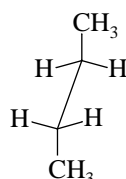


CHAPTER 3

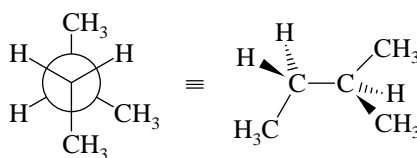
CONFORMATIONS OF ALKANES AND CYCLOALKANES

SOLUTIONS TO TEXT PROBLEMS

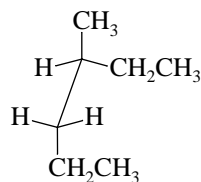
- 3.1 (b) The sawhorse formula contains four carbon atoms in an unbranched chain. The compound is butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$.



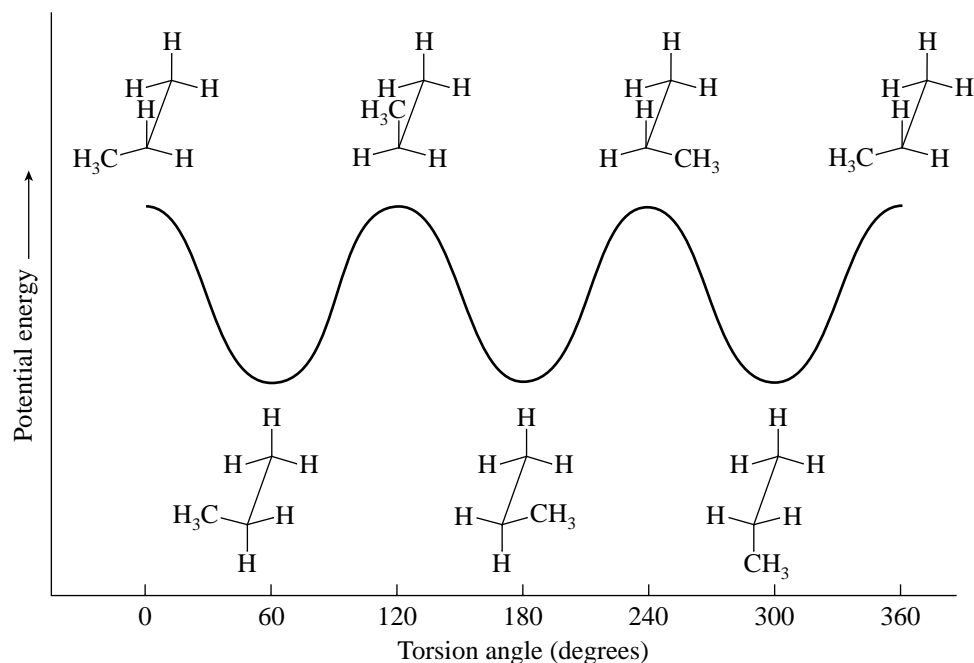
- (c) Rewrite the structure to show its constitution. The compound is $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)_2$; it is 2-methylbutane.



- (d) In this structure, we are sighting down the C-3—C-4 bond of a six-carbon chain. It is $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$, or 3-methylhexane.

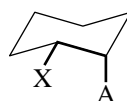


- 3.2 Red circles gauche: 60° and 300° . Red circles anti: 180° . Gauche and anti relationships occur only in staggered conformations; therefore, ignore the eclipsed conformations (0° , 120° , 240° , 360°).
- 3.3 All the staggered conformations of propane are equivalent to one another, and all its eclipsed conformations are equivalent to one another. The energy diagram resembles that of ethane in that it is a symmetrical one.



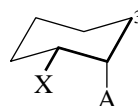
The activation energy for bond rotation in propane is expected to be somewhat higher than that in ethane because of van der Waals strain between the methyl group and a hydrogen in the eclipsed conformation. This strain is, however, less than the van der Waals strain between the methyl groups of butane, which makes the activation energy for bond rotation less for propane than for butane.

- 3.4 (b) To be gauche, substituents X and A must be related by a 60° torsion angle. If A is axial as specified in the problem, X must therefore be equatorial.

