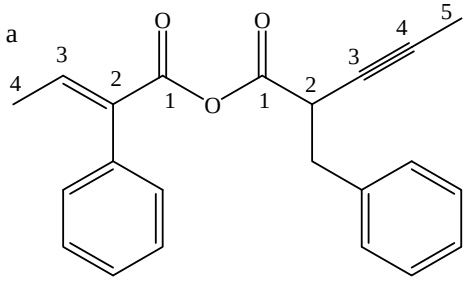
Chem 201 Sample Midterm
Beauchamp

Exams are designed so that no one question will make or break you. The best strategy is to work steadily, starting with those problems you understand best. Partial credit is given for anything done correctly, but no points are given for incorrect answers. Make sure you show all of your work. Draw in any lone pairs of electrons, formal charge and curved arrows to show electron movement where appropriate. Do your best to show me what you know in the time available.

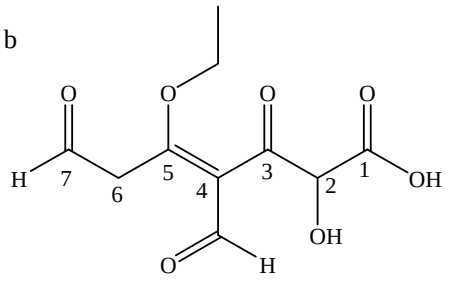
1. Provide an acceptable name for each of the following molecules.

a



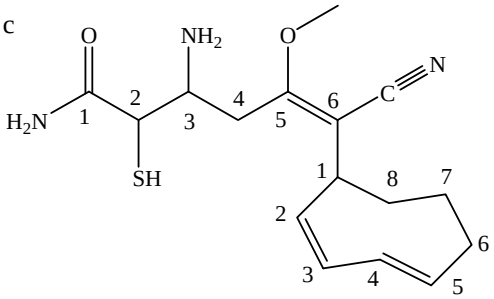
2-phenylbut-2E-enoic 2-benzylpent-3-ynoic anhydride

b



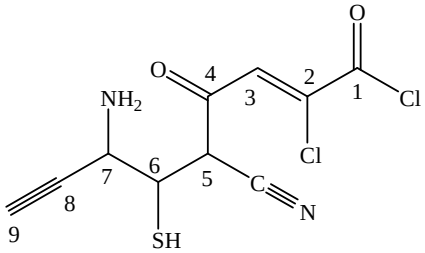
2-hydroxy-4-formyl-3,7-dioxo-5-ethoxyhept-4Z-enoic acid

c



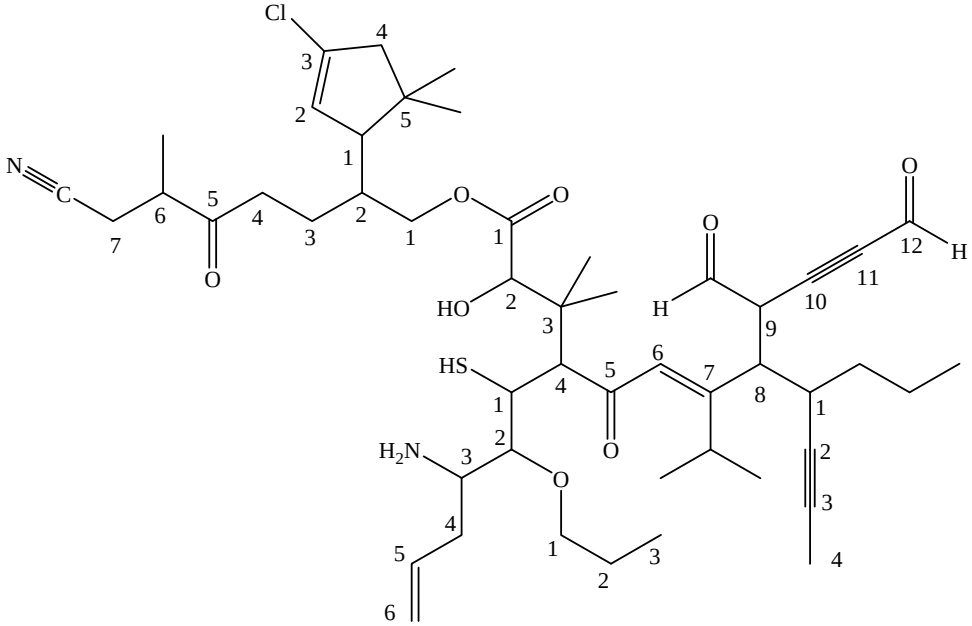
2-mercapto-3-amino-5-methoxy-6-cyano-6-(cycloocta-2Z,4E-dienyl)hexanamide

