals. When the appropriate *s*-homodesmotic model is chosen, the obtained SEs are in good agreement with the ones derived from group additivity schemes. The different BDEs in the title molecules are explained by the calculated SEs in the parent molecules and their radicals: (1) BDEs leading to alkyl radicals are ca. 10 kJ mol⁻¹ lower in cyclopentane and cyclopentene than in cyclohexane and cyclohexene, due to a smaller eclipsing strain in the five-membered radicals relative to the parent molecules (six-membered hydrocarbons and their radicals are essentially strain free). (2) C–H BDEs in cyclopentene and cyclohexene leading to the allyl radicals are similar because cyclopenten-3-yl has almost as much strain as its parent molecule, due to a synperiplanar configuration. (3) The C–H BDE in 1,3-cyclopentadiene is 27 kJ mol⁻¹ higher than in 1,4-cyclohexadiene due to the stabilizing effect of the conjugated double bond in 1,3-cyclopentadiene and not to a destabilization of the cyclopentadienyl radical. The chemical insight afforded by group additivity methods in choosing the correct model for SE estimation is highlighted.

Introduction

Some terpenes exhibit antioxidant properties comparable to those of α -tocopherol,¹ without the pro-oxidant effects of this

latter compound at higher concentrations.² Because this property is linked with the C–H BDE in the terpene, knowledge of the C–H BDEs in terpenes and other structurally related molecules is of great interest to understand which structural factors influence the antioxidant properties of these compounds.

The C–H BDE in an organic molecule RH, $DH^\circ(\text{C-H})$, corresponds to the enthalpy of reaction 1, where all of the

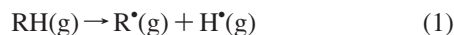
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molecules are in the ideal gas phase (isolated). It is related to the thermodynamic stability of the corresponding carbon-centered radical R^\bullet , as measured by its standard enthalpy of formation $\Delta_f H^\circ(R^\bullet, g)$, through eq 2.



$$DH^\circ(C-H) = \Delta_f H^\circ(R^\bullet, g) + \Delta_f H^\circ(H^\bullet, g) - \Delta_f H^\circ(RH, g) \quad (2)$$

Most well-known BDEs for organic compounds have been obtained in the gas phase from kinetics studies, ion cycles, and photoionization mass spectrometry, but chemical accuracy (i.e., values with errors smaller than ca. 4 kJ mol⁻¹) was achieved for only relatively few data.³⁻⁵ As the literature values for the C–H BDEs in many small hydrocarbons have uncertainties well above chemical accuracy, we investigated a number of those molecules using a combined approach of theoretical chemistry methods and time-resolved photoacoustic calorimetry (TR-PAC).^{6,7}

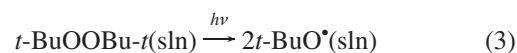
In a previous study we determined the C–H BDEs in a series of open-chain hydrocarbons containing the allyl group.⁸ We then used the results to select the “best” values for the C–H BDEs in these molecules, which allowed a quantitative discussion of the factors that determine the stability of the corresponding radicals, namely, hyperconjugation and resonance. Having dealt with all relevant molecules from the simplest propene to cyclohexadiene (viz., propane, propene, isobutene, 1-butene, 2-butene, 3-methyl-1-butene, 2-pentene, 1,3- and 1,4-pentadiene, cyclohexene, and 1,3- and 1,4-cyclohexadiene), we now turned our attention to the effect of ring strain on the C–H BDEs. To this end we need to compare the five-membered rings cyclopentane, cyclopentene, and 1,3-cyclopentadiene, with the six-membered ones, cyclohexane, cyclohexene, and 1,4-cyclohexadiene, respectively. In this work we report the TR-PAC determinations of C–H BDEs in cyclopentane and cyclohexane. The TR-PAC experimental results were complemented by quantum chemistry calculations for the same molecules and the corresponding radicals (cyclopentyl and cyclohexyl), plus cyclopentene, cyclopenten-3-yl, cyclopenten-4-yl, cyclohexen-4-yl, propane, and isopropyl. These and the previous results for the remaining cyclic hydrocarbons, together with the simpler molecules propene, 1-butene, (*E*)-2-pentene, 1,3- and 1,4-pentadiene,⁸ were then used to systematically investigate the structure–energetics relationship in the five- and six-membered ring hydrocarbons (see Supporting Information for the complete list of molecules investigated).

Strain is the central concept in this discussion, used in the conventional sense of Cox and Pilcher,⁹ i.e., including all the stabilizing and destabilizing effects in relation to a strain-

free reference molecule, regardless of the cause. To relate BDEs to strain we need to consider it both in the parent molecule and in its radical. However, evaluating strain in the radicals is considerably more complex than in the parent molecules. An important part of this work was therefore the selection of a method that allows quantifying the strain in the radicals studied.

Results

The strategy used to obtain BDEs from photoacoustic calorimetry was based on the photochemical process below: di-*tert*-butylperoxide (*t*-BuOOBu-*t*) is photolyzed, generating *tert*-butoxyl radicals (reaction 3), each abstracting an hydrogen atom from the organic molecule RH, reaction 4.



Deconvolution of the resulting waveform (see Experimental Section) first made it possible to confirm the reaction scheme (reactions 3 and 4) and then afforded the observed fraction of photon energy released as heat, $\phi_{\text{obs},i}$ for each process, and the lifetime of the second, τ_2 . An estimate of the rate constant can be obtained from this lifetime.¹⁰ The enthalpy of the hydrogen abstraction reaction was derived from eq 5, where $\Delta_{\text{obs}}H_2$ corresponds to the observed enthalpy change and is calculated by multiplying $\phi_{\text{obs},2}$ (the observed heat fraction associated with reaction 2) by $E_m = N_A h\nu$ (the molar photon energy). Φ_r is the reaction quantum yield for the photolysis of di-*tert*-butylperoxide.¹¹

$$\Delta_r H_2 = \frac{-\Delta_{\text{obs}}H_2}{\Phi_r} \quad (5)$$

As the enthalpy of reaction 4 is simply twice the difference between the solution BDEs of the hydrocarbon C–H and *tert*-butyl alcohol O–H, $DH_{\text{sln}}^\circ(C-H)$ can be derived from eq 6, where the subscript “sln” indicates that both BDEs are solution values.

$$DH_{\text{sln}}^\circ(C-H) = \frac{\Delta_r H_2}{2} + DH_{\text{sln}}^\circ(t\text{-BuO-H}) \quad (6)$$

In a previous work we determined $DH_{\text{sln}}^\circ(t\text{-BuO-H}) = 455.2 \pm 5.2$ kJ mol⁻¹ in benzene.¹² To derive the gas-phase value $DH^\circ(C-H)$, the solvation terms illustrated in eq 7 must be considered.¹³

$$DH^\circ(C-H) = DH_{\text{sln}}^\circ(C-H) + \Delta_{\text{sln}}H^\circ(RH, g) - \Delta_{\text{sln}}H^\circ(R^\bullet, g) - \Delta_{\text{sln}}H^\circ(H^\bullet, g) \quad (7)$$

The solvation of the hydrogen atom was estimated as $\Delta_{\text{sln}}H^\circ(H^\bullet, g) = 5 \pm 1$ kJ mol⁻¹ for organic solvents.¹³ On the other hand, for carbon-centered radicals $\Delta_{\text{sln}}H^\circ(RH, g) \approx \Delta_{\text{sln}}H^\circ(R^\bullet, g)$,¹² so the difference between solution and gas-phase

