

# Organic Chemistry I

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# 4. Cycloalkanes

Hydrocarbons containing single-bonded carbon atoms arranged in rings are known as **cyclic alkanes**, **carbocycles**, or **cycloalkanes**. The majority of organic compounds occurring in nature contain rings. Indeed, so many fundamental biological functions depend on the chemistry of ring-containing compounds that life could not exist in their absence.

Because of their cyclic nature, members of this class of compounds can exhibit new types of strain, such as ring strain and transannular interactions.

## **NAMES AND PHYSICAL PROPERTIES OF CYCLOALKANES**

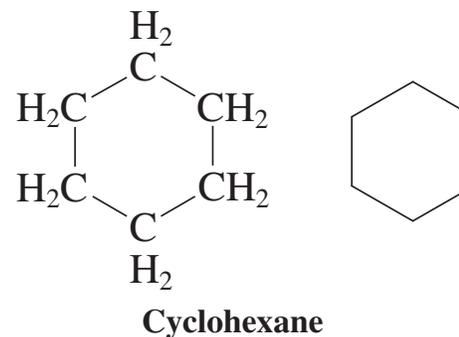
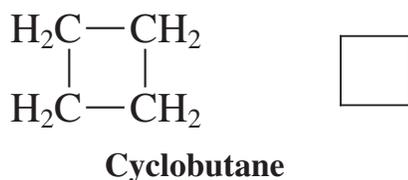
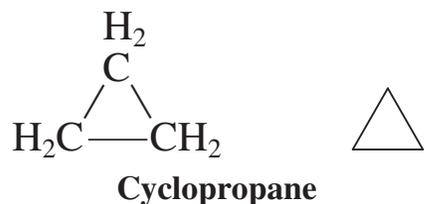
Cycloalkanes have their own names under IUPAC rules, and their properties are generally different from those of their noncyclic (also called acyclic) analogs with the same number of carbons.

**The names of the cycloalkanes follow IUPAC rules**

We can construct a molecular model of a cycloalkane by removing a hydrogen atom from each terminal carbon of a model of a straight-chain alkane and allowing these carbons to form a bond. The empirical formula of a cycloalkane is  $C_nH_{2n}$  or  $(CH_2)_n$ .

The system for naming members of this class of compounds is straightforward: Alkane names are preceded by the prefix **cyclo-**.

Three members in the homologous series—starting with the smallest, cyclopropane.

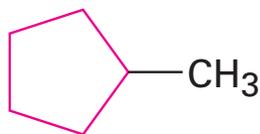


## Find the parent

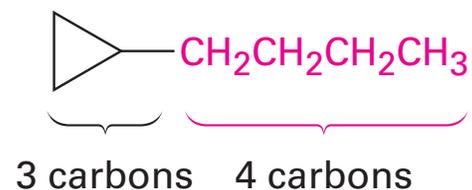
Count the number of carbon atoms in the ring and the number in the largest substituent.

If the **number of carbon atoms** in the ring is **equal to or greater than** the **number in the substituent**, the compound is named as an **alkyl-substituted cycloalkane**.

If the number of carbon atoms in the largest substituent is greater than the number in the ring, the compound is named as a **cycloalkyl-substituted alkane**.



Methyl**cyclopentane**

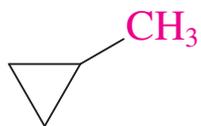


1-Cyclopropyl**butane**

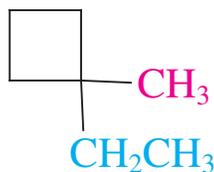
Naming a substituted cyclic alkane requires numbering the individual ring carbons only if more than one substituent is attached to the ring. In monosubstituted systems, the carbon of attachment is defined as carbon 1 of the ring.

For polysubstituted compounds, take care to provide the lowest possible numbering sequence. When two such sequences are possible, the alphabetical order of the substituent names takes precedence.