d



2-chloro-4-oxo-5-cyano-6-mercapto-7-amino-non-2Z-en-8-ynoyl chloride

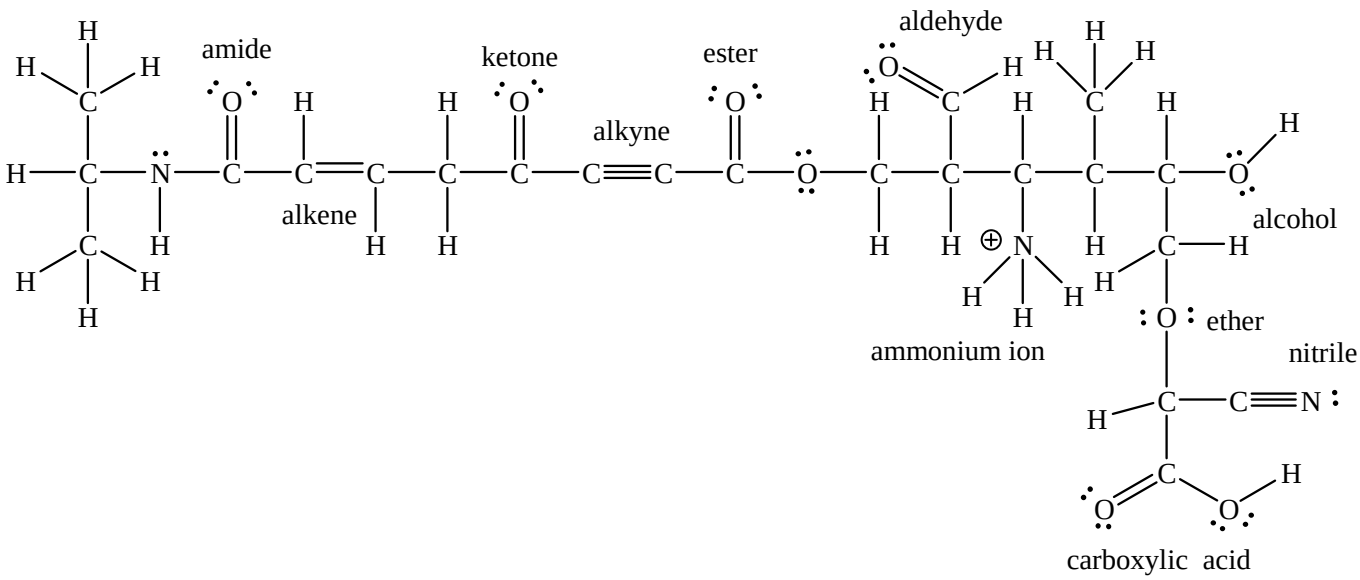
e



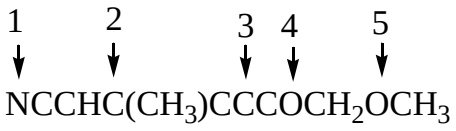
2-(5,5-dimethyl-3-chlorocyclopent-2-enyl)-5-oxo-6-methyl-7-cyanoheptyl 2-hydroxy-3,3-dimethyl-4-(1-mercapto-2-propoxy-3-aminohex-5-enyl)-5,12-dioxo-7-(1-methylethyl)-8-(1-propylbut-2-ynyl)-9-formyldodec-6Z-en-10-ynoate

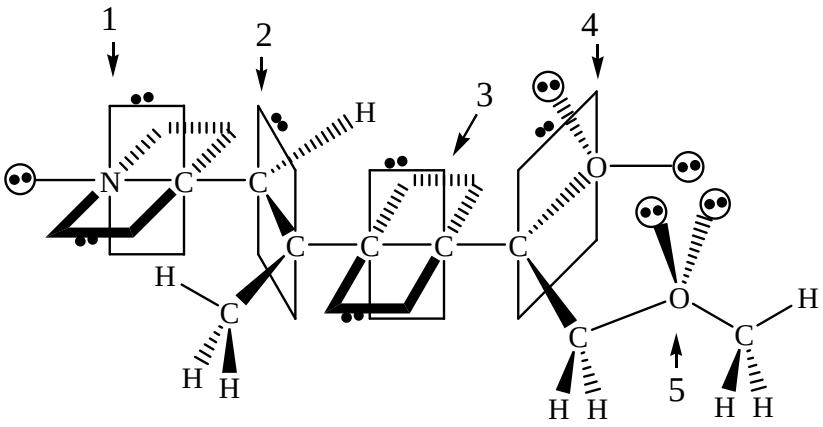
2. Draw an acceptable Lewis structure (2D) for the following molecule. Show <u>all</u> single, double and triple bonds with one, two or three lines. Include all lone pairs of electrons as two dots. Include any formal charge, if present. Identify any functional groups by name (i.e. ketone, amide, etc.)

$$\left[(CH_3)_2HCHNOCCHCHCH_2COCCCO_2CH_2CH(CHO)CHNH_3CHCH_3CHOHCH_2OCHCNCO_2H\right]$$



3. Draw a 3-D structure for the following molecule. Show bonds in front of the page as wedges, bonds in back of the page as dashed lines and bonds in the page as simple lines. Show orbitals for pi bonds and lone pairs along with their electrons. Identify the hybridization, bond angles and descriptive shape for all numbered atoms.