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TABLE 1. Theoretical and Experimental C–H Bond Dissociation Enthalpies (in kJ mol⁻¹) at 298.15 K

| molecule | radical | B3LYP-TZ ^a | CBS-Q ^a | CBS-QB3 ^a | CCSD(T) ^a | exptl ^b |
|----------------------------------|------------------------------|----------------------------|----------------------------|----------------------------|----------------------------|--------------------------|
| propene ^c | allyl | 352.2 | 361.3 | 364.9 | 371.5 | 371.5 ± 1.7 ^d |
| propane | isopropyl | 397.5 | 410.9 | 413.9 | 416.3 | 412.5 ± 1.7 ^e |
| cyclopentane | cyclopentyl | 388.4 [403.3] ^f | 404.1 [405.7] ^f | 403.7 [402.3] ^f | 406.8 [403.0] ^f | 401.8 ± 5.8 |
| cyclopentene | cyclopenten-4-yl | 390.5 [405.5] ^f | 406.6 [408.2] ^f | 406.1 [404.7] ^f | 408.7 [404.8] ^f | |
| | cyclopenten-3-yl | 335.5 [354.9] ^g | 347.3 [357.5] ^g | 350.5 [357.1] ^g | 358.7 ^h | 344.3 ± 4.2 ⁱ |
| 1,3-cyclopentadiene ^j | cyclopentadienyl | 333.4 [352.7] ^g | 346.1 [356.4] ^g | 345.9 [352.5] ^g | 353.4 ^h | 357.8 ± 7.1 ^j |
| cyclohexane | cyclohexyl | 399.4 [414.3] ^f | 417.8 [419.4] ^f | 416.1 [414.7] ^f | 418.5 [414.6] ^f | 419.8 ± 6.0 |
| cyclohexene | cyclohexen-4-yl | 398.1 [413.1] ^f | 418.3 [419.9] ^f | 415.1 [413.7] ^f | 417.7 [413.9] ^f | |
| | cyclohexen-3-yl ^f | 333.8 [353.2] ^g | 347.2 [357.5] ^g | 349.5 [356.1] ^g | 357.9 ^h | 350.0 ± 5.6 |
| 1,4-cyclohexadiene ^c | cyclohexadienyl | 297.0 [316.4] ^g | 307.8 [318.0] ^g | 311.0 [317.6] ^g | 326.3 ^h | 312.8 ± 6.1 ^c |

^a Results from the direct homolysis reaction 1 and, in brackets, from the isodesmic and isogyric reaction 9. This work unless noted otherwise.

^b TR-PAC results from this work, unless noted otherwise. The error is twice the standard deviation of the mean for 5–6 independent experiments.

^c From ref 8. ^d From ref 3. ^e From ref 4. ^f Using the literature value for the C2–H BDE in propane as the anchor (412.5 ± 1.7 kJ mol⁻¹). ^g Using the literature value for the C(sp³)–H BDE in propene as the anchor (371.5 ± 1.7 kJ mol⁻¹). ^h In this case there is no need to derive the BDEs from reaction 9 since the computed C(sp³)–H BDE in propene matches the experimental result. ⁱ From ref 16. ^j From ref 17.

C–H BDEs is equal to the solvation enthalpy of the hydrogen atom indicated above.¹⁴

Regarding the theoretical results, bond dissociation enthalpies were computed from eq 8, equivalent to eq 2 but with the standard enthalpies of formation replaced by the theoretically obtained enthalpies H .

$$DH^\circ(\text{C-H}) = H(\text{R}^\bullet) + H(\text{H}^\bullet) - H(\text{RH}) \quad (8)$$

The C–H BDEs for the molecules investigated in this work are presented in Table 1. The touchstone for discussing the energetics of the allyl radicals is the C(sp³)–H BDE in propene, which is well established as 371.5 ± 1.7 kJ mol⁻¹.³ Similarly, the basis for discussing the energetics of the alkyl radicals in this work is the also well-known C2–H BDE in propane that corresponds to the formation of the isopropyl radical (412.5 ± 1.7 kJ mol⁻¹).⁴ These BDEs were used as the anchors to derive more accurate computational results in Table 1. Indeed, C–H BDEs calculated from eq 8, which relies on reaction 1, are usually low limits of the exact values. This problem can be avoided by using a particular type of reaction, eq 9, in which the structural features of reactants and products (such as the number of electron pairs, the number of carbon atoms in a given state of hybridization, etc.) are matched to some degree (for a more complete description see Calculating the Strain Energy).



The differences $DH^\circ(\text{R-H}) - DH^\circ(\text{R}'\text{-H})$, which are equal to the enthalpies of reaction 9, are largely method-independent and usually more accurate than the BDEs obtained from eq 8, because reaction 9 takes advantage of error cancelation.¹⁵ Moreover, these differences may yield absolute BDE values by using a reliable value for the anchor, $DH^\circ(\text{R}'\text{-H})$. The bracketed values in Table 1 were obtained from reaction 9 with $\text{R}' =$ isopropyl and using the experimental C2–H BDE for propane, 412.5 kJ mol⁻¹, whenever alkyl radicals are formed, and with $\text{R}' =$ allyl and using the experimental C(sp³)–H BDE for propene, 371.5 kJ mol⁻¹, when allylic radicals are involved. Note that the accurately known C–H BDE in methane could in principle be used instead of the C2–H BDE in propane, but

then the structural features in reaction 9 would be matched to a lesser extent, since R^\bullet would be a primary radical, whereas the product is a secondary radical. When the C2–H BDE in propane is used, both radicals are secondary.

As expected, Table 1 shows that the BDEs computed from reaction 1 have larger discrepancies than the bracketed values obtained with reaction 9. A closer analysis reveals that when alkyl radicals are involved, this difference is only important for the DFT calculations, but when allylic radicals are formed, the discrepancy is also noticeable for the complete basis set methods. These results also follow our previous observation⁸ that the discrepancies are smaller for CBS-QB3 than for CBS-Q, indicating that the former is the most accurate of these two methods for the systems under study. We will however favor the results of the CCSD(T) calculations, which are expected to be the most reliable. It is also observed that the CBS-QB3 and CCSD(T) results are in excellent agreement, with the previously noted exception of the BDE for 1,4-cyclohexadiene (and the remaining dienes, (*E*)-1,3- and 1,4-pentadiene, and 1,3-cyclohexadiene), but even then the discrepancy is smaller than 8 kJ mol⁻¹.⁸

The BDEs corresponding to the C–H bond cleavages yielding the cyclopentadienyl, cyclohexen-3-yl, and cyclohexadienyl radicals (Table 1) were also the subject of previous studies by our group and the corresponding selected values were 355,¹⁷ 357.9, and 326.3 kJ mol⁻¹,⁸ respectively. The first value corresponds to a rounded average of the CCSD(T) calculation with the TR-PAC result, while the remaining values are simply the CCSD(T) results (which are in good agreement with the experimental TR-PAC values). For the sake of consistency, in the present study we will also use the CCSD(T) result for the C–H BDE in cyclopentadienyl, 353.4 kJ mol⁻¹. To compare the new results with the literature data we followed our previous strategy and relied mainly on the compilation by Luo,⁵ complemented with a brief analysis of the data collected by this author.

The experimental results for the C–H BDE in cyclopentane vary in a narrow range, 397 ± 4 to 400 ± 4 kJ mol⁻¹.⁵ The latter value, selected by Luo, is based on the EPR determination of the equilibrium constant for the exchange reaction between methyl radical and cyclopentyl iodide.¹⁸ It should be revised

(14) The final uncertainty of the TR-PAC determination of $DH^\circ(\text{C-H})$ (eq 7) is equal to the uncertainty of $DH^\circ_{\text{sin}}(\text{C-H})$ (eq 6), since the error in $\Delta_{\text{sin}}H^\circ(\text{H}^\bullet, \text{g})$ cancels out and the error in $\Delta_{\text{sin}}H^\circ(\text{RH, g}) - \Delta_{\text{sin}}H^\circ(\text{R}^\bullet, \text{g})$ is negligible, see e.g., ref 12.

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taking into account the most recently auxiliary data, namely, the enthalpy of formation of the methyl radical ($146.7 \pm 0.3 \text{ kJ mol}^{-1}$).⁴ The revision is however small, yielding $402.9 \text{ kJ mol}^{-1}$. Both our calculated and experimental values are in conformity with this result, and we selected $403.0 \text{ kJ mol}^{-1}$ (CCSD(T)), in excellent agreement with our TR-PAC result of $401.8 \pm 5.8 \text{ kJ mol}^{-1}$. The TR-PAC experiments were performed with cyclopentane concentrations of 4.0 and 10.1 M (this latter concentration referring to neat cyclopentane plus the peroxide). From the lifetime obtained for reaction 4, τ_2 , we estimate $7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant of hydrogen abstraction from cyclopentane (k_2), in good agreement with the reported laser flash photolysis values, e.g., $8.51 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ The value of the C–H BDE in cyclopentane is very close to the calculated β -C–H BDE in cyclopentene yielding the alkyl radical cyclopenten-4-yl, $404.8 \text{ kJ mol}^{-1}$ (CCSD(T)).