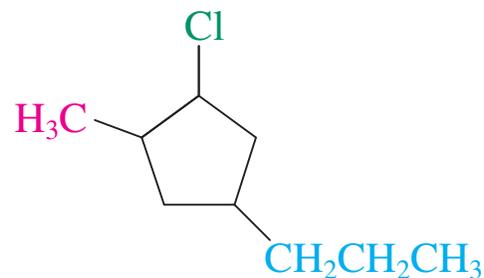
Radicals derived from cycloalkanes by abstraction of a hydrogen atom are **cycloalkyl radicals**. Substituted cycloalkanes are therefore sometimes named as cycloalkyl derivatives. In general, the smaller unit is treated as a substituent to the larger one.



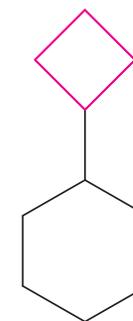
**Methyl**cyclopropane  
(No numbering)



**1-Ethyl-1-methyl**cyclobutane  
(Alphabetical)



**1-Chloro-2-methyl-4-propyl**cyclopentane  
(Alphabetical; not 2-chloro-1-methyl-4-propylcyclopentane)



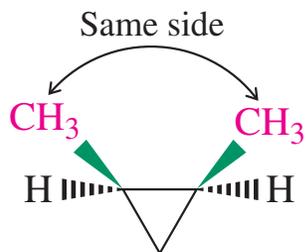
**Cyclobutyl**cyclohexane  
(Smaller ring is substituent)

## Disubstituted cycloalkanes can be stereoisomers

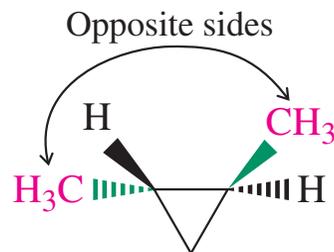
In disubstituted cycloalkanes, two substituents are located on different carbons shows *two isomers*: the two substituents are positioned on the *same* face, or side, of the ring; or they are on *opposite* faces.

Substituents on the same face are called **cis**; those on opposite faces, **trans**.

### Stereoisomers of 1,2-Dimethylcyclopropane

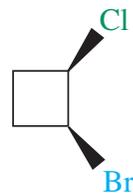


*cis*-1,2-Dimethylcyclopropane

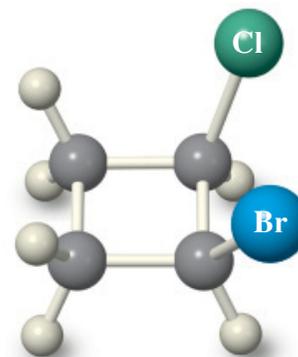


*trans*-1,2-Dimethylcyclopropane

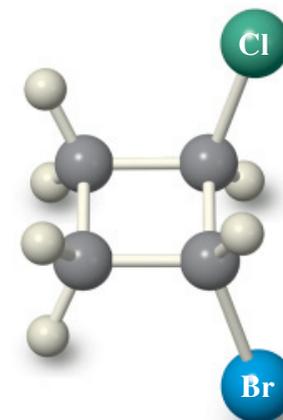
### Stereoisomers of 1-Bromo-2-chlorocyclobutane