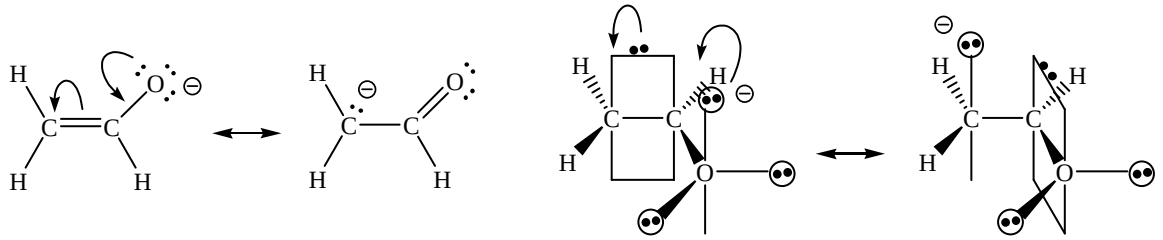




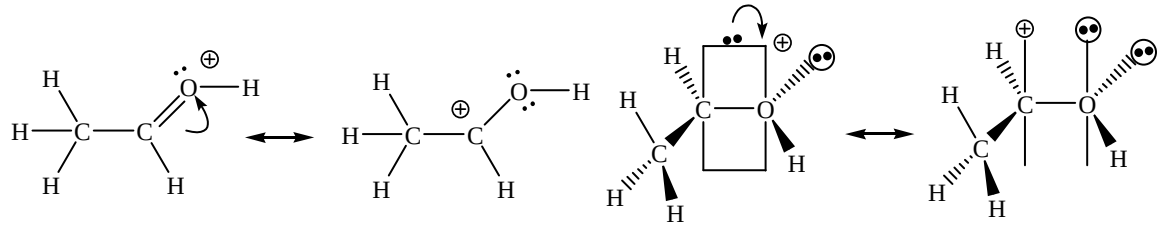
Atom	Shape	Hybridization	Bond Angles	# σ bond	# π bonds	# lone pairs
1	linear	sp	180	1	2	1
2	trigonal planar	sp^2	120	3	1	0
3	linear	sp	180	2	2	0
4	trigonal planar	sp^2	120	1	1	2
5	tetrahedral	sp^3	109	2	0	2

4. Write all reasonable 2D resonance structures for the following formulas. Include formal charge where appropriate and use proper curved arrows to show electron movement. Draw at least 2 resonance structures in 3D.