For the α -C–H BDE in cyclopentene, which leads to the allylic radical cyclopenten-3-yl, the results reported by Luo are again very close, 344 ± 4 and $343 \pm 8 \text{ kJ mol}^{-1}$.⁵ However, all of our calculations point to a higher BDE, varying in a narrow range, viz., 355 (B3LYP-TZ) to 359 kJ mol^{-1} (CCSD(T)), in keeping with previous high-level calculations of 352.3 (G3),^{20,21} 353.1 (G3B3),²² and $355.6 \text{ kJ mol}^{-1}$ (W1).²¹ We select the result of the CCSD(T) method for this BDE, 359 kJ mol^{-1} .

The reported values for the C–H BDE in cyclohexane range from 403 to 416 kJ mol^{-1} , the latter selected by Luo.⁵ The data presented by this author includes a non-time-resolved PAC result of 410 kJ mol^{-1} .²³ Since reaction 4 is too slow for PAC without deconvolution analysis, the experiment involved two competing reactions, namely, reaction 4 with cyclohexane and with 1,4-cyclohexadiene. Using this strategy, the derivation of the desired BDE for cyclohexane depends on the knowledge of both rate constants and the C–H BDE in the latter compound. TR-PAC directly affords the BDE in cyclohexane and also the rate constant for reaction 4. Our experiments led to $419.8 \pm 6.0 \text{ kJ mol}^{-1}$, in good agreement with Luo's selection, and were performed with cyclohexane concentrations ranging from 2.2 to 9.0 M (neat cyclohexane plus the peroxide). From the lifetime obtained for reaction 4, τ_2 , we derived $8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the rate constant of hydrogen abstraction from cyclohexane (k_2), which matches a recent laser flash photolysis result ($8.13 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)¹⁹ and is in fair agreement with the value used in the PAC study indicated above ($5.5 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$).²³ Our calculations are also in good agreement with Luo's recommendation, and we selected $414.6 \text{ kJ mol}^{-1}$ (CCSD(T)). The value of this BDE is very close to the calculated β -C–H BDE in cyclohexene that leads to the alkyl radical cyclohexen-4-yl, $413.9 \text{ kJ mol}^{-1}$ (CCSD(T)).

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TABLE 2. Selected Values for the Relative [$\Delta DH^\circ(\text{C-H})$] and Absolute [$DH^\circ(\text{C-H})$] C–H BDEs (in kJ mol^{-1}), and Recommended Enthalpies of Formation for the Corresponding Radicals^a

| molecule | radical | ΔDH° (C–H) | DH° (C–H) | $\Delta_f H^\circ$ (R \cdot ;g) ^b |
|----------------------------------|------------------|----------------------------|---------------------|---|
| propane | isopropyl | 0.0 | 412.5 | 89.8 |
| cyclopentane | cyclopentyl | −9.5 | 403.0 | 108.6 |
| cyclopentene | cyclopenten-4-yl | −7.7 | 404.8 | 220.8 |
| cyclohexane | cyclohexyl | 2.1 | 414.6 | 73.3 |
| cyclohexene | cyclohexen-4-yl | 1.4 | 413.9 | 191.0 |
| propene | allyl | 0.0 | 371.5 | 173.5 |
| 1-butene ^c | 1-methylallyl | −11.9 | 359.6 | 141.7 |
| (E)-2-pentene ^c | 2-penten-4-yl | −11.5 | 360.0 | 110.1 |
| (E)-1,3-pentadiene ^c | pentadienyl | −19.0 | 352.5 | 210.6 |
| 1,4-pentadiene ^c | pentadienyl | −46.5 | 325.0 | 212.7 |
| cyclopentene | cyclopenten-3-yl | −12.8 | 358.7 | 174.7 |
| cyclohexene ^c | cyclohexen-3-yl | −13.6 | 357.9 | 135.0 |
| 1,3-cyclopentadiene ^d | cyclopentadienyl | −18.1 | 353.4 | 269.7 |
| 1,4-cyclohexadiene ^c | cyclohexadienyl | −45.2 | 326.3 | 213.1 ^e |

^a Estimated uncertainty of ca. $\pm 4 \text{ kJ mol}^{-1}$ ^b Calculated using $\Delta_f H^\circ(\text{H}\cdot, \text{g}) = 217.998 \pm 0.006 \text{ kJ mol}^{-1}$ (ref 24) and $\Delta_f H^\circ(\text{RH}, \text{g})$ from ref 25. ^c From ref 8. ^d From ref 17. ^e $\Delta_f H^\circ(\text{RH}, \text{g})$ from ref 26.

Discussion

The above data analysis led to the set of recommended values collected in Table 2. They are all based on the values derived from CCSD(T), with exception of the anchor molecules propane and propene, for which the recommended literature values are given. The top part of the table lists the alkyl radicals. The allyl radicals presented next include mostly earlier results^{8,17} that are relevant for the present discussion.

In our previous work dealing with simple (and unstrained) alkanes, alkenes, and dienes, we explained the differences in C–H BDEs using the concepts of hyperconjugation and resonance. These effects are reflected by the structural changes that accompany radical formation. For instance, hyperconjugation can be measured by the shortening of the C–C bond(s) adjacent to the radical center; resonance in an allyl group is characterized by two carbon–carbon bonds of identical length, which were a single and a double bond in the parent molecule. Both factors are accompanied by a decrease in spin density at the carbon atom where abstraction occurs, which correlates rather well with the C–H BDEs in the alkanes and alkenes studied. This supports the view that those BDEs are mainly determined by alkyl and allyl radical stabilization through spin delocalization. In the case of the dienes we have also to consider the thermodynamic stabilities of the parent compounds, namely, the possibility of a strongly stabilizing conjugated double bond.⁸

In the present study, deviations from the above behavior will be attributed to strain and assessed by comparing the title molecules with a suitable reference. This reference should obviously be a strain-free compound but having stabilization effects that are identical to those in the molecule under study. Suitable references that will be used throughout this discussion are displayed in Figure 1.

To rationalize the effect of strain on the BDEs, we will start by inspecting the geometries of the parent molecules and radicals for “anomalous” (with regard to the references) C–C bond lengths (Figure 2) and C–C–C angles (Figure 3).

Cyclohexane versus Cyclopentane. The C–H BDE in propane leading to isopropyl ($412.5 \text{ kJ mol}^{-1}$) is similar to the C–H BDE in cyclohexane ($414.6 \text{ kJ mol}^{-1}$). This is consistent with the known fact that cyclohexane and its radical have little or no strain. However, the C–H BDE in cyclopentane is some

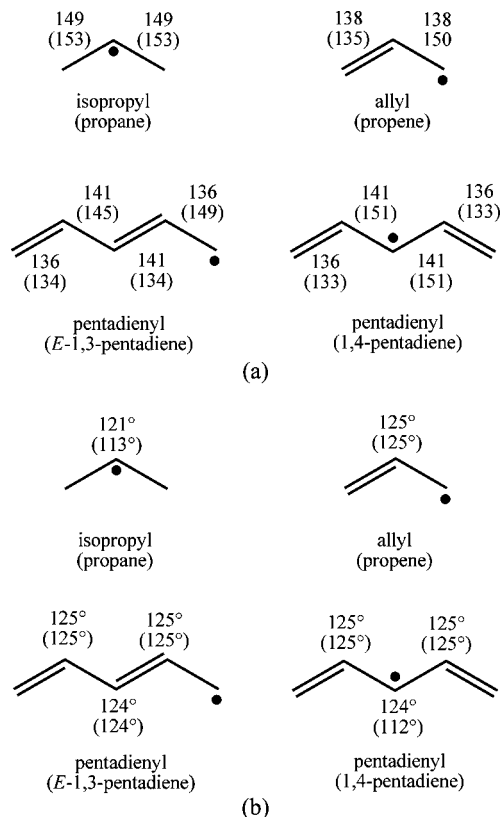
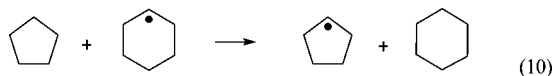


FIGURE 1. (a) Bond lengths (pm) and (b) bond angles for the radicals and their parent molecules (in parentheses) to be used as the strain-free reference molecules, calculated with B3LYP/cc-pVTZ.

11 kJ mol⁻¹ lower than in the above compounds: The enthalpy of reaction 10, obtained from CCSD(T) calculations, is -11.6 kJ mol⁻¹.



The lower C-H BDE in cyclopentane can be qualitatively understood with the help of Figure 4, which relates the BDEs in cyclohexane and cyclopentane with the strain destabilizations of the parent molecule and its radical (for a quantitative description of strain energy, SE, see Calculating the Strain Energy). It is clear from Figure 4 that the lower C-H BDE in cyclopentane should result from a higher strain destabilization of cyclopentane (relative to cyclohexane) as compared with the strain destabilization of cyclopentyl (relative to cyclohexyl).