*cis*-1-Bromo-2-chlorocyclobutane



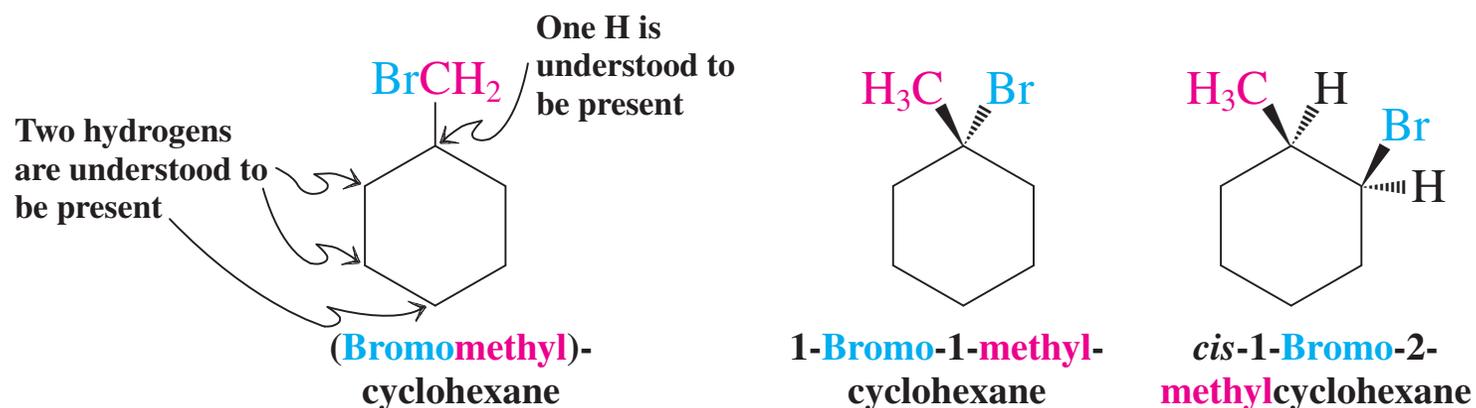
*trans*-1-Bromo-2-chlorocyclobutane



Cis and trans isomers are **stereoisomers**—compounds that have identical connectivities (i.e., their atoms are attached in the same sequence) but differ in the arrangement of their atoms in space.

They are distinct from constitutional or structural isomers, which are compounds with differing connectivities among atoms. Cis and trans isomers can be interconverted only by *breaking* bonds.

For example, there are eight isomeric bromomethylcyclohexanes (three of which are shown below), all with different and distinct physical and chemical properties.



## The properties of the cycloalkanes differ from those of their straight-chain analogs

Compared with the corresponding straight-chain alkanes, the cycloalkanes have higher boiling and melting points, and higher densities, **due to** increased London interactions of the relatively more rigid and more symmetric cyclic systems.

In lower cycloalkanes possessing an odd or even number of carbons, a pronounced alternation in their melting points is observed (differences in **crystal packing forces** between the two series).

Cycloalkane	Melting point (°C)	Boiling point (°C)	Density at 20°C (g mL <sup>-1</sup> )
Cyclopropane (C <sub>3</sub> H <sub>6</sub> )	-127.6	-32.7	0.617 <sup>b</sup>
Cyclobutane (C <sub>4</sub> H <sub>8</sub> )	-50.0	-12.5	0.720
Cyclopentane (C <sub>5</sub> H <sub>10</sub> )	-93.9	49.3	0.7457
Cyclohexane (C <sub>6</sub> H <sub>12</sub> )	6.6	80.7	0.7785
Cycloheptane (C <sub>7</sub> H <sub>14</sub> )	-12.0	118.5	0.8098
Cyclooctane (C <sub>8</sub> H <sub>16</sub> )	14.3	148.5	0.8349
Cyclododecane (C <sub>12</sub> H <sub>24</sub> )	64	160 (100 torr)	0.861
Cyclopentadecane (C <sub>15</sub> H <sub>30</sub> )	66	110 (0.1 torr <sup>a</sup> )	0.860

<sup>a</sup>Sublimation point.  
<sup>b</sup>At 25°C.

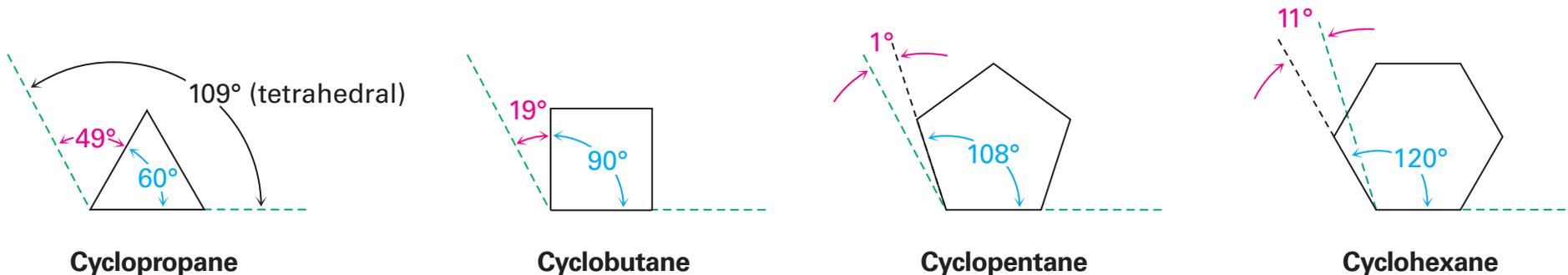
## RING STRAIN AND THE STRUCTURE OF CYCLOALKANES