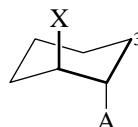


X and A are gauche.

- (c) For substituent X at C-1 to be anti to C-3, it must be equatorial.

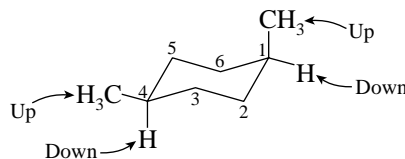


- (d) When X is axial at C-1, it is gauche to C-3.

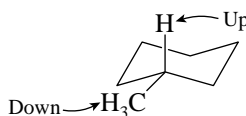


- 3.5 (b) According to the numbering scheme given in the problem, a methyl group is axial when it is "up" at C-1 but is equatorial when it is up at C-4. Since substituents are more stable when they

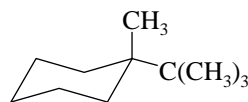
occupy equatorial rather than axial sites, a methyl group that is up at C-1 is less stable than one that is up at C-4.



- (c) An alkyl substituent is more stable in the equatorial position. An equatorial substituent at C-3 is “down.”

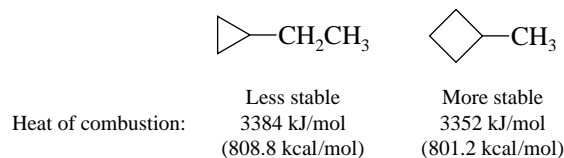


- 3.6 A *tert*-butyl group is much larger than a methyl group and has a greater preference for the equatorial position. The most stable conformation of 1-*tert*-butyl-1-methylcyclohexane has an axial methyl group and an equatorial *tert*-butyl group.

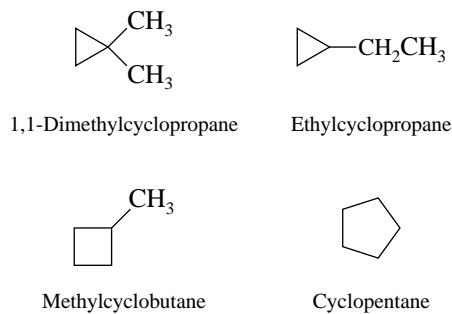


1-*tert*-Butyl-1-methylcyclohexane

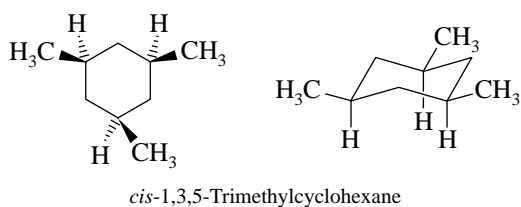
- 3.7 Ethylcyclopropane and methylcyclobutane are isomers (both are C_5H_{10}). The less stable isomer has the higher heat of combustion. Ethylcyclopropane has more angle strain and is less stable (has higher potential energy) than methylcyclobutane.



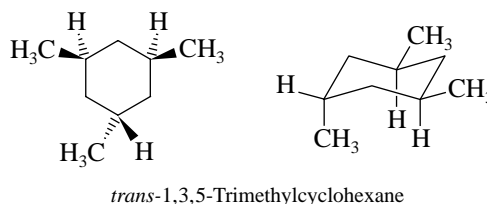
- 3.8 The four constitutional isomers of *cis* and *trans*-1,2-dimethylcyclopropane that do not contain double bonds are



- 3.9 When comparing two stereoisomeric cyclohexane derivatives, the more stable stereoisomer is the one with the greater number of its substituents in equatorial orientations. Rewrite the structures as chair conformations to see which substituents are axial and which are equatorial.

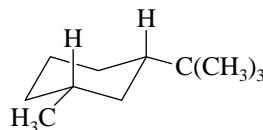


All methyl groups are equatorial in *cis*-1,3,5-trimethylcyclohexane. It is more stable than *trans*-1,3,5-trimethylcyclohexane (shown in the following), which has one axial methyl group in its most stable conformation.