C-C bond lengths in cyclopentane (155 pm) are slightly larger than in cyclohexane (153 pm), which are equal to the ones in propane. C-C-C bond angles in cyclopentane and cyclohexane are also different, and whereas in the latter they are close to the one in propane (112° vs 113°, respectively), in the former they are smaller (ca. 106°). Both facts are consistent with a destabilization of cyclopentane due to strain.

Concerning the radicals, bond lengths in cyclopentyl and cyclohexyl are equal, and the ones adjacent to the radical center are equal to isopropyl. However, the angle corresponding to this latter structure (C-C1-C) is narrower in cyclopentyl (112°) than in a typical sp² hybridization, such as in cyclohexyl (119°) or isopropyl (121°). Furthermore, the spin density at the radical center is higher in cyclopentyl (0.970) than in cyclohexyl (0.955), which is quite close to isopropyl (0.953), indicating

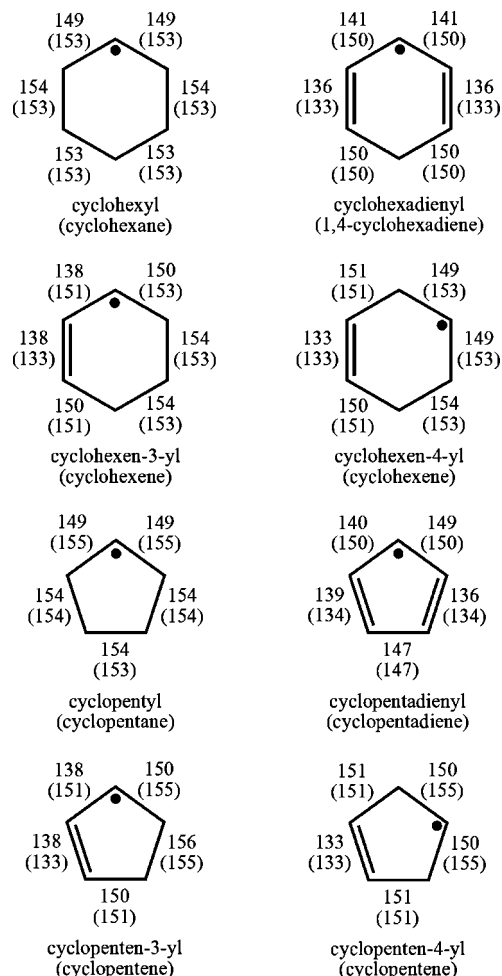
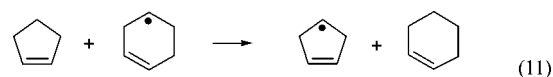


FIGURE 2. Bond lengths (pm) for the radicals and their parent molecules (in parentheses), calculated with B3LYP/cc-pVTZ.

less delocalization in cyclopentyl. All of these facts point to a destabilization of cyclopentyl due to strain.

Cyclohexene versus Cyclopentene. The BDEs leading to the alkyl radicals cyclohexen-4-yl and cyclopenten-4-yl are very close to the BDEs of the corresponding alkanes discussed above. Again, the C-H BDE in cyclohexene (413.9 kJ mol⁻¹) is equal to the C-H BDE in propane (412.5 kJ mol⁻¹) and the C-H BDE in cyclopentene is lower (404.8 kJ mol⁻¹), as illustrated by the enthalpy of reaction 11, -9.1 kJ mol⁻¹ (CCSD(T)).



Repeating the previous analysis of the structural features of these molecules leads to similar observations. Regarding the parent compounds, the bonds adjacent to the radical center (C4) are longer in cyclopentene (155 pm) than in cyclohexene (153 pm), which are equal to the ones in propane. The bond angle between the same bonds in cyclohexene is close to the one in propane (111° vs 113°, respectively), while in cyclopentene it is smaller (ca. 106°). Additionally, the angles defined by the double bond and the adjacent carbon atoms in cyclopentene are narrower (112°) than in cyclohexene (124°). These three facts point to a strain destabilization of cyclopentene, while cyclohexene should have little or no strain. Concerning the radicals, bond lengths adjacent to the radical center are equal in

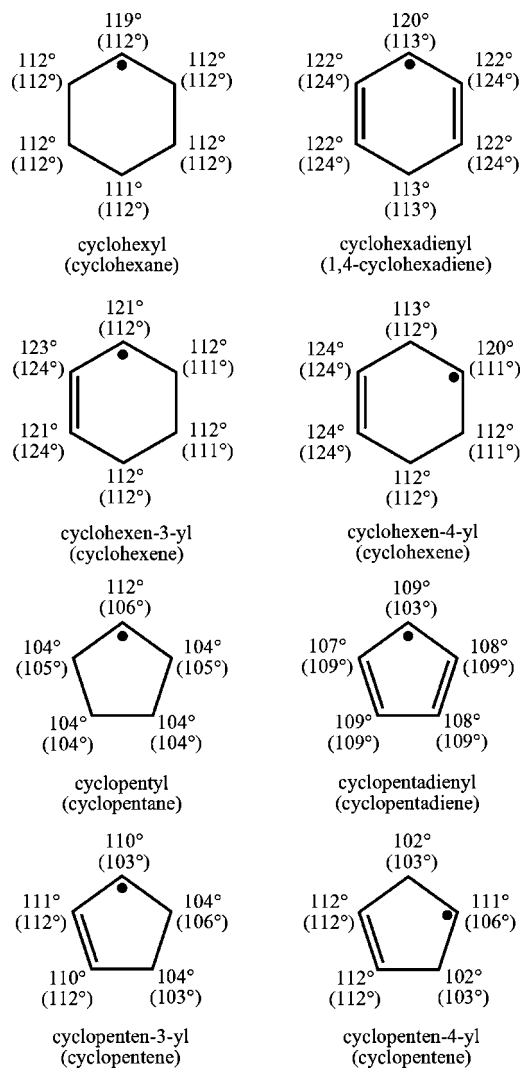


FIGURE 3. Bond angles for the radicals and their parent molecules (in parentheses), calculated with B3LYP/cc-pVTZ.

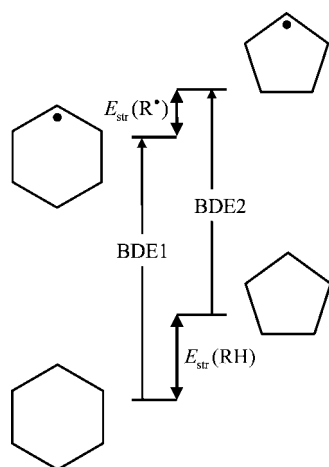


FIGURE 4. Relation between the BDEs in cyclohexane and cyclopentane, considering the destabilization of the parent molecule and its radical due to strain (E_{str}).

cyclohexen-4-yl and isopropyl (149 pm) and only slightly longer in cyclopentene-4-yl (150 pm). The radical centered angle is narrower in cyclopenten-4-yl (111°) than in cyclohexen-4-yl (120°) or isopropyl (121°). The spin density at the radical center

is higher in cyclopenten-4-yl (0.970) than in cyclohexen-4-yl (0.960) and isopropyl (0.953), indicating less delocalization in cyclopenten-4-yl. The remaining structural features of the radicals are unchanged from the parent molecule. Therefore, the difference in C–H BDEs between cyclopentene and cyclohexene may be explained as before: the strain destabilization of cyclopentene is larger than the strain destabilization of the cyclopentene-4-yl radical.

Regarding the formation of the allylic radicals, the C–H BDEs of cyclohexene (357.9 kJ mol⁻¹) and cyclopentene (358.7 kJ mol⁻¹) are rather close and similar to the C–H BDEs in 1-butene (359.6 kJ mol⁻¹) and 2-pentene (360.0 kJ mol⁻¹). The BDEs in the unstrained compounds 1-butene and 2-pentene can be explained solely by spin delocalization on the radical through hyperconjugation and resonance.⁸ This means that either cyclopentene, cyclohexene, and their allylic radicals are unstrained or the strain energies for each parent-radical pair are identical. However, the above discussion demonstrated that cyclopentene is strain-destabilized, whereas cyclohexene is not. Therefore, cyclopenten-3-yl radical and cyclopentene must have similar strain energies. Recall that cyclopenten-4-yl radical has less strain than cyclopentene. Hence, cyclopenten-3-yl radical has more strain than cyclopenten-4-yl radical.