The molecular models reveal obvious differences between cyclopropane, cyclobutane, cyclopentane, and etc, and the corresponding straight-chain alkanes: **ring strain**.

The reason for it lies in the tetrahedral carbon model. The C–C–C bond angles in cyclopropane ( $60^\circ$ ) and cyclobutane ( $90^\circ$ ) differ considerably from the tetrahedral value of  $109.5^\circ$ .

As the ring size increases, strain diminishes. Thus, cyclohexane can be assembled without distortion or strain.

The relative stability of the cycloalkanes is measured by their heats of combustion,  $\Delta H^\circ_{\text{comb}}$ .



## The heats of combustion of the cycloalkanes reveal the presence of ring strain

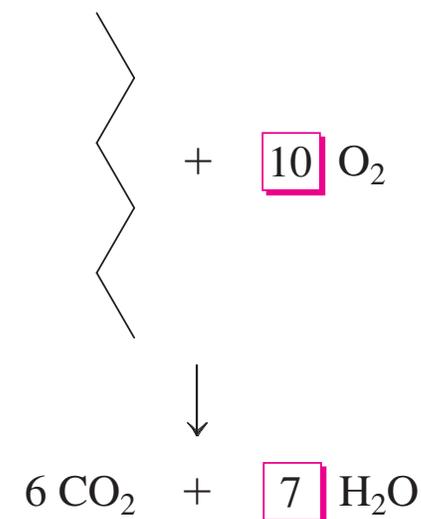
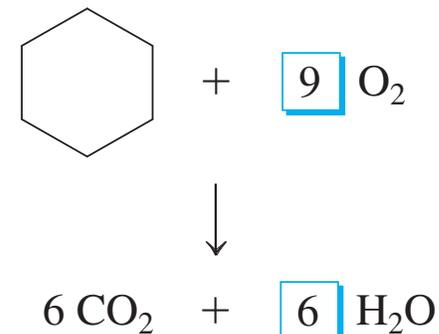
The stability of cycloalkanes could compare with their heats of combustion with those of the analogous straight-chain alkanes. Such a direct comparison is flawed because the empirical formula of cycloalkanes,  $C_nH_{2n}$ , differs from that of normal alkanes,  $C_nH_{2n+2}$ , by two hydrogens.

The formula for cycloalkanes can be rewrite as  $(CH_2)_n$ . Thus, if we had an experimental number for the contribution of a “strain-free”  $CH_2$  fragment to the  $\Delta H^\circ_{\text{comb}}$  of straight-chain alkanes, then the corresponding  $\Delta H^\circ_{\text{comb}}$  of a cycloalkane should simply be multiples of this number.

**The  $\Delta H^\circ_{\text{comb}}$  of a Strain-Free Cycloalkane Should Be Multiples of  $\Delta H^\circ_{\text{comb}}(CH_2)$**

$$\Delta H^\circ_{\text{comb}}(C_nH_{2n}) = n \times \Delta H^\circ_{\text{comb}}(CH_2)$$

### Combustion of Cyclohexane Versus Hexane



The  $\Delta H^\circ_{\text{comb}}$  increases by about the same amount with each successive member of the homologous series: about 157 kcal mol<sup>-1</sup> for each additional CH<sub>2</sub> moiety.