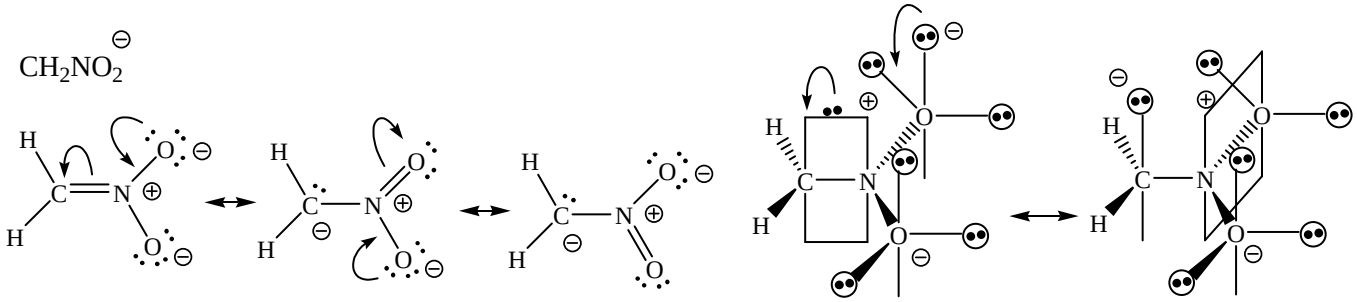
$CH_2CHO^{\ominus}$



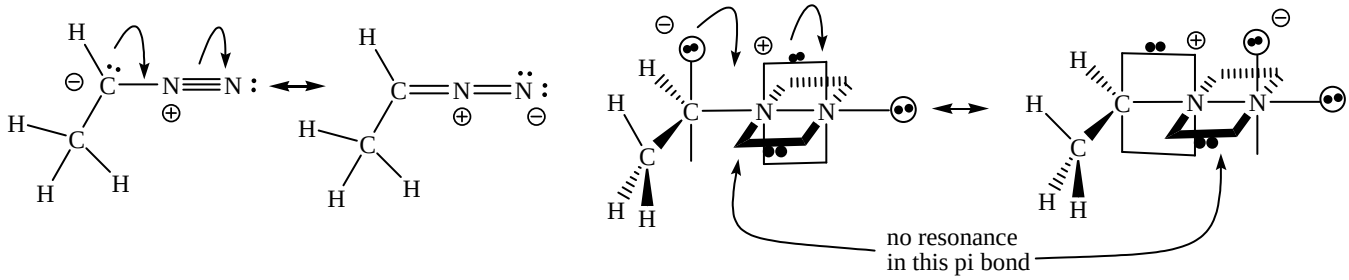
$CH_3CHOH^{\oplus}$

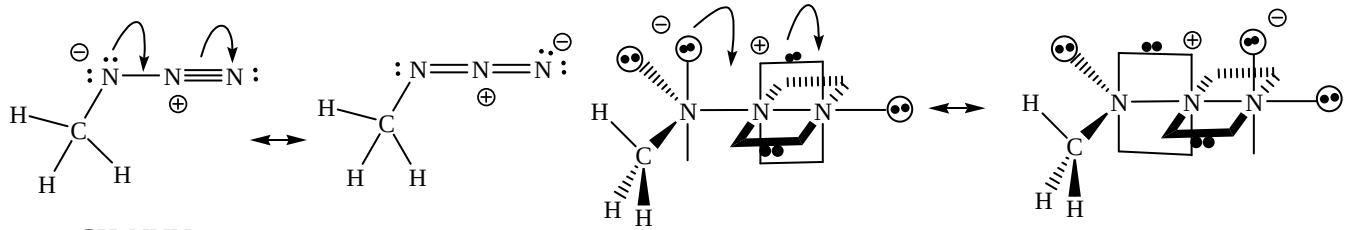


$CH_2NO_2^{\ominus}$



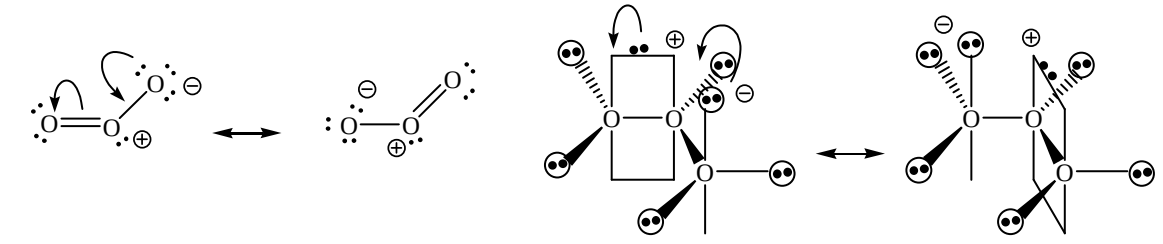
CH_3CHNN

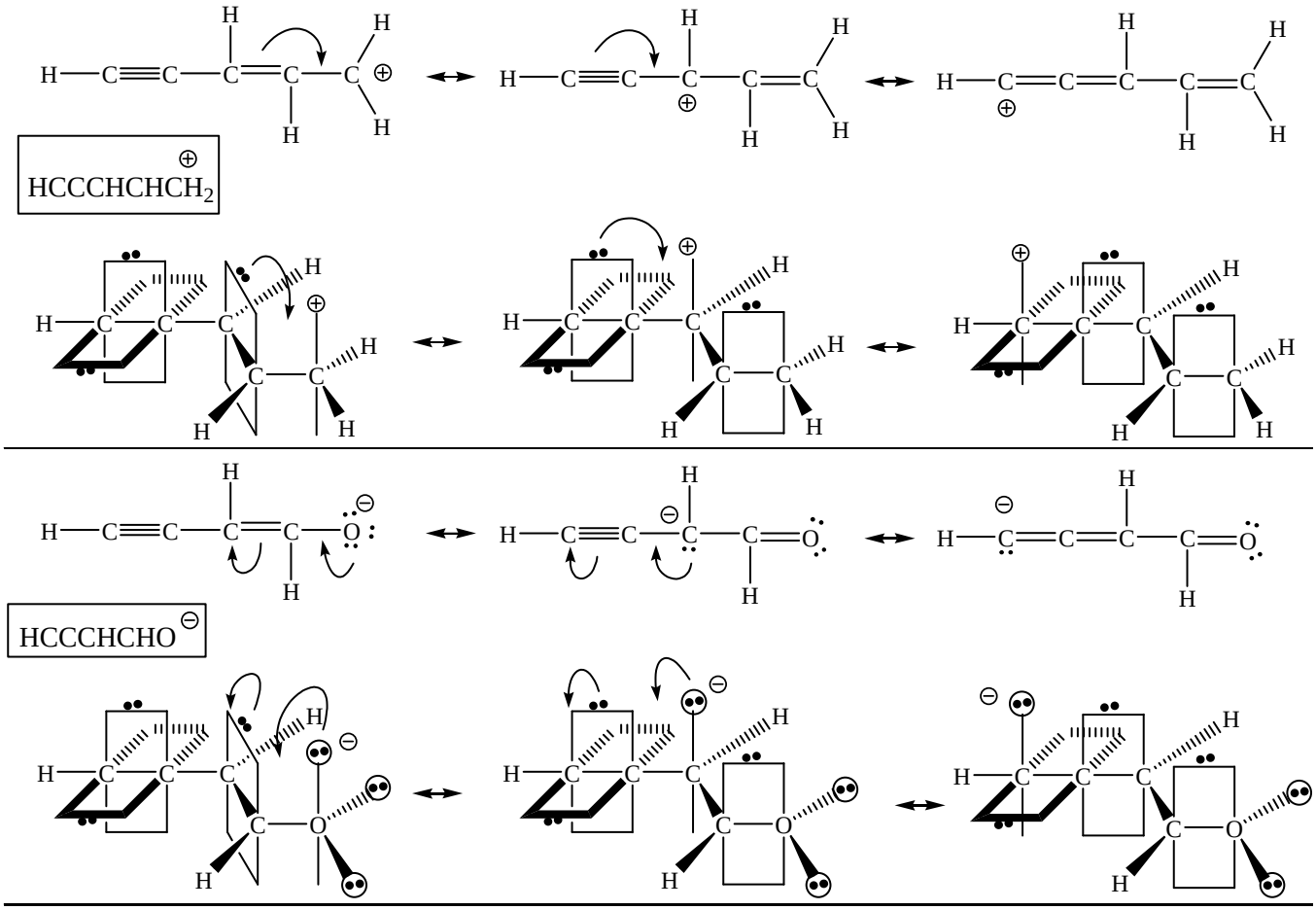




CH_3NNN

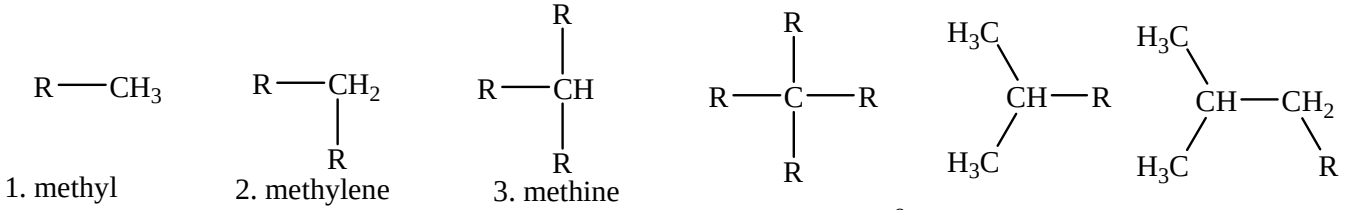
OOO





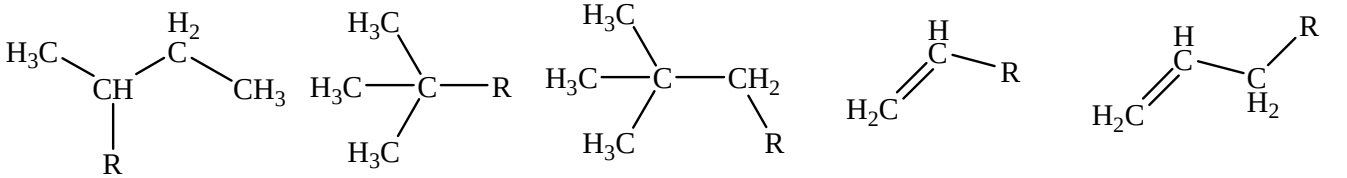
5. Draw an example of each of the following. Use "R" as a carbon portion for unspecified parts of your structures.