By comparing the structures of cyclopenten-3-yl and cyclohexen-3-yl radicals, it is easy to accept that the former should be more strained. Indeed, the angles in cyclopenten-3-yl are around 111° in the allyl system and 104° in the sp³ carbons, whereas in cyclohexen-3-yl they are much closer to regular values (around 122° in the allyl system and 112° in the sp³ carbons). However, it is more difficult to demonstrate, on the basis of structural features, that the cyclopenten-3-yl radical is more strained than cyclopentyl or cyclopenten-4-yl. To make progress we need to quantify strain, which we will do in the next section before returning to this question.

Calculating the Strain Energy. As described by Feng et al.,²² strain can be quantified in a number of ways, the most popular being the “bent bond” model introduced by Coulson²⁷ and developed by Bader and co-workers^{28,29} in the “bond path” theory. Feng et al. also proposed a new and perhaps more chemically intuitive way to measure the effect of ring strain on BDEs, by calculating the hybridization in the parent molecule and in the radical using natural bond orbital (NBO) analysis.^{30,31} Hybridization in the parent molecule is evaluated by calculating the $p\%$ character associated with the C–H bond orbital where abstraction will occur. Deviation from 0.75 (sp³ hybridization) points to a destabilization of the molecule due to strain. Likewise, hybridization in the radical is assessed by calculating the $p\%$ of the odd electron, and $p\% < 1.00$ indicates strain. The authors then proposed a three-parameter structure-energetics equation to predict C–H BDEs in strained hydrocarbons. It includes the two parameters above to quantify strain in addition to the spin density that accounts for hyperconjugation and resonance, but while the model can predict the BDEs for a variety of saturated and unsaturated strained hydrocarbons rather well, it does not explain the finer issues, like the questions raised in the previous section. Indeed, the $p\%$ of the odd electron is

(27) Coulson, C. A.; Goodwin, T. H. *J. Chem. Soc.* **1962**, 2851–2854.

(28) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985–1001.

(29) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001–1012.

(30) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.

(31) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

TABLE 3. Strain Energies (E_{str} , in kJ mol^{-1}) Derived from Experimental Data

| molecule | $\Delta_f H^\circ(\text{RH}, \text{g})^a$ | $\Delta_f H^\circ(\text{RH}^*, \text{g})^b$ | $E_{\text{str}}(\text{RH})$ | RSC ^c |
|---------------------|---|---|-----------------------------|------------------|
| cyclopentane | -76.4 | -103.6 | 27.2 | 30.9 |
| cyclopentene | 34.0 | 11.1 | 22.9 | 23.8 |
| cyclohexane | -123.3 | -124.3 | 1.0 | 3.2 |
| cyclohexene | -4.9 | -9.6 | 4.7 | 5.3 |
| 1,3-cyclopentadiene | 134.3 | 109.3 | 25.0 | 21.0 |
| 1,4-cyclohexadiene | 104.8 ^d | 105 | -0.2 | -0.7 |

^a From ref 25 except when noted otherwise. ^b For the hypothetical strain-free compound RH^* , using the extended Laidler terms from ref 32. The corrective terms that account for strain were obviously *not* used. ^c Ring strain corrections ($\text{RSC} \equiv E_{\text{str}}$) of Benson group additivity method from ref 34. ^d From ref 26.

calculated as 1.00 in the five-membered radicals cyclopentyl, cyclopenten-3-yl, and cyclopenten-4-yl, meaning that it is completely in the p orbital and therefore strain had no effect in any of these radicals. Consequently, the structure-energetics equation applied to cyclopentane, cyclopentene, and cyclohexane (yielding the alkyl radicals) leads to similar BDEs, around 418 kJ mol^{-1} , missing the trends discussed above.

A different and, to our purpose, a better approach, would be to directly calculate the strain energy (E_{str}). Conventionally, this is defined as the difference between the enthalpies of formation of the compound of interest RH and a strain-free reference compound RH^* , usually obtained through a bond additivity scheme, eq 12.⁹

$$E_{\text{str}}(\text{RH}) = \Delta_f H^\circ(\text{RH}, \text{g}) - \Delta_f H^\circ(\text{RH}^*, \text{g}) \quad (12)$$

Table 3 presents the calculated E_{str} for the title molecules, using the extended Laidler terms tabulated by Leal³² to estimate the enthalpies of formation of the corresponding unstrained compounds. Our calculated E_{str} are in excellent agreement with the ring strain corrections (RSC, which are equivalent to E_{str}) obtained from the popular Benson group additivity method.^{33,34} The results in Table 3 confirm the previous conclusions regarding the strain in the parent molecules: cyclopentane and cyclopentene are considerably strained while cyclohexane and cyclohexene are not. Although this agreement is reassuring, we still need to quantify the strain in the radicals.

A set of RSCs for hydrocarbon radicals, based on a consistent database of enthalpies of formation of radicals determined using ab initio calculations, was recently reported by Sabbe et al.³⁴ Unfortunately, this set of RSCs does not include all of the radicals investigated in the present study. However, computational chemistry also provides an alternative basis for evaluating SEs, as proposed by George et al.³⁵ These authors designed reactions that compare each carbon atom in the strained ring to a similar environment in an unstrained analogue and thus provide an estimate of SE. The construction of these reactions was systematized by Zhao and Gimarc in the *s*-homodesmotic model,³⁶ illustrated in eqs 13–15 for cyclopentane:³⁷

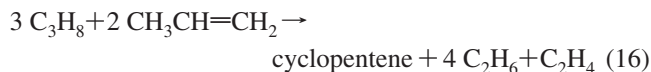


In the above reactions, each reactant molecule taken from the ring system has a length of $s + 2$ carbon atoms, and n

TABLE 4. Theoretical Strain Energies (E_{str} , in kJ mol^{-1}) Calculated by Using 1-Homodesmotic Reactions (See Text) for the Parent Molecules

| molecule | B3LYP-TZ | CBS-Q | CBS-QB3 | CCSD(T) |
|--------------|----------|-------|---------|---------|
| cyclopentane | 22.9 | 27.4 | 28.3 | 28.2 |
| cyclopentene | 22.1 | 24.9 | 25.0 | 26.4 |
| cyclohexane | 2.1 | -1.9 | 1.4 | 3.0 |
| cyclohexene | 6.6 | 4.3 | 5.9 | 8.4 |

reactant molecules are needed for an n -membered ring. An easy mnemonic to build these reactions is to go around the ring n times and take fragments of $s + 2$ carbon atoms for the reactants and $s + 1$ carbon atoms for the products. For instance, the $s = 1$ model for cyclopentene corresponds to reaction 16.



As detailed in Supporting Information, for $s = 0$ the reaction conserves both the number and formal types of bonds and is called isodesmic; when $s = 1$, the reaction also conserves the valence around each atom and is called homodesmotic; for $s = 2$, the valence environment around neighboring atoms is preserved as well and the reaction is said to be hyperhomodesmotic; and so on. In principle, computation of the enthalpy of any of reactions 13–15 yields an estimate of E_{str} in cyclopentane. However, the matching of structural elements increases as we consider larger fragments, and so should the accuracy of the calculated value. Indeed, Magers and co-workers have shown that the greater chemical similarity implicit in homodesmotic as compared to isodesmic reactions is essential for correct estimates, while results obtained with the homodesmotic and hyperhomodesmotic models were essentially identical. However, they also alerted to the possibility that an $s = 2$ and even an $s = 3$ *s*-homodesmotic model might be necessary in some cases,³⁷ as indeed we found out.

Table 4 compiles the results of the calculated E_{str} using the homodesmotic model ($s = 1$) for the molecules discussed so far (the more complicated dienes will be analyzed separately), with the enthalpies of each species computed at various theory levels. There is a general good agreement not only between the results at the various theory levels in Table 4 but, most importantly, between the theoretical SEs and the corresponding data in Table 3. We thus feel confident to take the final step and use the same strategy to calculate the SEs of the radicals.

Construction of the homodesmotic reactions for the radicals follows the same rules as before.³⁸ Reaction 17 exemplifies this exercise for the cyclopentyl radical ($s = 1$).



Table 5 presents the results of these calculations for the radicals discussed so far. Again the results from the various theory levels are in good agreement and close to the available RSCs, with DFT displaying a slight tendency to underestimate the strain energies.

(35) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1222–1227.

(36) Zhao, M.; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4023–4030.