### $\Delta H^\circ_{\text{comb}}$ Values for the Series of Straight-Chain Alkanes

CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub> (gas)	-530.6	}	Increment = -156.8	kcal mol <sup>-1</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> (gas)	-687.4		Increment = -157.8	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub> (gas)	-845.2		Increment = -157.3	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub> (gas)	-1002.5			

Calculate the  $\Delta H^\circ_{\text{comb}}$  of the cycloalkanes, (CH<sub>2</sub>)<sub>n</sub>, by using  $-(n \times 157.4)$  kcal mol<sup>-1</sup>, e.g. for cyclopropane ( $n = 3$ ), its  $\Delta H^\circ_{\text{comb}}$  should be -472.2 kcal mol<sup>-1</sup>, and for cyclobutane, it should be -629.6 kcal mol<sup>-1</sup>.

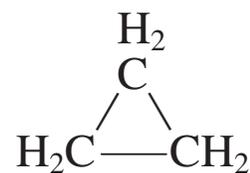
The actual heats of combustion is generally larger in magnitude compared to the calculated values.

For cyclopropane, the experimental value is  $-499.8 \text{ kcal mol}^{-1}$ , a discrepancy between the expected and observed values of  $27.6 \text{ kcal mol}^{-1}$ . Therefore, cyclopropane is more energetic than expected for a strainless molecule. The extra energy is attributed to **ring strain**. The strain per  $\text{CH}_2$  group in this molecule is  $9.2 \text{ kcal mol}^{-1}$ .

### Ring Strain in Cyclopropane

Calculated for strainless molecule:

$$\Delta H_{\text{comb}}^{\circ} = -(3 \times 157.4) = -472.2 \text{ kcal mol}^{-1}$$



$$\text{Measured: } \Delta H_{\text{comb}}^{\circ} = -499.8 \text{ kcal mol}^{-1}$$

$$\text{Strain: } 499.8 - 472.2 = 27.6 \text{ kcal mol}^{-1}$$

A similar calculation for cyclobutane reveals a ring strain of  $26.3 \text{ kcal mol}^{-1}$ , or about  $6.6 \text{ kcal mol}^{-1}$  per  $\text{CH}_2$  group. In cyclopentane, this effect is much smaller, the total strain amounting to only  $6.5 \text{ kcal mol}^{-1}$ , and **cyclohexane** is virtually **strain free**.

However, succeeding members of the series again show considerable strain until we reach very large rings.

Because of these trends, four groups of cycloalkanes defined as:

1. *Common Small rings* (cyclopropane, cyclobutane)
2. *Common rings* (cyclopentane, cyclohexane, cycloheptane)
3. *Medium rings* (from 8- to 12-membered)
4. *Large rings* (13-membered and larger)

Table 4-2		Calculated and Experimental Heats of Combustion in kcal mol <sup>-1</sup> (kJ mol <sup>-1</sup> ) of Various Cycloalkanes						
Ring size (C <sub>n</sub> )	$\Delta H^\circ_{\text{comb}}$ (calculated)		$\Delta H^\circ_{\text{comb}}$ (experimental)		Total strain		Strain per CH <sub>2</sub> group	
3	-472.2	(-1976)	-499.8	(-2091)	27.6	(115)	9.2	(38)
4	-629.6	(-2634)	-655.9	(-2744)	26.3	(110)	6.6	(28)
5	-787.0	(-3293)	-793.5	(-3320)	6.5	(27)	1.3	(5.4)
6	-944.4	(-3951)	-944.5	(-3952)	0.1	(0.4)	0.0	(0.0)
7	-1101.8	(-4610)	-1108.2	(-4637)	6.4	(27)	0.9	(3.8)
8	-1259.2	(-5268)	-1269.2	(-5310)	10.0	(42)	1.3	(5.4)
9	-1416.6	(-5927)	-1429.5	(-5981)	12.9	(54)	1.4	(5.9)
10	-1574.0	(-6586)	-1586.0	(-6636)	14.0	(59)	1.4	(5.9)
11	-1731.4	(-7244)	-1742.4	(-7290)	11.0	(46)	1.1	(4.6)
12	-1888.8	(-7903)	-1891.2	(-7913)	2.4	(10)	0.2	(0.8)
14	-2203.6	(-9220)	-2203.6	(-9220)	0.0	(0.0)	0.0	(0.0)

