Ring Strain in Cycloalkanes

The semi-empirical AM1 method is used to calculate heats of hydrogenation of cycloalkanes which in turn are employed to obtain strain energies.

Small-ring cycloalkanes are thermodynamically less stable than the corresponding n-alkanes. This is due to a variety of factors, most notably distortion of C-C-C bond angles away from idealized tetrahedral values, and eclipsing interactions between CH bonds in cycloalkanes that are unable to assume fully staggered arrangements. The destabilization of small-ring cycloalkanes, relative to open chain alkanes, is generally referred to as "ring strain".

In this experiment, you will employ semi-empirical AM1 calculations to evaluate the energetics of isodesmic reactions (see: Isodesmic Reactions).

\[
\begin{align*}
\text{CH}_2\text{CH}_2 + 2 \text{CH}_3\text{CH}_3 & \longrightarrow \text{CH}_3\text{CH}_2\text{C}_n\text{H}_{2n+1} + \text{CH}_3\text{CH}_2\cdot \text{CH}_2\text{CH}_3 \\
\end{align*}
\]

This reaction energy is equivalent to the difference in the hydrogenation energy of a small-ring cycloalkane and the corresponding hydrogenation energy of a "standard" acyclic alkane (in this case, n-butane), i.e.,

\[
E \left[ \begin{array}{c}
\text{CH}_2\text{CH}_2 \\
\text{CH}_3 \text{H}_5\text{C}
\end{array} \right] + E \left[ \begin{array}{c}
\text{CH}_3\text{CH}_2\cdot \text{CH}_2\text{CH}_3 \\
\text{H}_2 \longrightarrow 2 \text{CH}_3\text{CH}_3
\end{array} \right],
\]

and will allow you to assess the magnitude of ring strain as a function of ring size.

Procedure

Build and optimize using the AM1 method, cyclopropane, cyclobutane, cyclopentane, cyclohexane and cycloheptane. Try to select a conformer for cycloheptane which minimizes obvious steric interactions. Evaluate strain energies according to the above definition. (AM1 heats of formation of acyclic hydrocarbons are provided in the table below, and ΔH° for hydrogen is -5.2 kcal/mol at the AM1 level.)

<table>
<thead>
<tr>
<th>AM1 Heats of formation (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
</tr>
<tr>
<td>propane</td>
</tr>
<tr>
<td>n-butane</td>
</tr>
<tr>
<td>n-pentane</td>
</tr>
<tr>
<td>n-hexane</td>
</tr>
<tr>
<td>n-heptane</td>
</tr>
</tbody>
</table>

1. Carey and Sundberg A, p.157; March, p.150.
According to this measure, which rings are the most strained and which are the least strained? In particular, what is the relationship between strain energy and ring size? Examine the AM1 geometries of each of the cycloalkanes. Point out any significant deviations from tetrahedral CCC bond angles ("angle strain") and any eclipsing CH bonds ("torsional strain"). How do the CC bond distances in the cycloalkanes compare to those in the analogous n-alkanes? Try to explain why some bond distances, bond angles, and torsional angles are similar in cycloalkanes and alkanes, and why some are different.

Experimentally, cycloheptane is more strained than cyclohexane. Do your calculations support this result? Try to explain why with reference to specific geometrical features.

2. Experimental strain energies (kcal/mol): cyclopropane, 27; cyclobutane, 26; cyclopentane, 7; cyclohexane, 0; cycloheptane, 6; Isaacs, p.320.