(37) Lewis, L. L.; Turner, L. L.; Salter, E. A.; Magers, D. H. *THEOCHEM* **2002**, *592*, 161–171.

(38) To apply the *s*-homodesmotic model to the radicals, some new molecules are needed whose enthalpy was not previously calculated, such as the ethyl and the propyl radicals. The values for these molecules, which are not relevant for the discussion except in this regard, are given in Supporting Information.

(32) Leal, J. P. *J. Phys. Chem. Ref. Data* **2006**, *35*, 55–76.

(33) Cohen, N. *J. Phys. Chem. Ref. Data* **1996**, *25*, 1411–1481.

(34) Sabbe, M. K.; Saeys, M.; Reyniers, M.-F.; Marin, G. B.; Van Speybroeck, V.; Waroquier, M. *J. Phys. Chem. A* **2005**, *109*, 7466–7480.

TABLE 5. Theoretical Strain Energies (E_{str} , in kJ mol^{-1}) Calculated by Using 1-Homodesmotic Reactions (See Text) for the Radicals

| molecule | B3LYP-TZ | CBS-Q | CBS-QB3 | CCSD (T) | RSC ^a | exptl ^b |
|------------------|----------|-------|---------|----------|------------------|--------------------|
| cyclopentyl | 7.8 | 15.1 | 12.2 | 12.6 | 19.7 | 17.7 |
| cyclopenten-4-yl | 9.2 | 15.1 | 11.2 | 12.7 | | 15.2 |
| cyclohexyl | -2.0 | -0.4 | -2.4 | -0.9 | 3.9 | 3.1 |
| cyclohexen-4-yl | 1.3 | 6.2 | 1.2 | 3.7 | | 6.1 |
| cyclopenten-3-yl | 18.3 | 22.8 | 19.2 | 20.5 | 23.8 | 22.0 |
| cyclohexen-3-yl | 1.2 | 2.1 | -0.9 | 1.7 | 3.5 | 3.0 |

^a Ring strain corrections (RSC $\equiv E_{\text{str}}$) of Benson group additivity method from ref 34. ^b "Experimental" E_{str} values for the radicals calculated using eq 18 and the values in Tables 2 and 3.

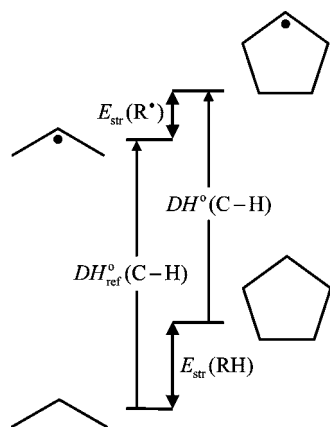
**FIGURE 5.** Relation between the strain energies (E_{str}) of the parent molecule and its radical, and the relative BDE, $\Delta DH^{\circ}(\text{C}-\text{H}) = DH^{\circ}(\text{C}-\text{H}) - DH_{\text{ref}}^{\circ}(\text{C}-\text{H})$, for cyclopentane.

Table 5 also displays "experimental" E_{str} values for radicals. These data are based in Figure 5, which is a more precise depiction of the relation between strain energies and BDEs than Figure 4.

It is assumed in Figure 5 that the BDEs difference between propane and cyclopentane is due only to the strain of cyclopentane and its radical. The C2-H BDE in propane is the correct anchor to assess that difference: (1) isopropyl and cyclopentyl can both be stabilized to the same extent by hyperconjugation (the same being true for all the alkyl radicals in Table 5); (2) propane and isopropyl radical are suitable strain-free references for evaluating the strain energies of alkanes and the corresponding alkyl radicals, which are "destabilized" in relation to the references only by SE.³⁹ From Figure 5, eq 18, relating the BDEs and strain energies differences, is obtained.

$$\Delta DH^{\circ}(\text{C}-\text{H}) = DH^{\circ}(\text{C}-\text{H}) - DH_{\text{ref}}^{\circ}(\text{C}-\text{H}) = E_{\text{str}}(\text{R}^{\bullet}) - E_{\text{str}}(\text{RH}) \quad (18)$$

The values for the alkyl radicals in the last column of Table 5 were obtained by solving eq 18 for $E_{\text{str}}(\text{R}^{\bullet})$, with $E_{\text{str}}(\text{RH})$ from Table 3 and $\Delta DH^{\circ}(\text{C}-\text{H})$ from Table 2. For the alkenes, a different reference has to be used when calculating $\Delta DH^{\circ}(\text{C}-\text{H})$. However, it cannot be the BDE in propene

(39) Stability is a precise thermodynamic concept, measured for instance by the enthalpy of formation of a molecule, as in the definition of E_{str} in eq 12. As such, it is meaningless in comparing molecules with a different number of atoms. We are not discussing the stability of, for instance, propane versus cyclopentane. The words "stabilization" and "destabilization" refer to the effect of strain in each individual molecule, which is defined in relation to the hypothetical unstrained molecule, modeled in this case by propane or its radical.

yielding the allyl radical, since this is only stabilized by resonance, whereas the cyclic allyl radicals in Table 5 are stabilized both by resonance and hyperconjugation. A suitable reference would then have to be either 1-butene or (*E*)-2-pentene, both yielding radicals stabilized in that same way (and therefore having equal BDEs). This is equivalent to adding the effect of one hyperconjugation, 11.9 kJ mol^{-1} , to the values of $\Delta DH^{\circ}(\text{C}-\text{H})$ in Table 2 before calculating $E_{\text{str}}(\text{R}^{\bullet})$ from eq 18 for the cycloalkenes. It is reassuring to find that the results from this procedure are in agreement with the theoretical SEs.⁴⁰

Table 5 presents the final piece of the puzzle. It confirms the hypothesis that the strain is negligible for the six-membered radicals but significant in the five-membered ones, although smaller than in the corresponding parent molecules. Furthermore, it shows that the cyclopenten-3-yl radical is indeed more strained than the other two five-membered ring radicals and that, as predicted above, its strain energy is similar to the one in cyclopentene. Therefore, the fact that the BDEs in cyclopentene and in cyclohexene (yielding the allyl radicals) are equal is due to the high strain of the cyclopenten-3-yl radical.

We are now well equipped to search for the structural features that are responsible for the strain in the molecules listed in Tables 4 and 5. In our first approach, we were essentially attributing strain to deviations from normal bond angles. Yet, this angle (or Bayer) strain is just one of molecular strain types. Indeed, cyclopentane is not planar⁴¹ due to eclipsing effects, responsible for torsional (or Pitzer) strain.⁴² To minimize these repulsions, cyclopentane adopts a puckered conformation, where three C-C bonds can rest on a smaller energy gauche configuration. There is, however, a price to pay, since the two remaining bonds cannot escape from a higher energy, almost synperiplanar, configuration. The situation is similar in cyclopentene, where two C-C bonds (involving the three carbon atoms opposite the double bond) also adopt an almost synperiplanar configuration. Yet, when the corresponding alkyl radicals (cyclopentyl and cyclopenten-4-yl) are formed, the removal of the hydrogen atom decreases the repulsions with both the adjacent CH_2 groups, stabilizing the radical. This stabilization and the fact that the remaining interactions are identical in the parent molecules, explain the significantly smaller SEs in the alkyl radicals in relation to the parent molecules. On the other hand, in cyclopenten-3-yl the allyl moiety forces the radical to become planar, so that the C-C bond opposite to the allyl moiety cannot escape from a full synperiplanar configuration. It is this repulsive interaction that is responsible for the high SE of cyclopenten-3-yl as compared with the other two five-membered ring radicals.

1,4-Cyclohexadiene versus 1,3-Cyclopentadiene. The C-H BDE in 1,4-cyclohexadiene ($326.3 \text{ kJ mol}^{-1}$) is essentially equal to the C-H BDE in 1,4-pentadiene ($325.0 \text{ kJ mol}^{-1}$), which is a suitable strain-free reference because both radicals, pentadienyl and cyclohexadienyl, can be stabilized by delocalization through a five-carbon-atom system. This suggests that cyclohexadiene and its radical should also be devoid of strain. Indeed, Table 3 shows that E_{str} for 1,4-cyclohexadiene is negligible, and since its BDE is very close to the BDE in the reference strain-free

(40) Note that the $E_{\text{str}}(\text{R}^{\bullet})$ values calculated with eq 18 used experimentally defined $E_{\text{str}}(\text{RH})$ values from Table 3 and $\Delta DH^{\circ}(\text{C}-\text{H})$ results from Table 2 (selected from computational and experimental results). In this sense, they can be called "experimental" strain energies.