1. methyl 2. methylene 3. methine 4. primary 5. secondary 6. tertiary 7. quarternary 8. isopropyl 9. isobutyl 10. sec-butyl 11. t-butyl 12. neopentyl 13. vinyl 14. allyl 15. propargyl 16. phenyl 17. benzyl 18. primary amine 19. secondary amine 20. tertiary amine 21. quaternary ammonium ion

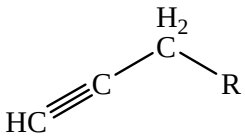


1. methyl 2. methylene 3. methine 7. quaternary = 4° 8. isopropyl 9. isobutyl

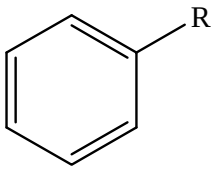
4. primary = 1° 5. secondary = 2° 6. tertiary = 3°



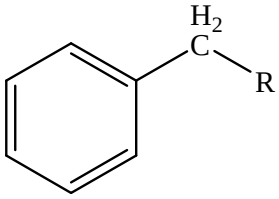
10. sec-butyl 11. t-butyl 12. neopentyl 13. vinyl 14. allyl



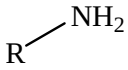
15. propargyl



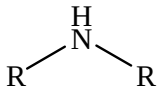
16. phenyl



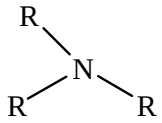
17. benzyl



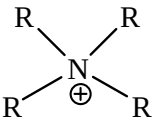
18. 1^o amine



19. 2^o amine



20. 3^o amine



21. 4^o ammonium ion

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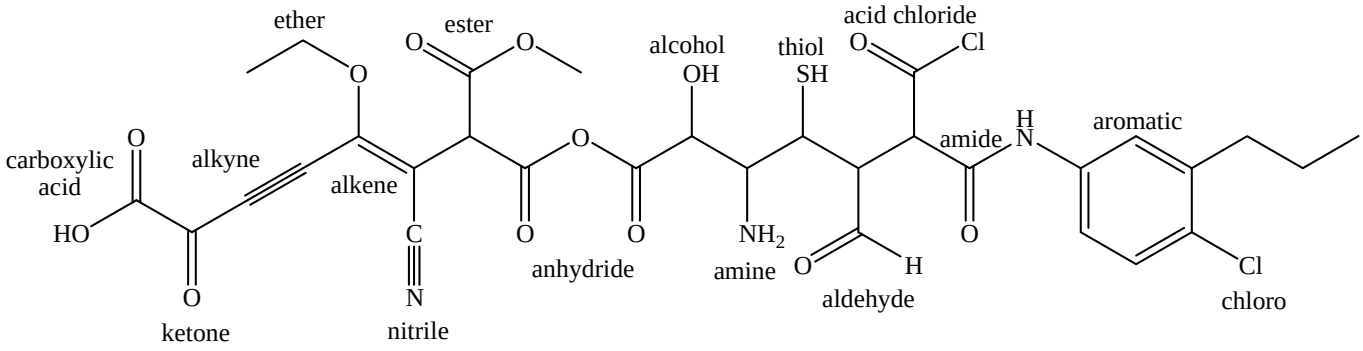
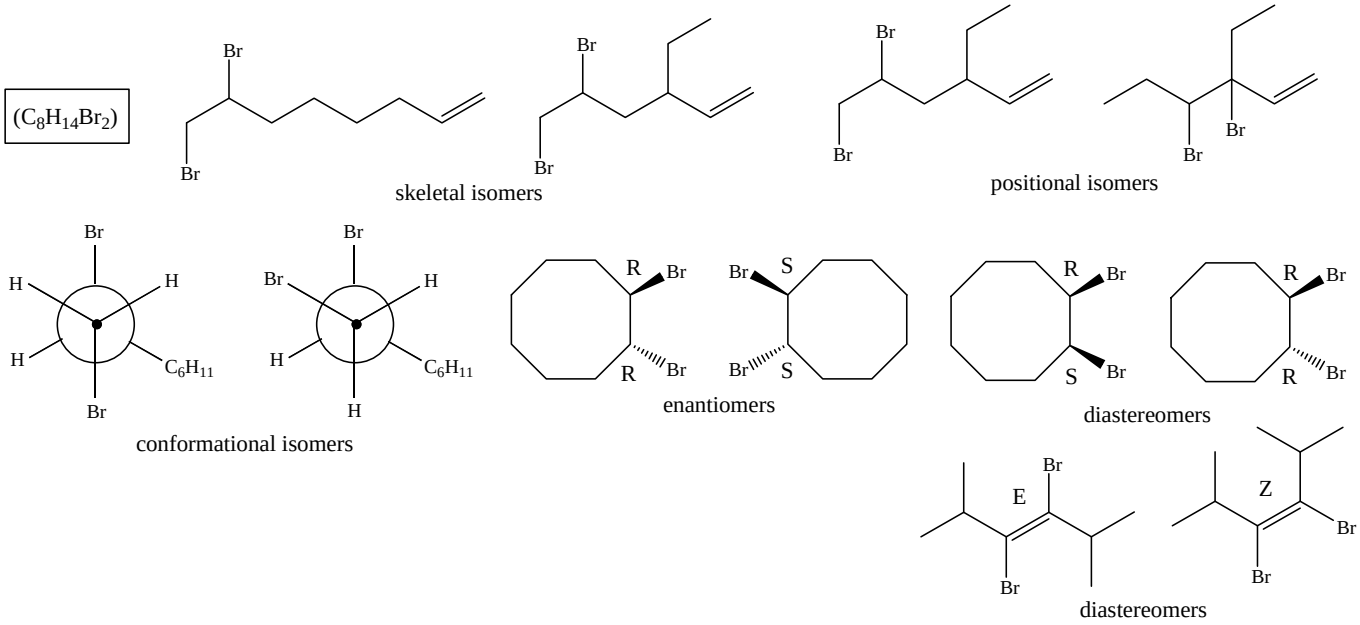
6. Use the given formula ($C_{31}H_{31}Cl_2N_3O_{13}S$) to draw a molecule with the following functional groups: carboxylic acid, anhydride, ester, acid chloride, amide, nitrile, aldehyde, ketone, alcohol, thiol, amine, ether, chloro, alkene, alkyne and aromatic. Identify each functional group by name. What is the degree of unsaturation?

