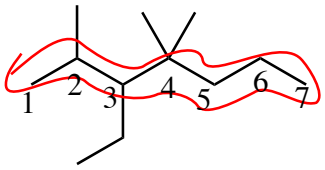
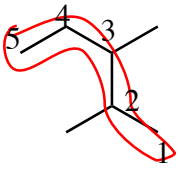
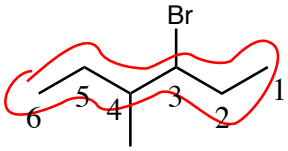
Chapter 4 Practice Problems
Solutions



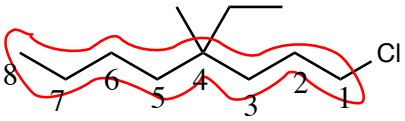
3-ethyl-2,4,4-trimethylheptane



2,3-dimethylpentane

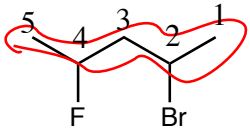


3-bromo-4-methylhexane

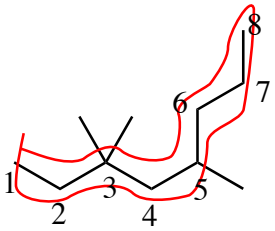


1-chloro-4-ethyl-4-methyloctane

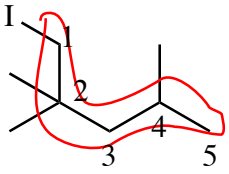
1



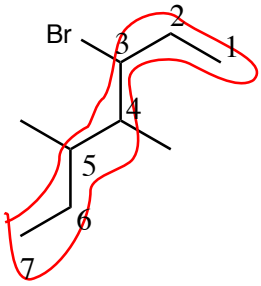
2-bromo-4-fluoropentane



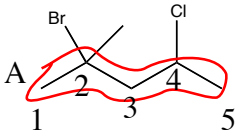
3,3,5-trimethyloctane



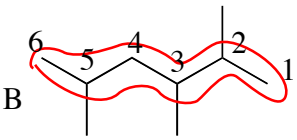
1-iodo-2,2,4-trimethylpentane



3-bromo-4,5-dimethylheptane

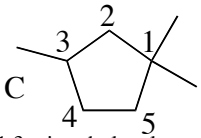


2-bromo-4-chloro-2-methylpentane

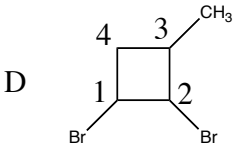


2,3,5-trimethylhexane

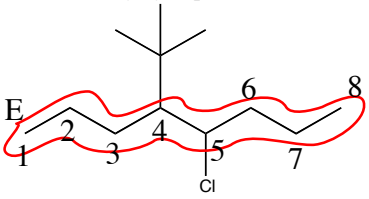
2



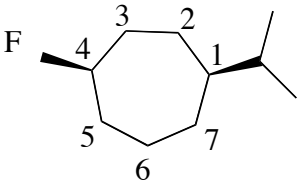
1,1,3-trimethylcyclopentane



1,2-dibromo-3-methylcyclobutane

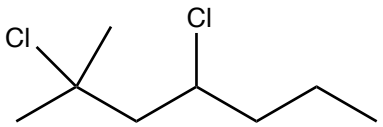


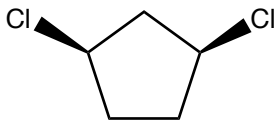
4-tert-**b**utyl-5-**c**hlorooctane

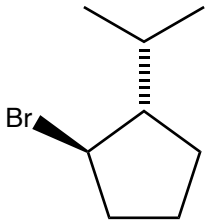


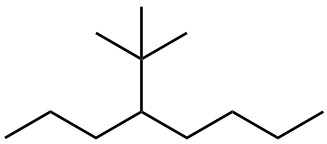
cis-1-**i**sopropyl-4-**m**ethylcycloheptane

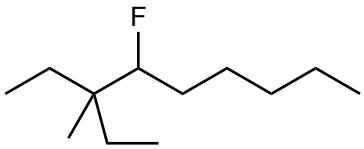
3

A. 

B. 

C. 

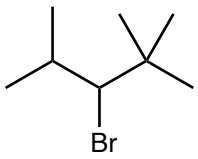
D. 

E. 