(41) Cyclopentane planarity would correspond to C-C-C angles of 108° , close to the 109° of a sp^3 hybridization.

(42) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed.; Wiley: New York, 2001.

TABLE 6. Theoretical Strain Energies (E_{str} , in kJ mol^{-1}) Calculated by Using s -Homodesmotic Reactions ($s = 1-3$, from Top to Bottom) for the More Complicated Molecules

| molecule | B3LYP-TZ | CBS-Q | CBS-QB3 | CCSD(T) | RSC ^a | exptl ^b |
|---------------------|----------|-------|---------|---------|------------------|--------------------|
| 1,4-cyclohexadiene | 4.2 | 0.9 | 4.1 | 7.0 | | |
| | -7.6 | 4.1 | -1.7 | -2.9 | | |
| | -8.3 | 14.2 | -0.8 | -2.1 | -0.7 | -0.2 |
| 1,4-cyclohexadienyl | 26.2 | 26.3 | 22.4 | 26.6 | | |
| | 41.7 | 46.1 | 37.6 | 36.2 | | |
| | -2.1 | 23.7 | -0.5 | 1.7 | -0.3 | 1.1 |
| 1,3-cyclopentadiene | 10.0 | 10.5 | 9.5 | 13.5 | | |
| | 17.2 | 27.5 | 19.2 | 18.7 | | |
| | 21.8 | 42.5 | 23.3 | 23.5 | 21.0 | 25.0 |
| | | | | | | |

^a Ring strain corrections ($\text{RSC} \equiv E_{\text{str}}$) of Benson group additivity method from ref.³⁴ ^b "Experimental" E_{str} values for the radicals calculated using eq 18 and the values in Tables 2 and 3.

molecule, the same can be predicted for E_{str} of cyclohexadienyl (cf. eq 18). Calculating E_{str} for 1,4-cyclohexadiene and its radical is considerably more demanding than in the previous examples but allows confirming this assertion. The summary of this exercise is displayed in Table 6, where it is shown that only a 3-homodesmotic model can provide a correct estimate of E_{str} for both 1,4-cyclohexadiene and its radical. The justification is based on the same simple chemical intuition that guided us to select the correct strain-free reference molecules for Figure 5 and eq 18. The reference for the 1,4-cyclohexadienyl radical is 1,4-pentadienyl. Therefore, an s -homodesmotic reaction whose enthalpy reflects only strain must include this reference, which is a fragment with $s + 2 = 5$ carbon atoms. Smaller reactants (e.g., reactions analogous to 16 and 17) cannot reproduce the bis-allylic stabilization in 1,4-cyclohexadienyl, and the resulting enthalpy would be in error by that difference. The same argument applies to the calculation of E_{str} for the parent molecule because 1,4-pentadiene must be included to balance all the relevant structural features. This can be confirmed by an analysis of the Benson groups or Laidler terms in both sides of the corresponding equation. A more detailed discussion on the application of s -homodesmotic reactions to evaluate SEs can be found in the Supporting Information.

Table 6 also shows that best estimates are obtained with CBS-QB3 and CCSD(T), which produce similar results. Surprisingly, DFT performs satisfactorily (having, nevertheless, a tendency to underestimate E_{str}) while CBS-Q largely overestimates E_{str} .

Regarding 1,3-cyclopentadiene, its C–H BDE is equal to the one in (*E*)-1,3-pentadiene. It is easy to understand that in this case 1,4-pentadiene would not be a suitable reference, because it does not possess the conjugated double bond that further stabilizes 1,3-pentadiene and 1,3-cyclopentadiene in relation to their 1,4- isomers. However, contrasting with the situation for 1,4-cyclohexadiene, Tables 3 and 6 indicate considerable strain in 1,3-cyclopentadiene. This fact is easily justified by angle strain alone. As shown in Figures 1 and 3, bond angles in 1,4-cyclohexadiene are close to standard values (124° for sp^2 and 113° for sp^3 carbons, identical to the corresponding angles in 1,4-pentadiene), whereas in 1,3-cyclopentadiene they are much narrower (109° for sp^2 and 103° for sp^3 carbons). Since its BDE is equal to the one in the strain-free reference, according to eq 18 cyclopentadienyl radical and 1,3-cyclopentadiene should have similar SEs. This is in keeping with the close geometric features of the two planar molecules. Hence, the strain, essentially angular, should affect both by a comparable amount.

A close inspection of cyclopentadienyl structure reveals additional interesting features. The normal bond lengths of a bis-allyl radical correspond to the ones in pentadienyl, which are equal to the ones in cyclohexadienyl radical (Figures 1 and 2). In relation to the parent molecule, they reflect a lengthening of the double bond (from 133 to 136 pm) and a shortening of the single (from 151 to 141 pm), symmetrically in relation to the radical center, indicative of delocalization through the five carbon atoms. However, the "bis-allyl" system in cyclopentadienyl (Figure 2) is not symmetrical. While bond lengths of one of the "allyl" groups change significantly, almost matching each other (139 and 140 pm), and are close to the bond lengths in the allyl radical (both 138 pm; see Figure 1), smaller changes are observed in the other allyl moiety.

The reason for the "asymmetry" in cyclopentadienyl radical is well studied and understood.⁴³ The more symmetrical D_{5h} geometry of this radical corresponds to a doubly degenerate state and therefore is subject to the Jahn–Teller effect: to lift the degeneracy, it will distort to a lower symmetry. A simple molecular orbital analysis shows that this can lead to either a compressed dienyl structure with a localized radical (2B_1 state) or to an elongated structure comprised of an allyl radical plus a localized double bond (2A_2 state), both with C_{2v} symmetry.⁴³ Recent calculations indicate that these two structures are very close in energy and ca. 19.3 kJ mol^{-1} more stable than the D_{5h} geometry.⁴⁴ The ground state of cyclopentadienyl was described as a Mexican hat case: the system pseudorotates around the D_{5h} geometry with little or no barrier, by alternately passing through the five equivalent geometries 2A_2 and the five 2B_1 .⁴⁵ This dynamic effect was demonstrated by EPR studies, which gave indication of Jahn–Teller distortion below 70 K, while at high temperature the odd electron appears with equal probability on all five carbon atoms, consistent with the rapid pseudorotation.⁴⁶ Rotationally resolved spectroscopy of asymmetrically deuterated cyclopentadienyl radicals made it possible to assign the distortions to the two geometries 2A_2 and 2B_1 .⁴⁷ Our computed ground-state geometry is compatible with the 2A_2 state and is in very good agreement with previous ones.^{43–45,48,49} This state is therefore a correct thermodynamic description of the ground-state cyclopentadienyl radical, further confirmed by the agreement between the calculated and experimental C–H BDE of 1,3-cyclopentadiene.¹⁷

Unfortunately, it is not possible to estimate the SE for cyclopentadienyl with the s -homodesmotic model. Even the corresponding 3-homodesmotic reaction is unbalanced because it results in three bis-allylic radicals versus one cyclopentadienyl, eq 19, a situation that does not happen with the cyclohexadienyl radical, eq 20.⁵⁰ Attempting to define a reaction with $s = 4$ is

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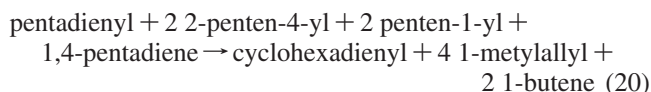
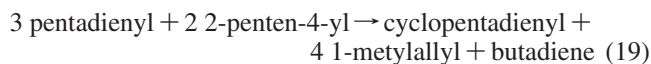
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(49) At our theory level for structure optimization (B3LYP/cc-pVTZ), vibrational frequency analysis shows that the dienyl-like structure (2B_1) is not a minimum on the potential energy surface but is essentially isoenergetic with the allylic structure (the energy difference is only ca. 3 J mol^{-1}), in agreement with the previous computations.

(50) When designing these equations, note that apparently different structures are in fact the same radical, such as 1,3-pentadien-5-yl, 1,4-pentadien-3-yl or simply pentadienyl, and 1-methylallyl or 2-buten-1-yl.

of course impossible for cyclopentadienyl for it would require fragments with $s + 2 = 6$ carbon atoms.