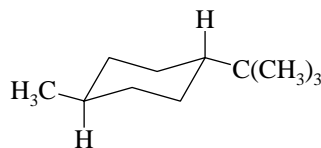


3.10 In each of these problems, a *tert*-butyl group is the larger substituent and will be equatorial in the most stable conformation. Draw a chair conformation of cyclohexane, add an equatorial *tert*-butyl group, and then add the remaining substituent so as to give the required *cis* or *trans* relationship to the *tert*-butyl group.

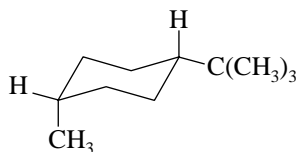
(b) Begin by drawing a chair cyclohexane with an equatorial *tert*-butyl group. In *cis*-1-*tert*-butyl-3-methylcyclohexane the C-3 methyl group is equatorial.



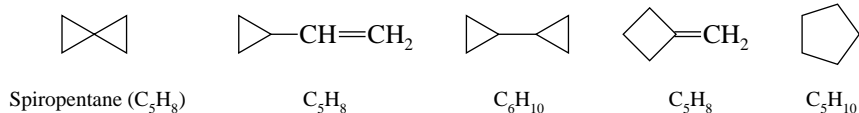
(c) In *trans*-1-*tert*-butyl-4-methylcyclohexane both the *tert*-butyl and the C-4 methyl group are equatorial.



(d) Again the *tert*-butyl group is equatorial; however, in *cis*-1-*tert*-butyl-4-methylcyclohexane the methyl group on C-4 is axial.



3.11 Isomers are different compounds that have the same molecular formula. Compare the molecular formulas of the compounds given to the molecular formula of spiropentane.

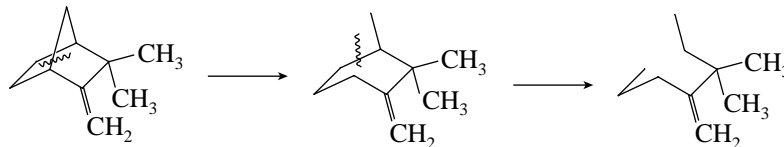


Only the two compounds that have the molecular formula C₅H₈ are isomers of spiropentane.

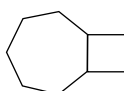
3.12 Two bond cleavages convert bicyclobutane to a noncyclic species; therefore, bicyclobutane is bicyclic.



The two bond cleavages shown convert camphene to a noncyclic species; therefore, camphene is bicyclic. (Other pairs of bond cleavages are possible and lead to the same conclusion.)

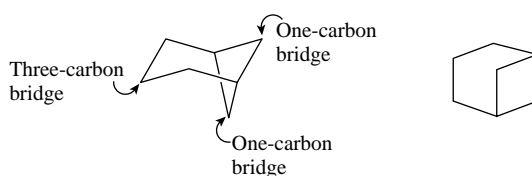


- 3.13 (b) This bicyclic compound contains nine carbon atoms. The name tells us that there is a five-carbon bridge and a two-carbon bridge. The 0 in the name bicyclo[5.2.0]nonane tells us that the third bridge has no atoms in it—the carbons are common to both rings and are directly attached to each other.

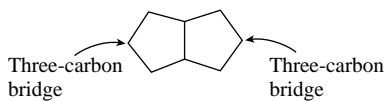


Bicyclo[5.2.0]nonane

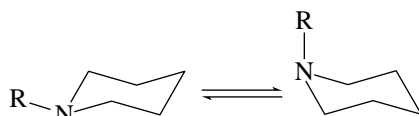
- (c) The three bridges in bicyclo[3.1.1]heptane contain three carbons, one carbon, and one carbon. The structure can be written in a form that shows the actual shape of the molecule or one that simply emphasizes its constitution.



- (d) Bicyclo[3.3.0]octane has two five-membered rings that share a common side.