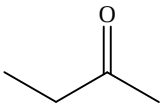


$C_{31}H_{31}Cl_2N_3O_{13}S$ degrees of unsaturation = [2(31)+2+3 - (33)] / 2 = (67 - 33) / 2 = 17 degrees

7. Use the given formula ($C_8H_{14}Br_2$) to write examples of each kind of isomerism: skeletal, positional, conformational, enantiomers, diastereomers.



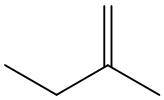
8. Match the given boiling points with the structures below and give a short reason for your answers.
(-7°C, +31 °C, +80 °C, +141°C, 1420°C)



2-butanone

MW = 72 g/mol

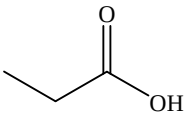
+80 °C



2-methyl-1-butene

MW = 70 g/mol

+31°C



propanoic acid

MW = 74 g/mol

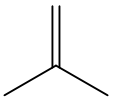
+141°C

KCl

potassium chloride

MW = 74.5 g/mol

1420°C



2-methylpropene

MW = 56 g/mol

-7°C

Structure 4 has ionic bonds, by far the strongest forces to overcome and has an extremely high bp. Structure 3 has strong H bonding possiblities and the second high bp. Structure 1 has polar C=O bond so higher than structures 2 and 5, which only have weak dispersion forces. Structure 2 is larger and has a larger surface area and more dispersion forces than structure 5, so has a higher bp.

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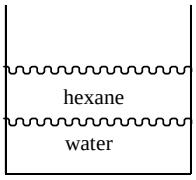
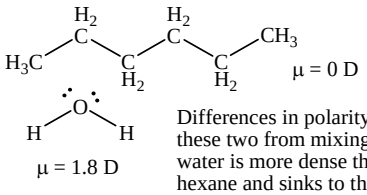
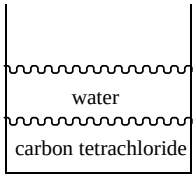
9. a. Hexane (density = 0.65 g/ml) and water (density = 1.0 g/ml) do not mix. Which layer is on top? Why don't they mix?
b. Carbon tetrachloride (density = 1.59 g/ml) and water (density = 1.0 g/ml) do not mix. Which layer is on top?

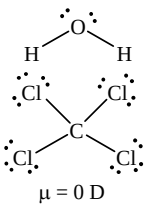




Differences in polarity keep these two from mixing and water is more dense than hexane and sinks to the bottom.

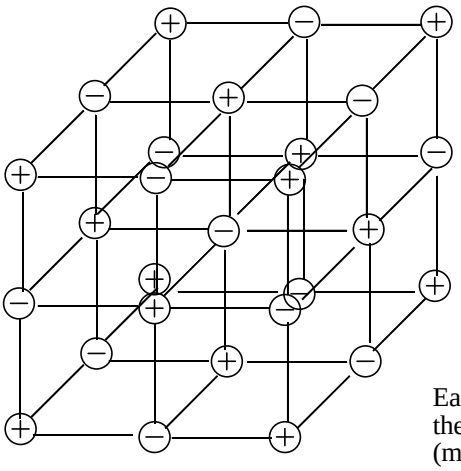
b



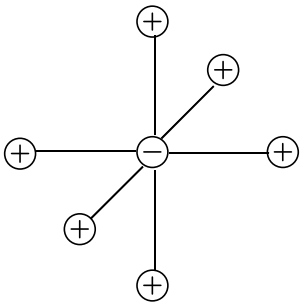


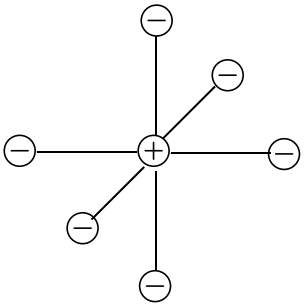
Differences in polarity keep these two from mixing and carbon tetrachloride is more dense than water and sinks to the bottom.

10. The melting point of NaCl is very high (≈ 800°C) and the boiling point is even higher (> 1400°C). Does this imply strong, moderate or weak forces of attraction between the ions? Considering your answer, is it surprising that NaCl dissolves so easily in water? Why does this occur? Consider another chloride salt, AgCl. How does your analysis work here? What changed?