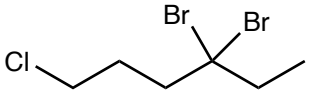
4

compound	Number of carbon atoms types				Number of hydrogen atoms types		
	1°	2°	3°	4°	1°	2°	3°
A	3	2	1	0	9	3	0
B	5	1	3	0	15	2	3
C	3	3	1	1	9	6	1
D	1	3	1	0	3	4	1
E	5	5	1	1	15	9	1
F	3	5	3	0	9	10	3

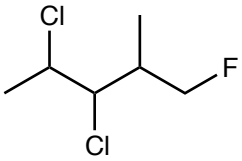
5



3-bromo-2,2,4-trimethylpentane

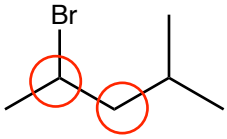


4,4-dibromo-1-chlorohexane



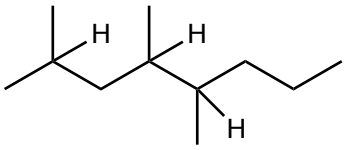
3,4-dichloro-1-fluoro-2-methylpentane

6

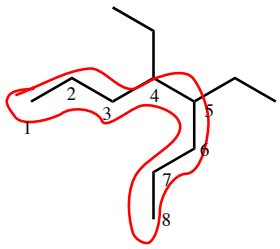


two 2° carbon atoms

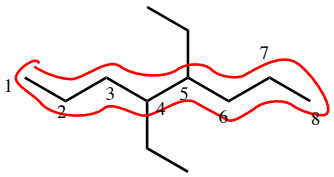
7



three 3° hydrogen atoms

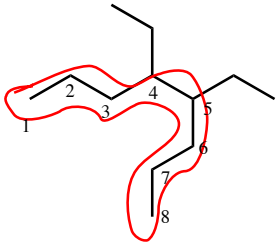


4,5-diethyloctane

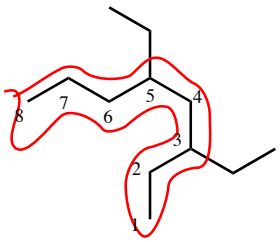


4,5-diethyloctane

8 **identical!**

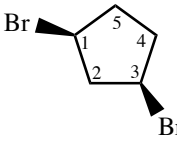


4,5-diethyloctane

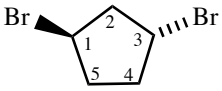


3,5-diethyloctane

constitutional isomers!

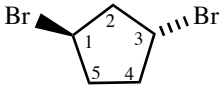


cis-1,3-dibromocyclopentane

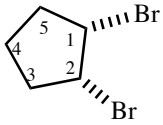


trans-1,3-dibromocyclopentane

stereoisomers!



trans-1,3-dibromocyclopentane



cis-1,2-dibromocyclopentane

constitutional isomers!

A.They all have the same molecular formula (C_7H_{14}), but have different connectivities (as evidenced by their drastically different names) and are therefore **constitutional isomers**.

B. Since they have the same molecular formula, they all have the same molecular weight. They are all nonpolar hydrocarbons. They only differ in extent of branching. Since branching decreases boiling point for similar compounds:

B (highest bp) > C > A (lowest bp)

9 *experimental 118 °C 101 °C 92 °C

C. Since they are all hydrocarbons of the same molecular weight, again the only thing that distinguishes them is extent of branching. Branching decreases heat of combustion:

B (highest HOC) > C > A (lowest HOC)

*note that there is not always agreement between HOC and boiling points! They measure two very different things (thermodynamic stability versus intermolecular forces)!

A. A = C_5H_{10} B = C_7H_{14} C = C_6H_{12}

They are unrelated other than sharing the characteristic that they are all cyclic hydrocarbons. NOTE that they are NOT isomers of any type.

B. Since the molecular weights are different and MW is the most important determinant of bp:

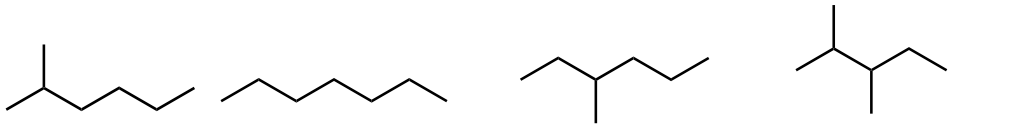
10

B (highest MW, highest bp) > C > A (lowest MW, lowest bp)

*experimental 118 °C 81 °C 49 °C

C. The more carbons present in the molecule, the more CO_2 and H_2O produced which releases more heat during combustion (think of how much heat is liberated when burning a small tree branch versus burning a large tree trunk). More heat produced translates into higher heats of combustion:

B (highest HOC) > C > A (lowest HOC)



	2-methylhexane	heptane	3-methylhexane	2,3-dimethylpentane
11	C_7H_{16}	C_7H_{16}	C_7H_{16}	C_7H_{16}

octane rating is determined by the extent of branching, more branching = higher octane rating:

2,3-dimethylpentane > 2-methylhexane ~ 3-methylhexane > heptane
highest *about the same* *lowest*

---

all are nonpolar hydrocarbons of the same molecular weight. Therefore, all else being equal, their boiling points will be determined by the extent of branching, the more branching, the lower the bp:

12

heptane > 2-methylhexane ~ 3-methylhexane > 2,3-dimethylpentane
highest *about the same* *lowest*

*experimental	98 °C	90 °C	92 °C	58 °C

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since these compounds are isomers of one another, it is OK to determine their relative stabilities using their relative heats of combustion (HOC). The HOC data is not provided, but we know that for isomeric molecules HOCs are affected by the extent of branching. The more branching, the lower the HOC, which translates into greater stability:

13

2,3-dimethylpentane > 2-methylhexane ~ 3-methylhexane > heptane
most stable *lowest HOC* *least stable* *highest HOC*

	octane	2-methylheptane	heptane	2-methylhexane
	C_8H_{18}	C_8H_{18}	C_7H_{16}	C_7H_{16}

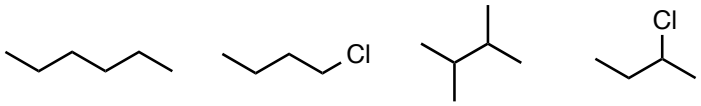
Note that these molecules have different molecular formulas! Octane and 2-methylheptane are constitutional isomers, and heptane and 2-methylhexane are consitutional isomers. Octane and 2-methylheptane have higher molecular weights than heptane and 2-methylhexane.

14

C_8H_{18} C_7H_{16}

octane > 2-methylheptane > heptane > 2-methylhexane
highest bp *lowest bp*
(unbranched) *(branched)* *(unbranched)* *(branched)*

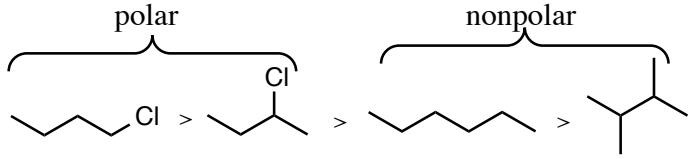
*experimental	126 °C	116 °C	98 °C	90 °C



• nonpolar • unbranched | • polar • unbranched | • nonpolar • branched | • polar • branched

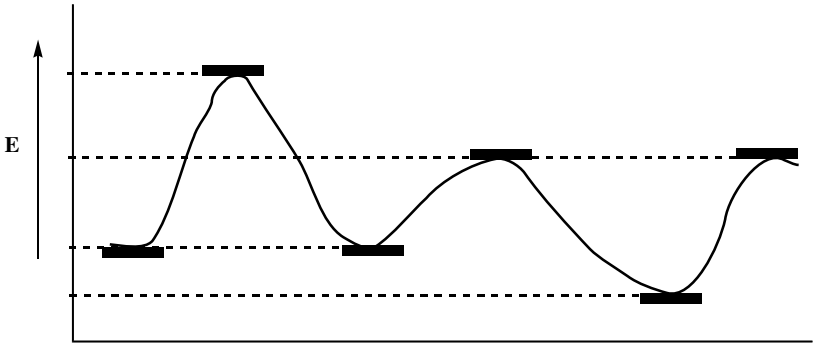
since all have about the same molecular weight, we need consider intermolecular forces and branching only. Generally, polar moleculars will have higher bp's than nonpolar molecules because the dipole-dipole interactions between polar molecules is stronger than the weak instantaneous dipole interactions between nonpolar molecules. Branching will decrease boiling points:

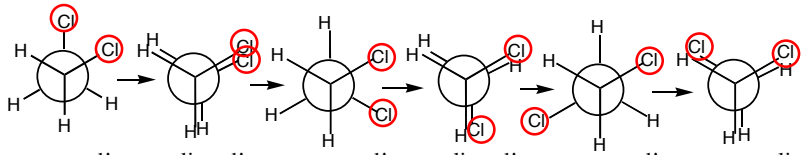
15



*experimental	78 °C	70 °C	69 °C	58 °C

16

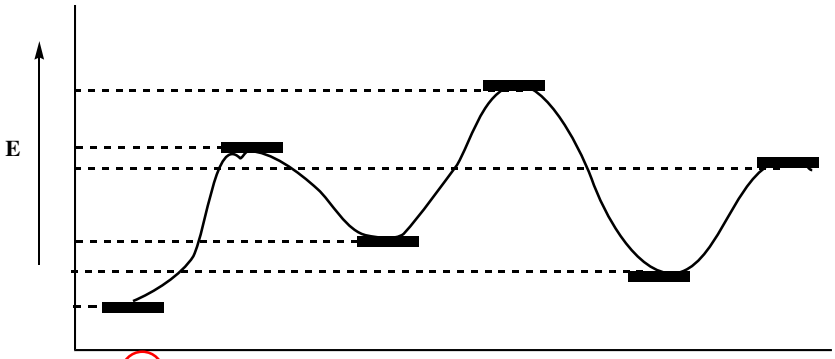


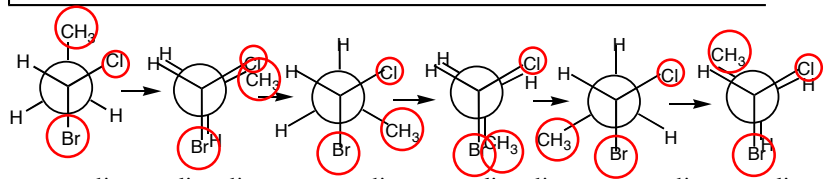


• staggered! • no torsional • gauche • some steric	• eclipsed! • torsional • **maximum steric** • **highest energy**	• staggered! • no torsional • gauche • some steric	• eclipsed! • torsional • some steric	• staggered! • no torsional • anti conformation • no steric • **most stable**	• eclipsed! • torsional • some steric

• *Cl is a large substituent and provides the greatest steric strain energy*
• *staggered conformations will always be at energy minima*
• *eclipsed conformations will always be at energy maxima*

17

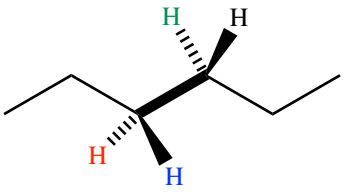


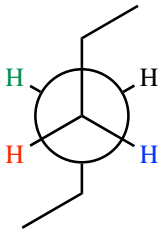


• staggered! • no torsional • some steric due to nearby CH_3/Cl	• eclipsed! • torsional • large steric due to eclipsed CH_3/Cl	• staggered! • no torsional • considerable steric due to nearby CH_3/Cl AND CH_3/Br	• eclipsed! • torsional • maximum steric due to eclipsed CH_3/Br	• staggered! • no torsional • some steric due to nearby CH_3/Br (greater than CH_3Cl)	• eclipsed! • torsional • some steric due to eclipsing of all groups with small H (but no big groups eclipsed with other big groups)

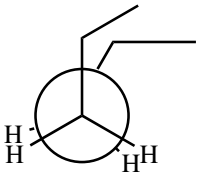
• *Br is larger than Cl and therefore provides the greater amount of steric strain energy*
• *the CH_3 groups is also large!*
• *staggered conformations will always be at energy minima*
• *eclipsed conformations will always be at energy maxima*

18



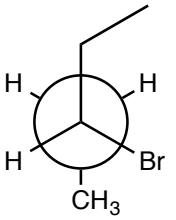


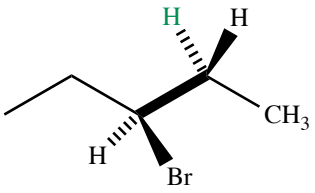
most stable
(staggered
with two large
groups anti)

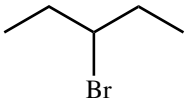


least stable
(eclipsed with
two large groups
on top of one another)

19

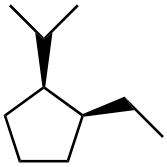




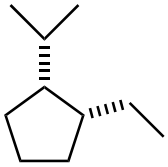


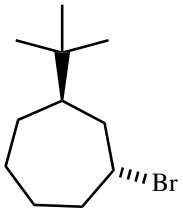
3-bromopentane

20



or





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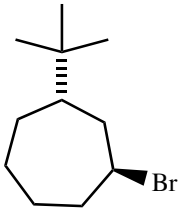