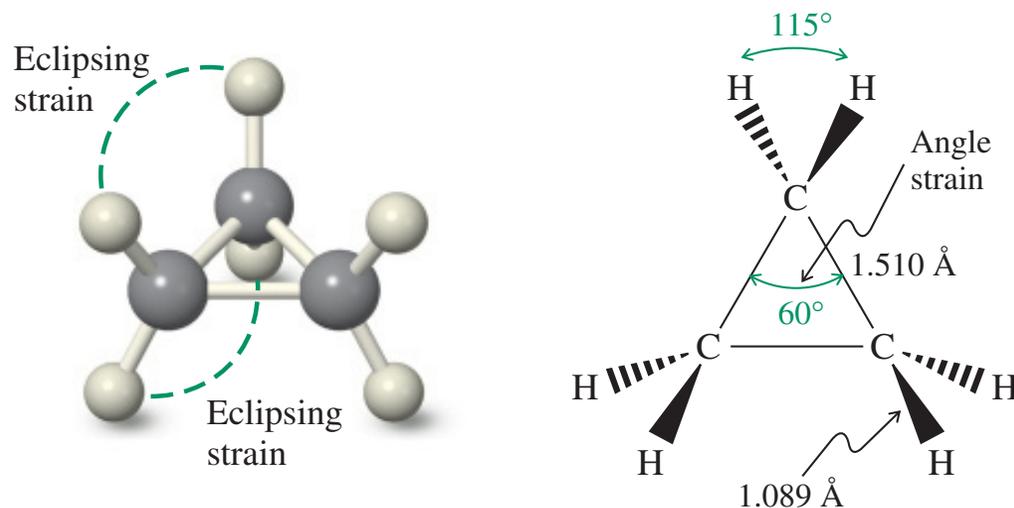
*Note:* The calculated numbers are based on the value of -157.4 kcal mol<sup>-1</sup> (-658.6 kJ mol<sup>-1</sup>) for a CH<sub>2</sub> group.

## Strain affects the structures and conformational function of the smaller cycloalkanes

The smallest cycloalkane, *cyclopropane*, is much less stable than expected for three methylene groups. The reason is twofold: **torsional strain** and **bond-angle strain**.

First, all methylene hydrogens are eclipsed, much like the hydrogens in the eclipsed conformation of ethane. The eclipsed form of ethane is higher than that of the more stable staggered conformation because of **eclipsing (torsional) strain**.

Moreover, the carbon skeleton in cyclopropane is by necessity **flat** and **quite rigid**, and **bond rotation** that might relieve eclipsing strain is **very difficult**.

