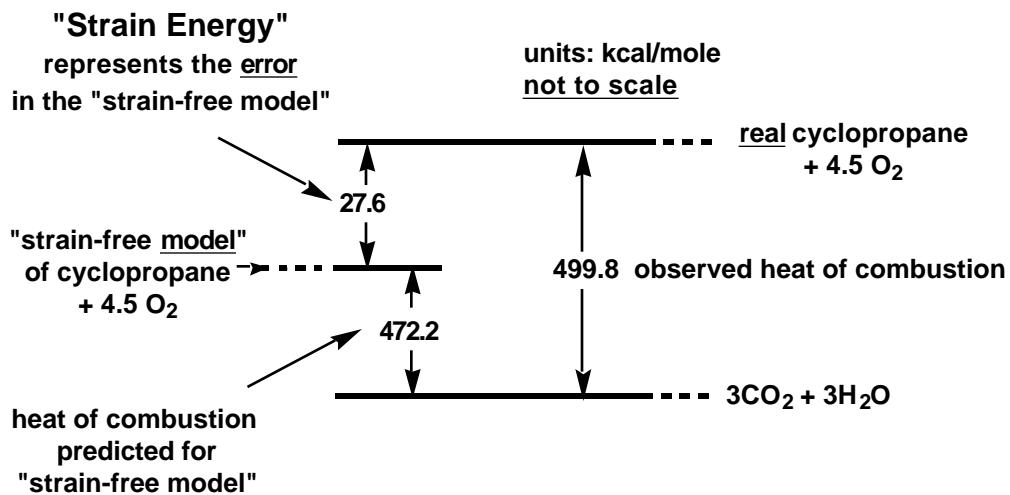
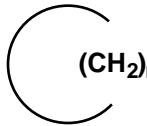


Text Related to Segment 5.02 ©2002 Claude E. Wintner

From the previous segment we have the value of the heat of combustion of an "unstrained" methylene unit as -157.4 kcal/mole. On this basis one would predict that combustion of "unstrained" cyclopropane should liberate $3 \times 157.4 = 472.2$ kcal/mole; however, when cyclopropane is burned, a value of 499.8 kcal/mole is measured for the actual heat of combustion. The difference of 27.6 kcal/mole is interpreted as representing the higher internal energy ("strain energy") of real cyclopropane as compared to a postulated strain-free "model." ("Model" in this usage speaks of a proposal, or postulate.) These facts are graphed conveniently on an energy diagram as follows:



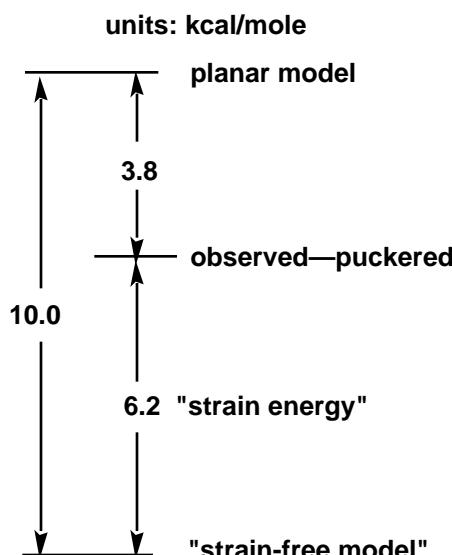
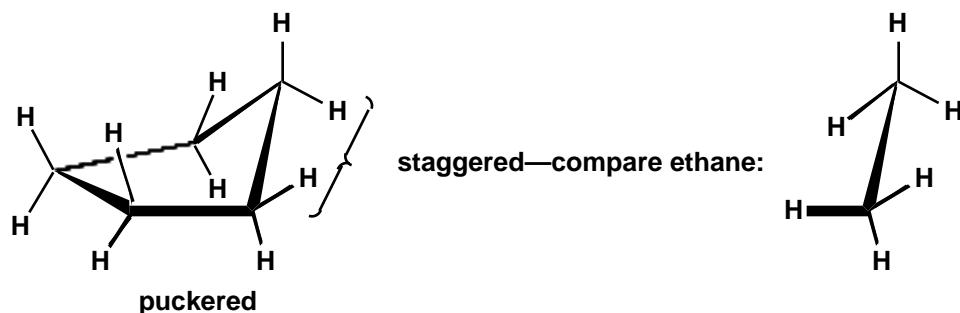
Note that this estimate of the strain energy in cyclopropane amounts to 9.2 kcal/mole of strain per methylene group (dividing 27.6 by 3, because of the three carbon atoms). Comparable values in kcal/mole for other small and medium rings are given in the following table. As one might expect, in general the strain decreases as the ring is enlarged.

| units: kcal/mole | | |
|--|----|--|
| | n | Total Strain Strain per CH ₂ |
|  $(\text{CH}_2)_n$ | 3 | 27.6 9.2 |
| | 4 | 26.3 6.6 |
| | 5 | 6.2 1.2 |
| | 6 | 0.1 0.0 ! ← |
| | 7 | 6.2 0.9 |
| | 8 | 9.7 1.2 |
| | 9 | 12.6 1.4 |
| | 10 | 12.4 1.2 |
| | 12 | 4.1 0.3 |
| | 15 | 1.9 0.1 |

Without entering into a discussion of the relevant bonding concepts here, and instead relying on geometry alone, interpretation of the source of the strain energy in cyclopropane and cyclobutane is to some extent self-evident. These molecules must pay the penalty for the distortion to (formally) 60° and 90°, respectively, of bond angles that should be tetrahedral (109°). For cyclobutane the total ring strain is hardly less than for cyclopropane, but the strain per methylene group is reduced considerably. Examination of a flexible model will make clear that the conformational rigidity of the carbon ring of cyclobutane is not complete; it can "wag" to some extent, as a bird in flight, whereas cyclopropane, for which the carbon ring is a triangle, formally is constrained to be conformationally rigid.

A few words regarding the conformation of cyclopentane are in order here. Referring again to the strain chart, at first glance it is less clear how one should interpret the value of 6.2 kcal/mole of strain energy in cyclopentane. The angle of a regular pentagon is 108°, almost the tetrahedral 109°. Given this very small difference, it hardly is surprising that models reveal no appreciable angle strain. On the other hand, for a cyclopentane molecule with all of its carbon atoms held in a plane, all of the hydrogen atoms must be eclipsed. In such a planar model there are ten eclipsing interactions, each costing about 1 kcal/mole, on the basis of the value found for ethane. The consequent predicted value of 10 kcal/mole for the strain

energy is too high. In fact, cyclopentane can escape some of this eclipsing strain by puckering, which allows one carbon atom to leave the plane, with the apparent partial relief of the better part of four eclipsing interactions:



conformation and strain in cyclopentane

The figure shows how, in the puckered form, the conformation about two of the carbon-carbon bonds approaches staggered ethane status. On the other hand, too

much puckering also will produce strain. The observed value of 6.2 kcal/mole strain represents a compromise between too much eclipsing and too much puckering. It should be noted, of course, that the cyclopentane molecule is in constant flux, with each carbon atom in turn moving out of the plane on a very rapid time scale.

We defer the very important observation of an apparently strain-free situation for cyclohexane to a later segment. In the so-called medium-sized rings, such as cyclononane and cyclodecane there is no appreciable angle strain, for they need not be planar, but examination of a model will show that no matter how one attempts to manipulate the conformation, there always must be some "bumping" interaction among hydrogen atoms (transannular strain) in the internal cavity of the ring. As the ring size becomes very large, these interactions no longer are obligatory.

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