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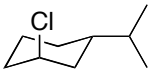
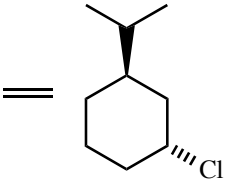
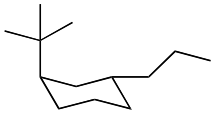
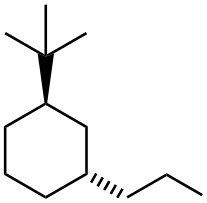




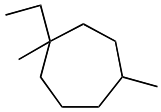
trans-1-chloro-3-isopropylcyclohexane





trans-1-tert-butyl-3-propylcyclohexane

1,1-dimethylcyclopentane



1-ethyl-1,4-dimethylcycloheptane

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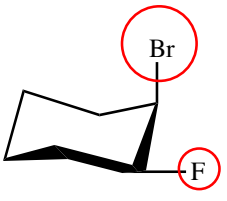
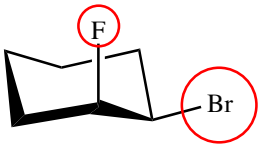


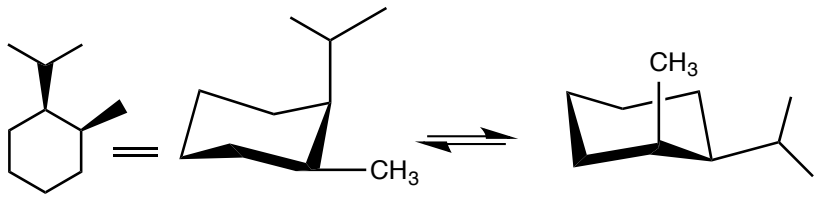
• ax Br
• eq F



• ax F
• eq Br

more stable

• Br is a larger atom than F so it experiences greater steric strain with the 1,3-diaxial interactions than does the smaller F atom.
• Therefore, the most stable chair conformation is when the larger Br is in the equatorial position



cis

• ax isopropyl
• eq methyl

• eq isopropyl
• ax methyl

• *both chair conformations have steric strain since each have at least on substituent axial*

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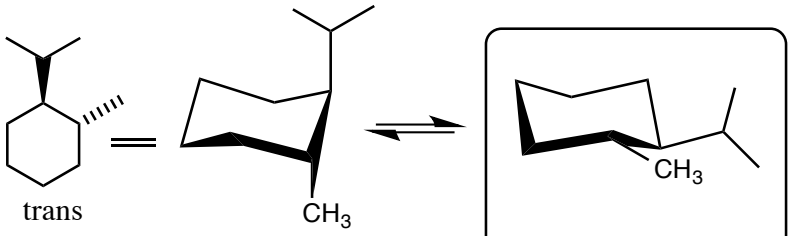

trans

• ax isopropyl
• ax methyl

•eq isopropyl
• eq methyl

• *most stable chair conformation since all substituents can be equatorial!*
• ***therefore, trans isomer is more stable than the cis isomer!***

cis-1,2-dimethylcyclopropane

trans-1,2-dimethylcyclopropane

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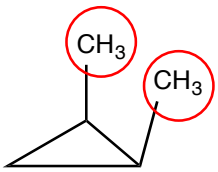
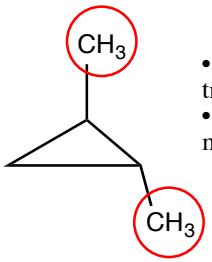
these are stereoisomers since they have the same connectivity and only differ in how the methyl groups are oriented in space.



• the cis isomer experiences **steric strain** between the two closely bonded methyl groups!
• this raises the energy of the cis isomer



• steric strain is avoided in the trans isomers
• the trans isomer is therefore more stable!

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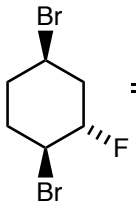

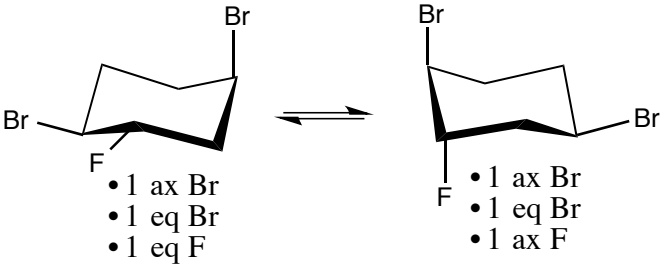

• 1 ax Br
• 1 eq Br
• 1 eq F

more stable chair conformation!

• 1 ax Br
• 1 eq Br
• 1 ax F

• *both have one axial and one equatorial Br*
• *the first has the F in the equatorial position*
• *the first is therefore more stable*

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