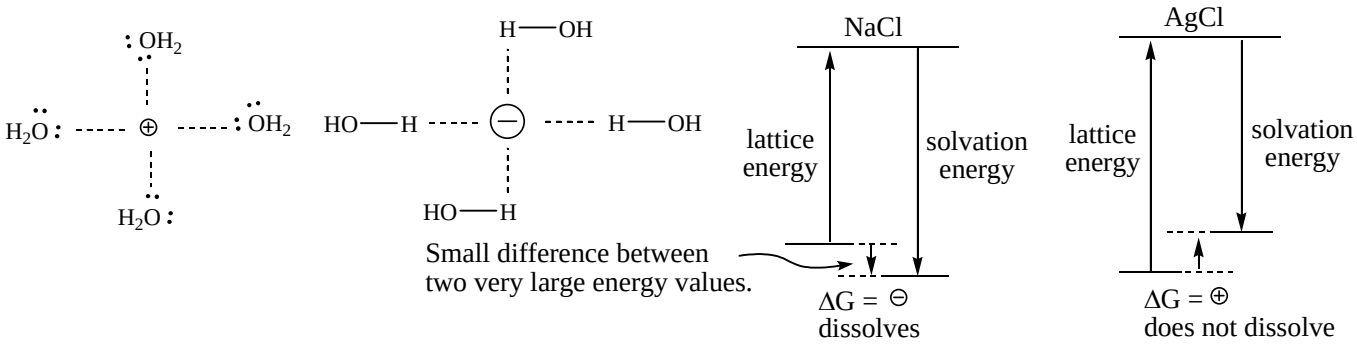
Lattic structure - depends on the size and charge of the ions.





Each ion is surrounded on many sides by oppositely charged ions. To introduce the disorder of a liquid (melt) or a gas (boil) requires a very large input of energy (mp indicates the amount of energy required to break down the ordered lattice structure and boiling point indicates the amount of energy required to remove an ion pair from the influence of all neighbors. Ionic bonds (ionic attractions on all sides) can only be bronke at great expense in energy.

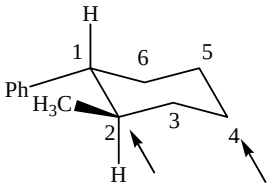
However, many water molucules working together can break down this structure by solvating both the cations and anions (solvation energy). When solvation energy > lattice energy, the salt will dissolve (NaCl). When solvation energy < lattice energy the salt will not dissolve (AgCl).



11. Draw all possible chair conformations of cis-1-phenyl-2-methylcyclohexane and trans-1-phenyl-2-methylcyclohexane. Which conformation is more stable? Draw it first. Provide a reason for your answer. Draw Newman projections of the most stable and least stable conformations using the $C_1 \rightarrow C_2$ and $C_5 \rightarrow C_4$ or the $C_2 \rightarrow C_1$ and $C_4 \rightarrow C_5$ bonds to sight along. Point out any gauche interactions shown in your Newman projection. Use the table on the next page to determine the gauche energy costs. Using the trans-1-phenyl-2-methylcyclohexane what are the relative percents of each conformation? Sketch an energy diagram that shows how the energy changes with the conformational changes for that isomer.

trans isomer

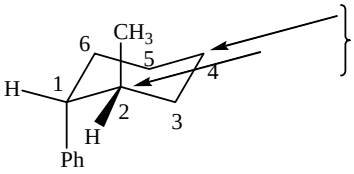
A = most stable conformation



costs = 1 gauche interaction = 1.4 kcal/mole

flip flop

B = least stable conformation



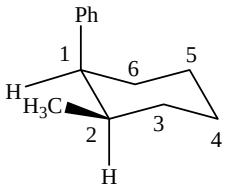
costs = 1 axial phenyl = 2.9 kcal/mole
= 1 axial methyl = 1.7 kcal/mole
total = 4.6 kcal/mole

relative stabilities = A > D > C > B

$$K_{eq} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-3,200}{1,380}} = 10^{-2.32} = \frac{1}{210} = \frac{B}{A}$$

cis isomer

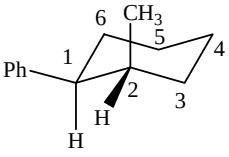
C



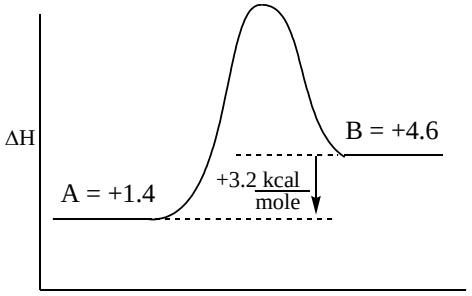
costs = 1 axial phenyl = 2.9 kcal/mole
= 1 gauche interaction = 1.4 kcal/mole
total = 4.3 kcal/mole

flip flop

D



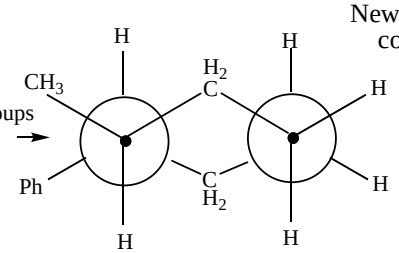
costs = 1 axial methyl = 1.7 kcal/mole
= 1 gauche interaction = 1.4 kcal/mole
total = 3.1 kcal/mole



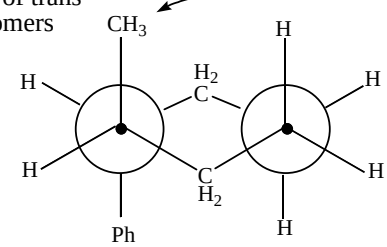
Newman projections of trans conformational isomers

Larger axial groups crowd the other axial positions on the same face.

Gauche groups crowd one another.