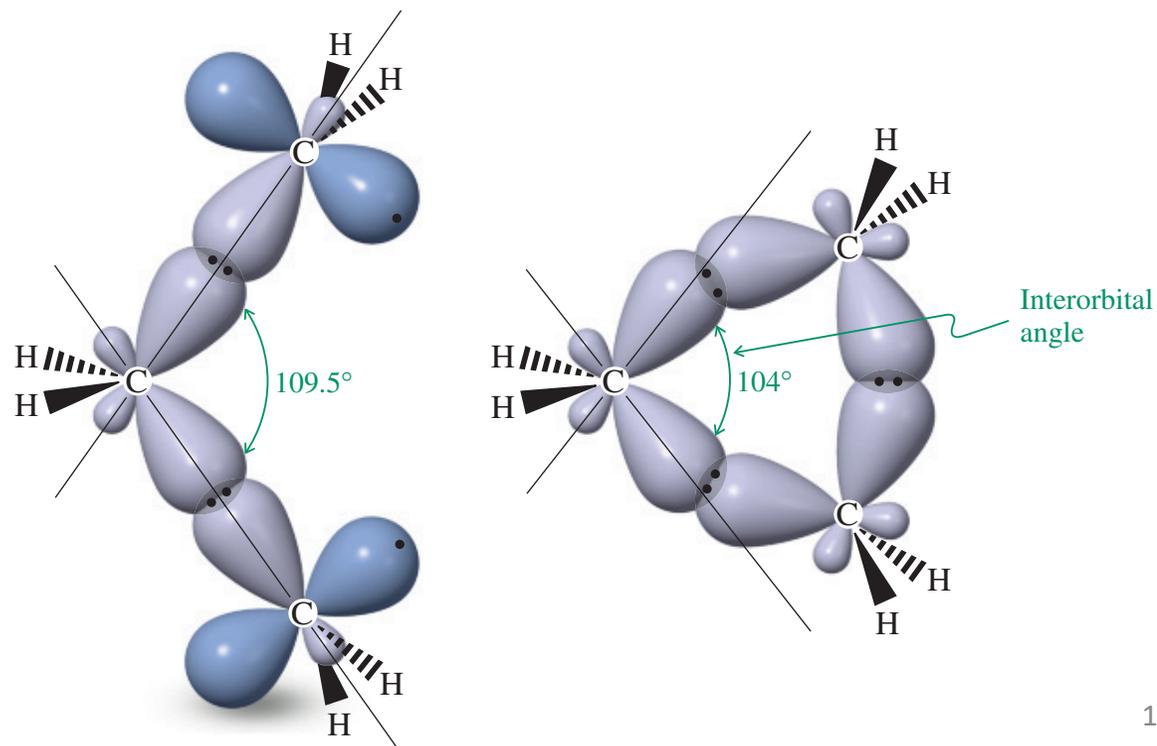


Second, the cyclopropane has C–C–C bond angles of  $60^\circ$ , a significant deviation from the “natural” tetrahedral bond angle of  $109.5^\circ$ .

The bonding in the strain-free “open cyclopropane,” the trimethylene diradical  $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\cdot$ , is compared with that in the closed form: the two ends of the trimethylene diradical cannot “reach” far enough to close the ring without “bending” the two C–C bonds already present.

If all three C–C bonds in cyclopropane adopt a bent configuration (interorbital angle  $104^\circ$ ), overlap is sufficient for bond formation.

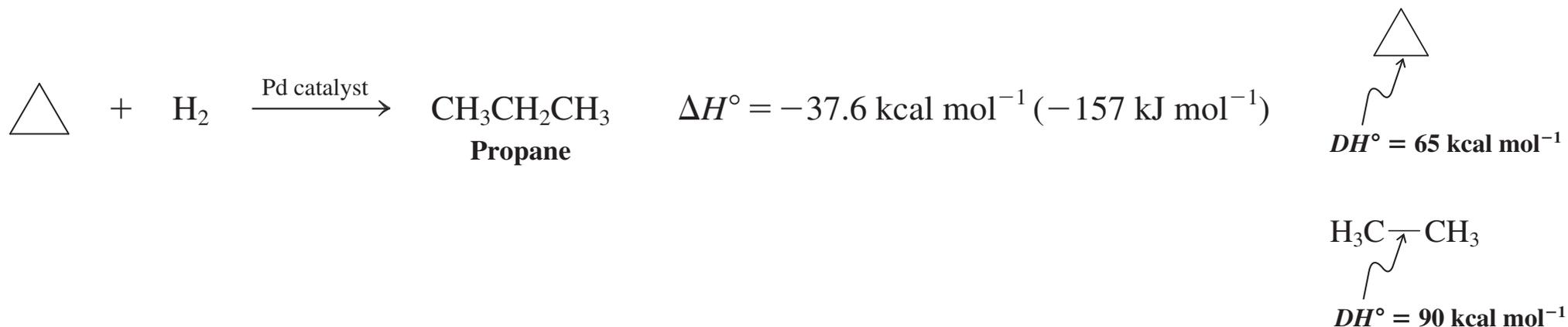
The energy needed to distort the tetrahedral carbons enough to close the ring is called **bond-angle strain**.



The ring strain in cyclopropane is derived from a combination of eclipsing and bond-angle contributions.