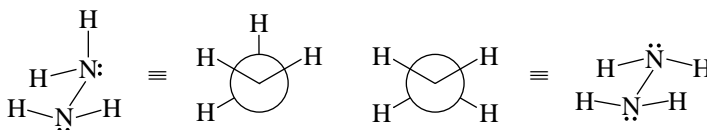


- 3.14 Since the two conformations are of approximately equal stability when $R = H$, it is reasonable to expect that the most stable conformation when $R = CH_3$ will have the CH_3 group equatorial.

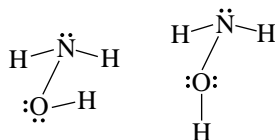


$R = H$: both conformations similar in energy
 $R = CH_3$: most stable conformation has CH_3 equatorial

- 3.15 (a) Recall that a neutral nitrogen atom has three covalent bonds and an unshared electron pair. The three bonds are arranged in a trigonal pyramidal manner around each nitrogen in hydrazine (H_2NNH_2).

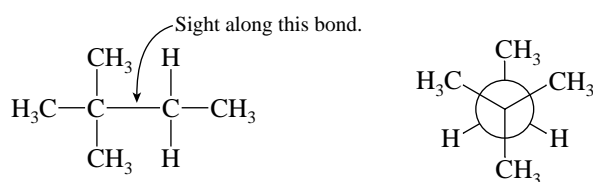


- (b) The O—H proton may be anti to one N—H proton and gauche to the other (left) or it may be gauche to both (right).

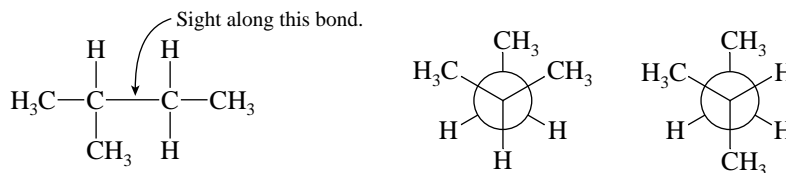


- 3.16** Conformation (a) is the most stable; all its bonds are staggered. Conformation (c) is the least stable; all its bonds are eclipsed.

- 3.17** (a) First write out the structural formula of 2,2-dimethylbutane in order to identify the substituent groups attached to C-2 and C-3. As shown at left, C-2 bears three methyl groups, and C-3 bears two hydrogens and a methyl group. The most stable conformation is the staggered one shown at right. All other staggered conformations are equivalent to this one.

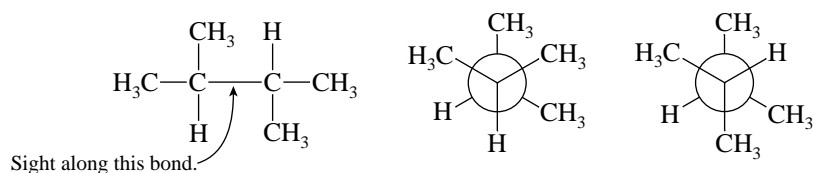


- (b) The constitution of 2-methylbutane and its two most stable conformations are shown.

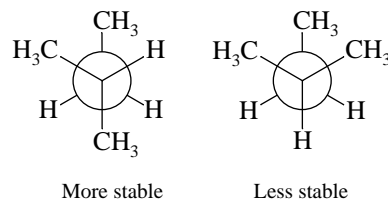


Both conformations are staggered. In one (left), the methyl group at C-3 is gauche to both of the C-2 methyls. In the other (right), the methyl group at C-3 is gauche to one of the C-2 methyls and anti to the other.

