

The Conformations of Cycloalkanes

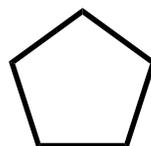
Ring-containing structures are a common occurrence in organic chemistry. We must, therefore spend some time studying the special characteristics of the parent **cycloalkanes**. Cyclical connectivity imposes constraints on the range of motion that the atoms in rings can undergo. Cyclic molecules are thus more rigid than linear or branched alkanes because cyclic structures have fewer internal degrees of freedom (that is, the motion of one atom greatly influences the motion of the others when they are connected in a ring). In this lesson we will examine structures of the common ring structures found in organic chemistry. The first four cycloalkanes are shown below.



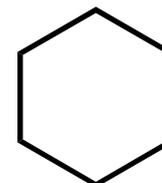
cyclopropane



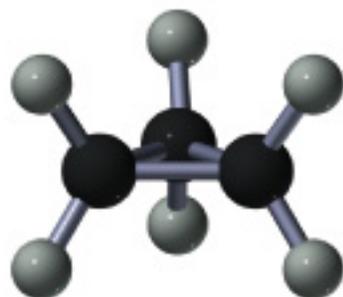
cyclobutane



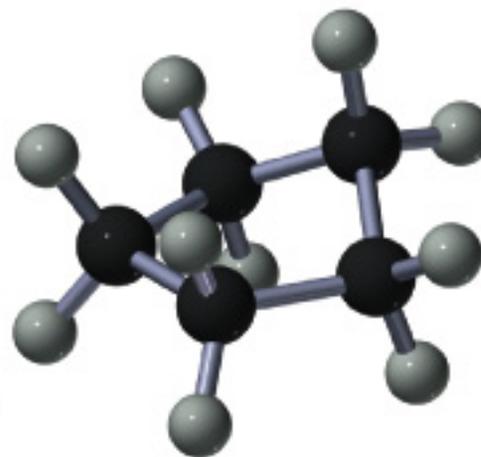
cyclopentane



cyclohexane



cyclopropane



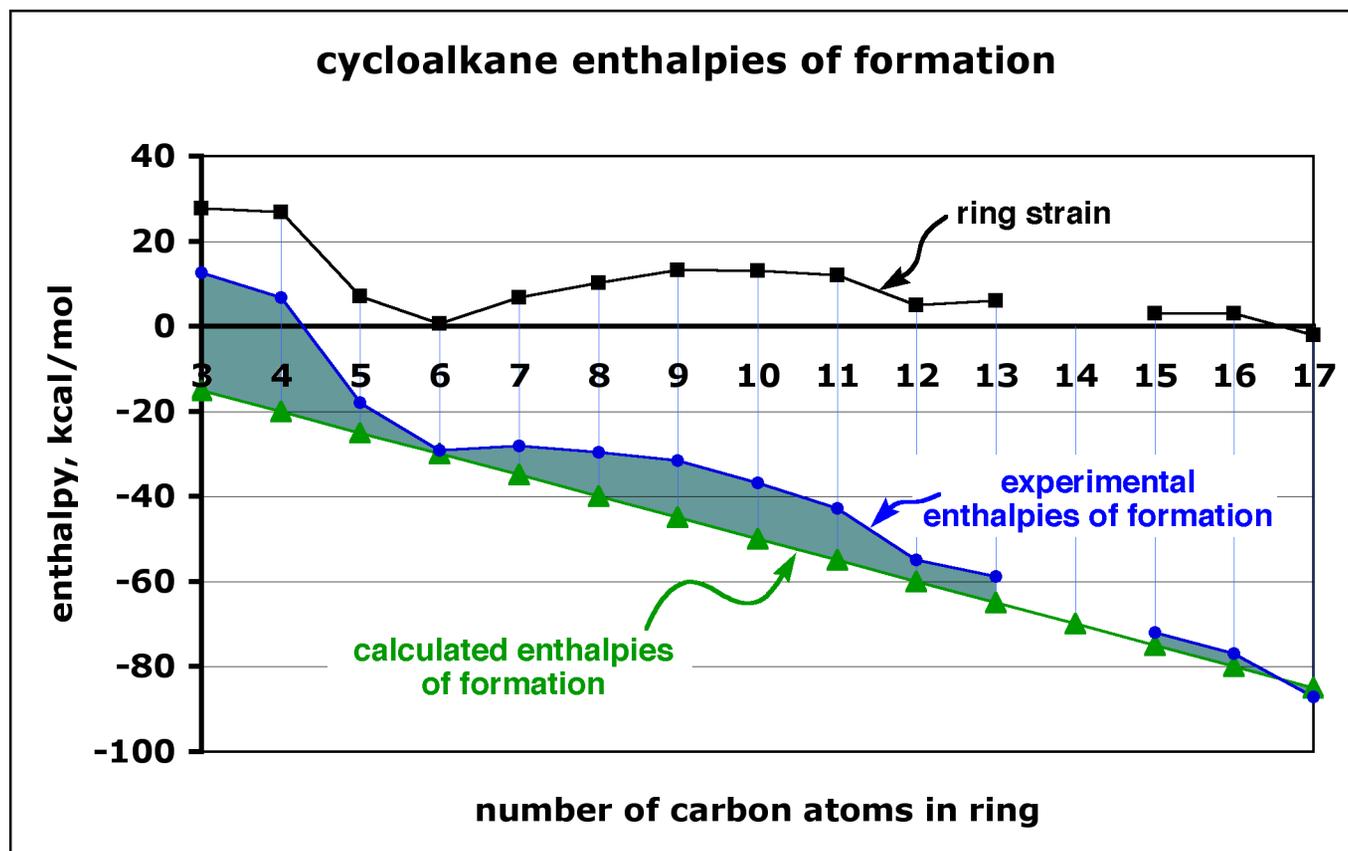
cyclopentane



The amount of energy stored in a strained ring is estimated by comparing the experimental heat of formation to the calculated heat of formation. The calculated heat of formation is based on the notion that, in the absence of strain, each $-\text{CH}_2-$ group contributes equally to the heat of formation, in line with the behavior found for the acyclic alkanes (i.e., open chains). Thus, the calculated heat of formation varies linearly with the number of carbon atoms in the ring. Except for the 6-membered ring, the experimental values are found to have a more positive heat of formation than the calculated value owing to ring strain. The plots of calculated and experimental enthalpies of formation and their difference (i.e., ring strain) are seen in the Figure. The 3-membered ring has about 27 kcal/mol of strain. It can be seen that the 6-membered ring possesses almost no ring strain.

Ring Strain

Strain energy vs. ring size based on heats of formation data for the cycloalkanes. Source of data: *Chem. Rev.* **1993**, *93*, 2419-2438. See also: Wikipedia, "Benson Group Increment Theory".



Bond Angles Bend: The Concept of Angle Strain

Carbon atoms prefer to adopt tetrahedral geometry, meaning that ideal bond angles are close to 109° . The 3-membered cyclopropane ring has C-C-C bond angles that are 60° and thus bent about 50° from the ideal angle. Cyclopropane is a known compound; at room temperature it exists as a gas that can be stored for long periods without decomposition. Obviously, molecules such as cyclopropane deform far from their ideal geometry. The potential energy as a function of bond angle for propane gives an estimate of how much energy is stored in deforming the molecule to make the 60° angle required of the 3-membered ring. Notice that the lowest energy for propane is at an angle slightly more open than 109° . This is probably because the methyl groups are larger than hydrogen, and to minimize crowdedness, the bond angle deforms ever so slightly away from 109° . Notice also that the bond angle can be opened or closed several degrees without costing much energy