Despite the shortcomings of the *s*-homodesmotic model in predicting the SE of cyclopentadienyl radical, it was possible to conclude that the SEs in cyclopentadienyl and 1,3-cyclopentadiene must be comparable (see above). Therefore, the higher BDE in 1,3-cyclopentadiene in relation to the BDE in 1,4-cyclohexadiene is essentially due to a ground-state or parent effect (identical to the relation between 1,3- and 1,4-pentadiene).⁸ It is a stabilization of 1,3-cyclopentadiene due to the conjugated double bond rather than a destabilization of the radical due to impaired delocalization, that is responsible for the higher BDE.

Conclusions

The carbon–hydrogen BDEs in the five- and six-membered ring hydrocarbons differ noticeably, and the difference is attributed to strain, a concept that we use in the conventional way of Cox and Pilcher,⁹ i.e., including all the stabilizing and destabilizing effects relative to strain-free reference molecules. The relation between BDEs and strain energy (SE) is given by Figure 5 or eq 18. Since strain can affect parent molecules and radicals differently, a comprehensive discussion must discriminate between these two. Although the evaluation of SE in radicals is more complex than in parent molecules, both cases can be addressed through quantum chemistry calculations by using the *s*-homodesmotic model. This methodology is a rather convenient way to design chemical reactions whose enthalpies can be identified with the SE of a given molecule. The results can then be assessed by comparison with experimental data through eq 18.

The systematization of the structural features provided by group additivity methods helps selecting the adequate *s*-homodesmotic model for a given molecule. Furthermore, the calculation of SEs with the same *s*-homodesmotic model should afford good estimates (due to error cancelation), and failure to verify eq 18 alerts to faults in the chosen model (see Supporting Information). The sources of error can then be easily identified by checking the balance of group additivity terms. It was also noted that CBS-QB3 yields SE results very similar to the much more expensive CCSD(T) method. DFT performance is poorer but acceptable in most cases, while CBS-Q shows a somewhat erratic behavior.

We concluded that a correct estimate of SE is obtained for alkanes, alkenes, and alkyl radicals with the 1-homodesmotic model, whereas allyl radicals are best described with 2-homodesmotic reactions (although a good approximation is obtained with the 1-homodesmotic). For unconjugated dienes like 1,4-cyclohexadiene, the 2-homodesmotic model must be used, while for conjugated dienes like 1,3-cyclopentadiene the requirement increases to 3-homodesmotic. For the corresponding bis-allyl radicals, the SE of cyclohexadienyl is only satisfactorily described by the 3-homodesmotic model, which however cannot be applied to cyclopentadienyl.

Our results justified the trends in BDEs by determining that the five-membered hydrocarbons all have considerable and

similar strain, in the order 1,3-cyclopentadiene < cyclopentene < cyclopentane. Analysis of the corresponding structures indicates that the strain in 1,3-cyclopentadiene is essentially angular. This, together with torsional strain, should also affect cyclopentene, with torsional strain being stronger in cyclopentane. The six-membered hydrocarbons are nearly strain-free, in the order 1,4-cyclohexadiene < cyclohexane < cyclohexene. The small strain in cyclohexene relative to cyclohexane might be due to its increased rigidity, which prevents the carbon atoms from adopting fully staggered configurations, leading to an increase of torsional strain. Six-membered radicals are also almost devoid of strain, while their five-membered counterparts display considerable strain. However, the alkyl radicals cyclopentyl and cyclopenten-4-yl have SEs that are ca. 10–15 kJ mol⁻¹ less than those of the corresponding parent molecules. The corresponding BDEs are, therefore, smaller than the equivalent BDEs in the six-membered hydrocarbons by a similar amount. The SE in the rigid cyclopenten-3-yl is closer to the SE in the parent molecule, leading to a BDE similar to those in the unstrained molecules cyclohexene and cyclohexen-3-yl. Finally, the BDE in 1,3-cyclopentadiene is considerable higher than in the unstrained 1,4-cyclohexadiene. However, we estimate that the conventional strain is similar in 1,3-cyclopentadiene and in its radical. Therefore, the higher BDE in 1,3-cyclopentadiene is attributed not to a destabilizing strain effect in the radical but to a stabilizing effect in the parent molecule due to the conjugated double bond, thus mimicking the relation between the BDEs in the 1,3- and 1,4-pentadienes.

Finally, we would like to refer to the recent statement⁵¹ that, even in these days of increasingly accurate quantum chemistry methods, empirical schemes still have an important role to play, thanks to the chemical insight that they afford. We feel the present study to be a good example of this.

Experimental Section

Materials. Benzene (HPLC grade, 99.9+ %), was used without further purification. Cyclopentane (purity >99%) was used as received. Cyclohexane (HPLC grade, 99.9+%) was used as received. Di-*tert*-butylperoxide was purified according to a literature procedure.⁵² *o*-Hydroxybenzophenone was recrystallized twice from an ethanol–water mixture.

Photoacoustic Calorimetry. The basis of photoacoustic calorimetry,^{6,53} our photoacoustic calorimeter setup,^{17,54} and the experimental technique are described in detail elsewhere.^{17,55} Briefly, argon-purged solutions in benzene of ca. 0.4 M di-*tert*-butylperoxide and an adequate concentration (see Results) of each organic molecule studied (cyclopentane and cyclohexane) were flowed through a quartz flow cell (Hellma 174-QS) and photolyzed with pulses from a nitrogen laser (337.1 nm, pulse width 800 ps). The incident laser energy was varied by using neutral density filters (ca. 5–30 μJ/pulse at the cell, flux <40 J m⁻²). Each laser pulse triggered a photochemical process (see below) that induced a sudden volume change in solution, which generated an acoustic wave, detected by a piezoelectric transducer (0.5 MHz) in contact with the bottom of the cell. The signals were amplified and measured by a digital oscilloscope. The signal-to-noise ratio was improved by averaging 32 acquisitions for each data point obtained at a given

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laser energy. The apparatus was calibrated by carrying out a photoacoustic run using an optically matched solution of *o*-hydroxybenzophenone (in the same mixtures but without the peroxide), which dissipates all of the absorbed energy as heat.⁵³ All experiments were performed at 293 ± 1 K. For each run (experiment or calibration), four data points were collected corresponding to four different laser intensities obtained using the neutral density filters. The resulting waveforms from each data point were recorded for subsequent mathematical analysis, affording two waveforms for each point: sample and calibration. The analysis involved, for each laser energy, first the normalization of both waveforms and then the deconvolution of the sample waveform with the calibration waveform⁵⁶ using the software Sound Analysis.⁵⁷

Theoretical Calculations. The theoretical procedures used in the present work were essentially the same outlined in our foregoing study.⁸ Briefly, all geometries were optimized by density functional theory (DFT), using the B3LYP hybrid functional⁵⁸ together with the cc-pVTZ basis set.⁵⁹ The selection of this method was dictated by its known accuracy and cost-effectiveness.^{60,61} In fact, it is known to outperform highly correlated (and thus, computationally demanding) wave-function-based methods such as MP2⁶² or CCSD(T)⁶³ in this particular domain.⁶⁴ Vibrational frequencies were computed for all optimized geometries, allowing further confirmation that these were minima of the respective potential energy surfaces. Additionally, this analysis afforded the thermal correction to the energy at 298.15 K as well as the zero-point energy correction for each species. The corresponding enthalpies were then computed by adding these corrections to the energies of the respective optimized geometries. Enthalpies were also computed using two composite procedures, namely, CBS-Q and CBS-QB3,^{65–67} as well as with a dual (D,T) scheme to complete basis set extrapolation of CCSD(T) energies relying on cc-pVDZ and cc-pVTZ calculations proposed by Truhlar.⁶⁸ This was necessary since previous works

have shown that DFT behaves erratically in the determination of bond dissociation enthalpies.^{69,70} The CBS methods, particularly CBS-QB3, as well as the (D,T) extrapolation, have shown to be adequate tools for the study of BDEs.⁸ The B3LYP/cc-pVTZ calculations were also used to determine Mulliken atomic spin densities^{71–74} for the radical species under study. Although this population analysis can prove to be unreliable and is, by definition, basis-set-dependent, it has been successfully used, for example, in the study of heterosubstituted allyl radicals⁷⁵ and in our previous study on the allylic moiety.⁸ All calculations were carried out using the Gaussian-03⁷⁶ or the PSI3⁷⁷ programs.

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Supporting Information Available: Detailed description of the rules for selecting the *s*-homodesmotic model. Tables containing computed optimized geometries and total energies for radicals and parent compounds. Complete list of reactions used to estimate strain energies with the *s*-homodesmotic model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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