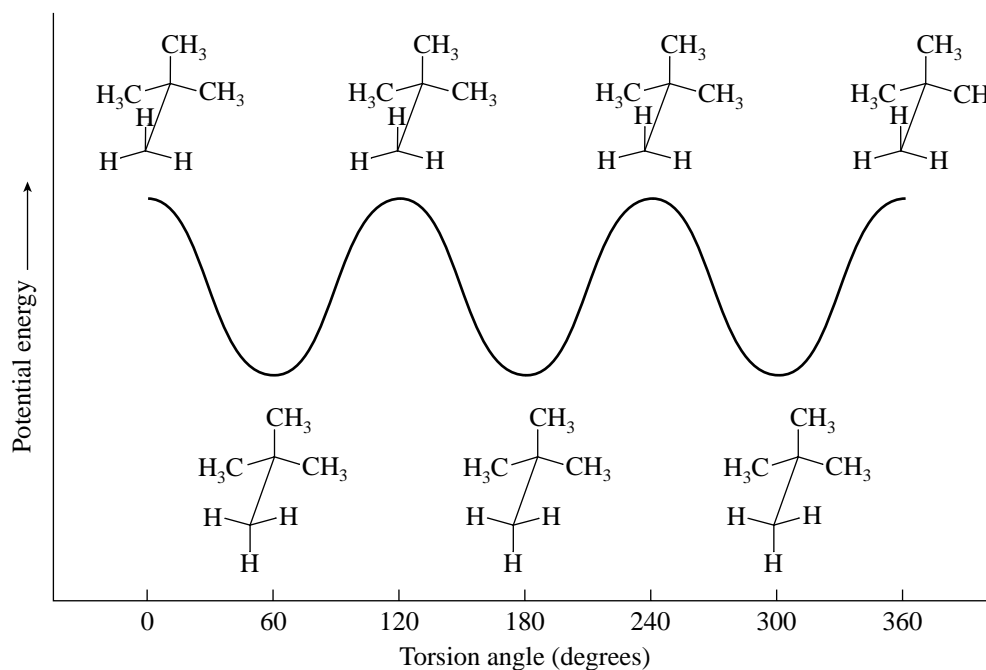
- (c) The hydrogens at C-2 and C-3 may be gauche to one another (left), or they may be anti (right).



- 3.18** The 2-methylbutane conformation with one gauche $\text{CH}_3 \cdots \text{CH}_3$ and one anti $\text{CH}_3 \cdots \text{CH}_3$ relationship is more stable than the one with two gauche $\text{CH}_3 \cdots \text{CH}_3$ relationships. The more stable conformation has less van der Waals strain.

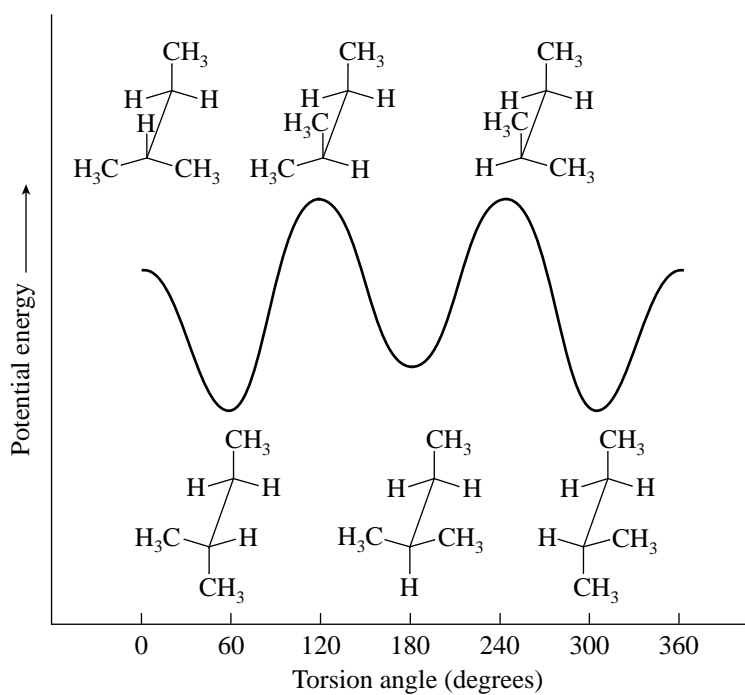


- 3.19 All the staggered conformations about the C-2—C-3 bond of 2,2-dimethylpropane are equivalent to one another and of equal energy; they represent potential energy minima. All the eclipsed conformations are equivalent and represent potential energy maxima.