As a consequence of its structure, cyclopropane has relatively weak C–C bonds [ $\Delta H^\circ = 65 \text{ kcal mol}^{-1}$  ( $272 \text{ kJ mol}^{-1}$ )]. This value is low [recall that the C–C strength in ethane is  $90 \text{ kcal mol}^{-1}$  ( $377 \text{ kJ mol}^{-1}$ )] because breaking the bond opens the ring and relieves ring strain.

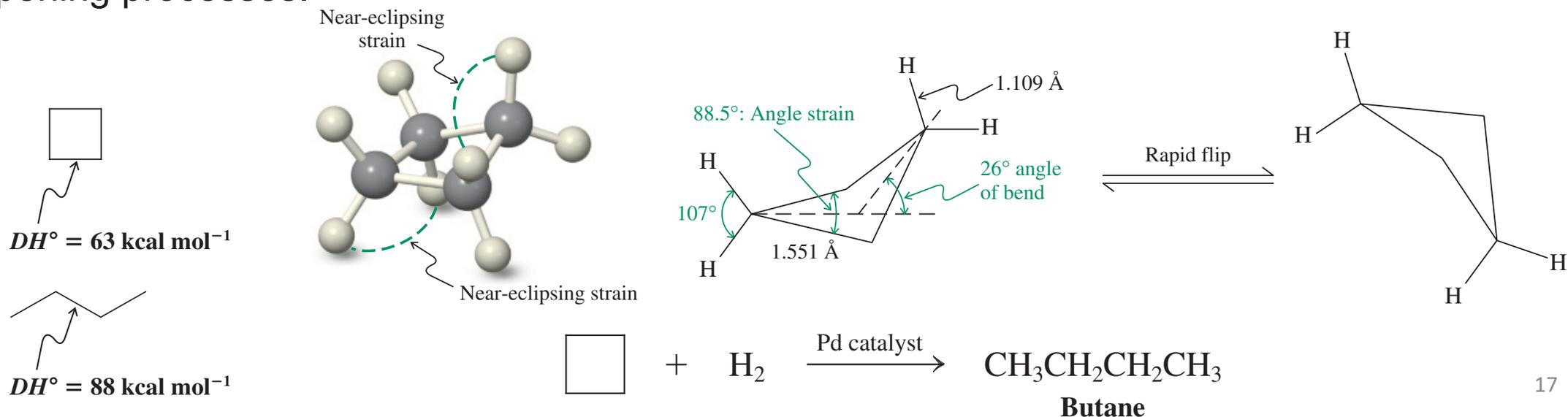
For example, reaction with hydrogen in the presence of a palladium catalyst opens the ring to give propane.



The structure of **cyclobutane** reveals that this molecule is not planar but puckered, with an approximate bending angle of  $26^\circ$ . The **nonplanar structure** of the ring is not very rigid. The molecule “**flips**” rapidly from one puckered conformation to the other.

Distorting the four-membered ring from planarity is favorable: It partly relieves the strain introduced by the eight eclipsing hydrogens. Bond-angle strain is reduced relative to that in cyclopropane, although maximum overlap is only possible with the use of bent bonds.

The C–C bond strength in cyclobutane is low [about  $63 \text{ kcal mol}^{-1}$  ( $264 \text{ kJ mol}^{-1}$ )] because of the release of ring strain on ring opening and the consequences of relatively poor overlap in bent bonds. Cyclobutane is less reactive than cyclopropane but undergoes similar ring-opening processes.



*Cyclopentane* might be expected to be planar because the angles in a regular pentagon are  $108^\circ$ , close to tetrahedral. However, such a planar arrangement would have *ten* H–H eclipsing interactions.

The puckering of the ring reduces this effect, as indicated by the **envelope** structure of the molecule. Although puckering relieves eclipsing, it also increases bond-angle strain. The envelope conformation is a compromise in which the energy of the system is minimized.

Overall, cyclopentane has relatively little ring strain, and its C–C bond strength [ $\Delta H^\circ = 81 \text{ kcal mol}^{-1}$  ( $338 \text{ kJ mol}^{-1}$ )] approaches that in acyclic alkanes. As a consequence, it does not show the unusual reactivity of three- or four-membered rings.