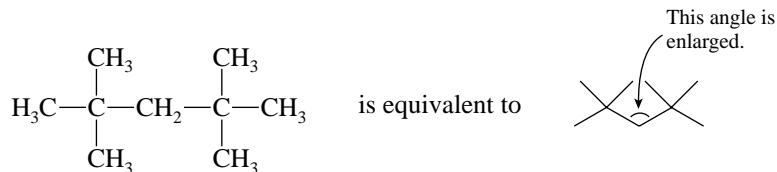


The shape of the potential energy profile for internal rotation in 2,2-dimethylpropane more closely resembles that of ethane than that of butane.

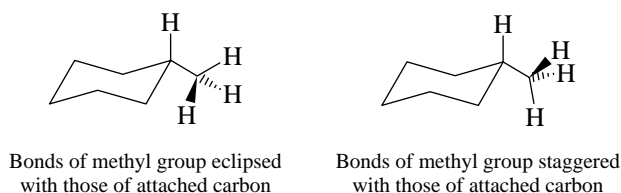
- 3.20 The potential energy diagram of 2-methylbutane more closely resembles that of butane than that of propane in that the three staggered forms are not all of the same energy. Similarly, not all of the eclipsed forms are of equal energy.



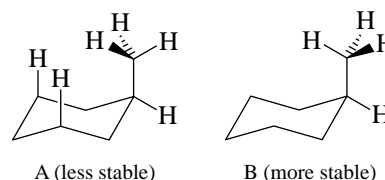
- 3.21 Van der Waals strain between the *tert*-butyl groups in 2,2,4,4-tetramethylpentane causes the C-2—C-3—C-4 angle to open to 125–128°.



- 3.22 The structure shown in the text is not the most stable conformation, because the bonds of the methyl group are eclipsed with those of the ring carbon to which it is attached. The most stable conformation has the bonds of the methyl group and its attached carbon in a staggered relationship.



- 3.23 Structure A has the hydrogens of its methyl group eclipsed with the ring bonds and is less stable than B. The methyl group in structure B has its bonds and those of its attached ring carbon in a staggered relationship.



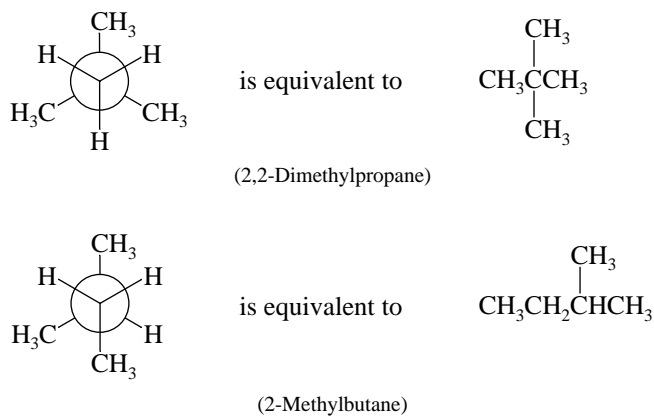
Furthermore, two of the hydrogens of the methyl group of A are uncomfortably close to two axial hydrogens of the ring.

- 3.24 Conformation B is more stable than A. The methyl groups are rather close together in A, resulting in van der Waals strain between them. In B, the methyl groups are farther apart.

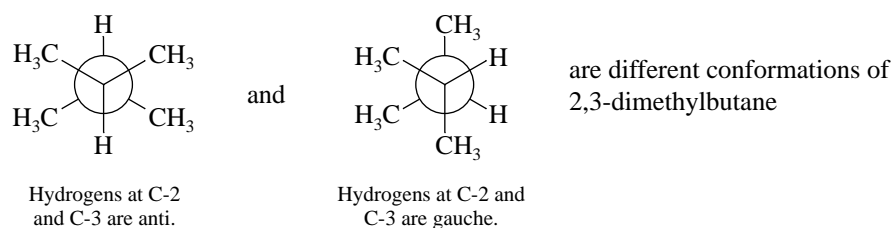
Van der Waals strain between cis methyl groups. Methyl groups remain cis, but are far apart.



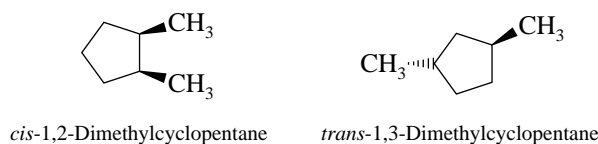
- 3.25 (a) By rewriting the structures in a form that shows the order of their atomic connections, it is apparent that the two structures are constitutional isomers.



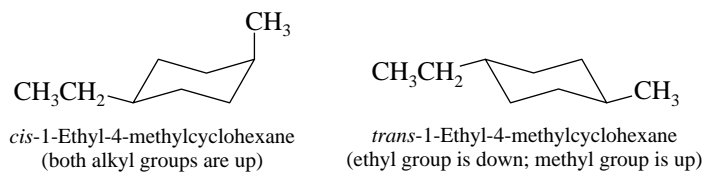
- (b) Both models represent alkanes of molecular formula C_6H_{14} . In each one the carbon chain is unbranched. The two models are different conformations of the same compound, $CH_3CH_2CH_2CH_2CH_2CH_3$ (hexane).
- (c) The two compounds have the same constitution; both are $(CH_3)_2CHCH(CH_3)_2$. The Newman projections represent different staggered conformations of the same molecule: in one the hydrogens are anti to each other, whereas in the other they are gauche.



- (d) The compounds differ in the *order* in which the atoms are connected. They are constitutional isomers. Although the compounds have different stereochemistry (one is *cis*, the other *trans*), they are not stereoisomers. Stereoisomers must have the same constitution.

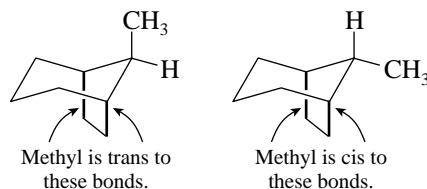


- (e) Both structures are *cis*-1-ethyl-4-methylcyclohexane (the methyl and ethyl groups are both “up”). In the structure on the left, the methyl is axial and the ethyl equatorial. The orientations are opposite to these in the structure on the right. The two structures are ring-flipped forms of each other—different conformations of the same compound.
- (f) The methyl and the ethyl groups are *cis* in the first structure but *trans* in the second. The two compounds are stereoisomers; they have the same constitution but differ in the arrangement of their atoms in space.

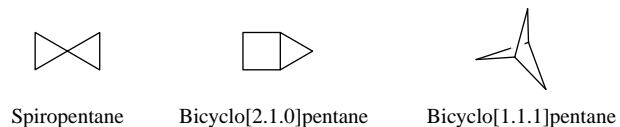


Do not be deceived because the six-membered rings look like ring-flipped forms. Remember, chair–chair interconversion converts all the equatorial bonds to axial and vice versa. Here the ethyl group is equatorial in both structures.

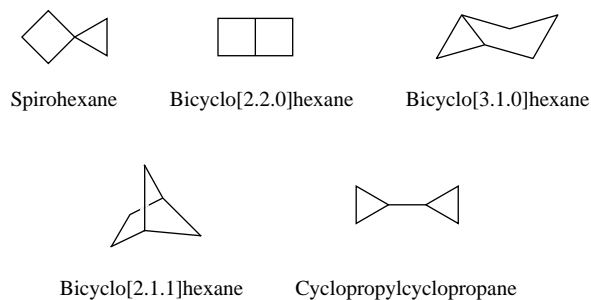
- (g) The two structures have the same constitution but differ in the arrangement of their atoms in space; they are stereoisomers. They are not different conformations of the same compound, because they are not related by rotation about C–C bonds. In the first structure as shown here the methyl group is *trans* to the darkened bonds, whereas in the second it is *cis* to these bonds.






- 3.26 (a) Three isomers of C_5H_8 contain two rings and have no alkyl substituents:



- (b) Five isomers of C_6H_{10} contain two rings and have no alkyl substituents:

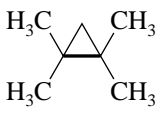
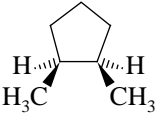



- 3.27 (a) The heat of combustion is highest for the hydrocarbon with the greatest number of carbons. Thus, cyclopropane, even though it is more strained than cyclobutane or cyclopentane, has the lowest heat of combustion.

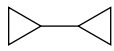


	Cyclopentane	Heat of combustion 3291 kJ/mol (786.6 kcal/mol)
	Cyclobutane	Heat of combustion 2721 kJ/mol (650.3 kcal/mol)
	Cyclopropane	Heat of combustion 2091 kJ/mol (499.8 kcal/mol)

A comparison of heats of combustion can only be used to assess relative stability when the compounds are isomers.

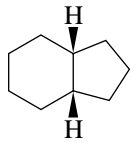
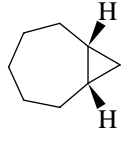
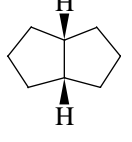
- (b) All these compounds have the molecular formula C_7H_{14} . They are isomers, and so the one with the most strain will have the highest heat of combustion.

	1,1,2,2-Tetramethylcyclopropane (high in angle strain; bonds are eclipsed; van der Waals strain between cis methyl groups)	Heat of combustion 4635 kJ/mol (1107.9 kcal/mol)
	<i>cis</i> -1,2-Dimethylcyclopentane (low angle strain; some torsional strain; van der Waals strain between cis methyl groups)	Heat of combustion 4590 kJ/mol (1097.1 kcal/mol)
	Methylcyclohexane (minimal angle, torsional, and van der Waals strain)	Heat of combustion 4565 kJ/mol (1091.1 kcal/mol)

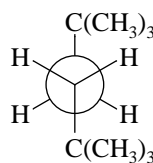
- (c) These hydrocarbons all have different molecular formulas. Their heats of combustion decrease with decreasing number of carbons, and comparisons of relative stability cannot be made.

	Cyclopropylcyclopropane (C ₆ H ₁₀)	Heat of combustion 3886 kJ/mol (928.8 kcal/mol)
	Spiropentane (C ₅ H ₈)	Heat of combustion 3296 kJ/mol (787.8 kcal/mol)
	Bicyclo[1.1.0]butane (C ₄ H ₆)	Heat of combustion 2648 kJ/mol (633.0 kcal/mol)

- (d) Bicyclo[3.3.0]octane and bicyclo[5.1.0]octane are isomers, and their heats of combustion can be compared on the basis of their relative stabilities. The three-membered ring in bicyclo[5.1.0]octane imparts a significant amount of angle strain to this isomer, making it less stable than bicyclo[3.3.0]octane. The third hydrocarbon, bicyclo[4.3.0]nonane, has a greater number of carbons than either of the others and has the largest heat of combustion.

	Bicyclo[4.3.0]nonane (C ₉ H ₁₆)	Heat of combustion 5652 kJ/mol (1350.9 kcal/mol)
	Bicyclo[5.1.0]octane (C ₈ H ₁₄)	Heat of combustion 5089 kJ/mol (1216.3 kcal/mol)
	Bicyclo[3.3.0]octane (C ₈ H ₁₄)	Heat of combustion 5016 kJ/mol (1198.9 kcal/mol)

- 3.28 (a) The structural formula of 2,2,5,5-tetramethylhexane is (CH₃)₃CCH₂CH₂C(CH₃)₃. The substituents at C-3 are two hydrogens and a *tert*-butyl group. The substituents at C-4 are the same as those at C-3. The most stable conformation has the large *tert*-butyl groups anti to each other.



Anti conformation of
2,2,5,5-tetramethylhexane

- (b) The zigzag conformation of 2,2,5,5-tetramethylhexane is an alternative way of expressing the same conformation implied in the Newman projection of part (a). It is more complete,