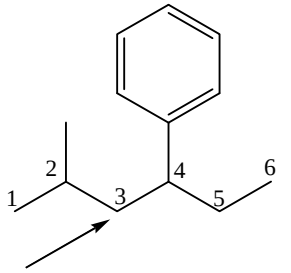


most stable isomer



least stable isomer

12. Use a Newman projection of the C3→C4 bond of 2-methyl-4-phenylhexane to **show the most stable conformation first**. Rotate through all of the eclipsed and staggered conformations. Using the energy values provided in the table below, calculate the relative energies of the different conformations. Plot the changes in energy in the graph diagram provided. Hint: Draw a 2D structure first and "bold" the bond viewed in your Newman projection, then decide your line of sight. What is the relative percent distribution between the 2 lowest energy conformations?



2-methyl-4-phenylhexane

$\Delta G \approx \Delta H$

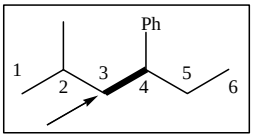
$K_{eq} = 10^{\frac{-\Delta H}{2.3RT}}$

Approximate Eclipsing Energy Values (kcal/mole)

	H	Me	Et	i-Pr	t-Bu	Ph
H	1.0	1.4	1.5	1.6	3.0	1.7
Me	1.4	2.5	2.7	3.0	8.5	3.3
Et	1.5	2.7	3.3	4.5	10.0	3.8
i-Pr	1.6	3.0	4.5	7.8	13.0	8.1
t-Bu	3.0	8.5	10.0	13.0	23.0	13.5
Ph	1.7	3.3	3.8	8.1	13.5	8.3

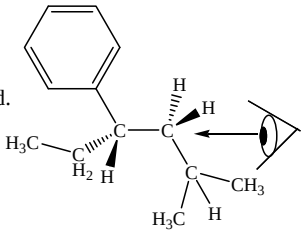
Approximate Gauche Energy Values (kcal/mole)

	H	Me	Et	i-Pr	t-Bu	Ph
H	0	0	0.1	0.2	0.5	0.2
Me	0	0.8	0.9	1.1	2.7	1.4
Et	0.1	0.9	1.1	1.6	3.0	1.5
i-Pr	0.2	1.1	1.6	2.0	4.1	2.1
t-Bu	0.5	2.7	3.0	4.1	8.2	3.9
Ph	0.2	1.4	1.5	2.1	3.9	2.3



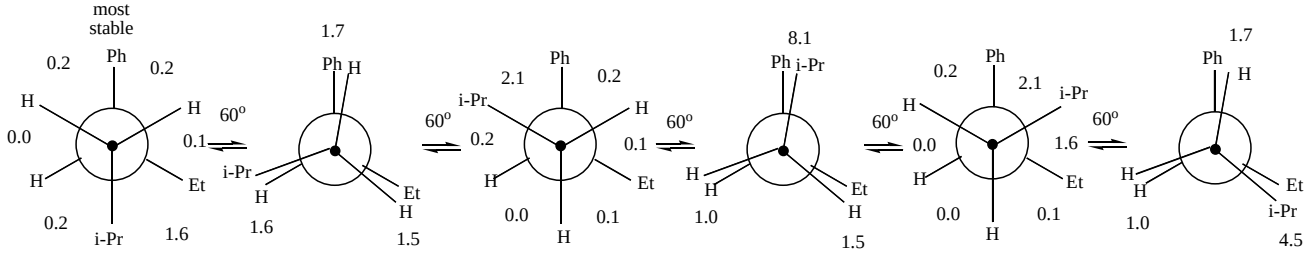
2-methyl-4-phenylhexane

Use the $C_3 \rightarrow C_4$ bond.

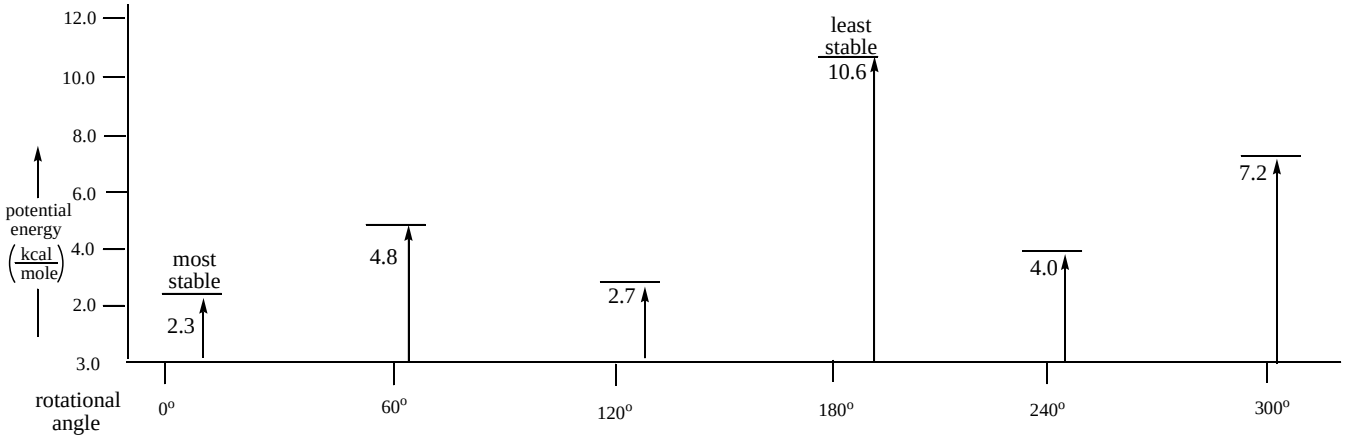


$K_{eq} = 10^{\frac{-\Delta G}{2.3RT}} = 10^{\frac{-400}{1{,}380}}$

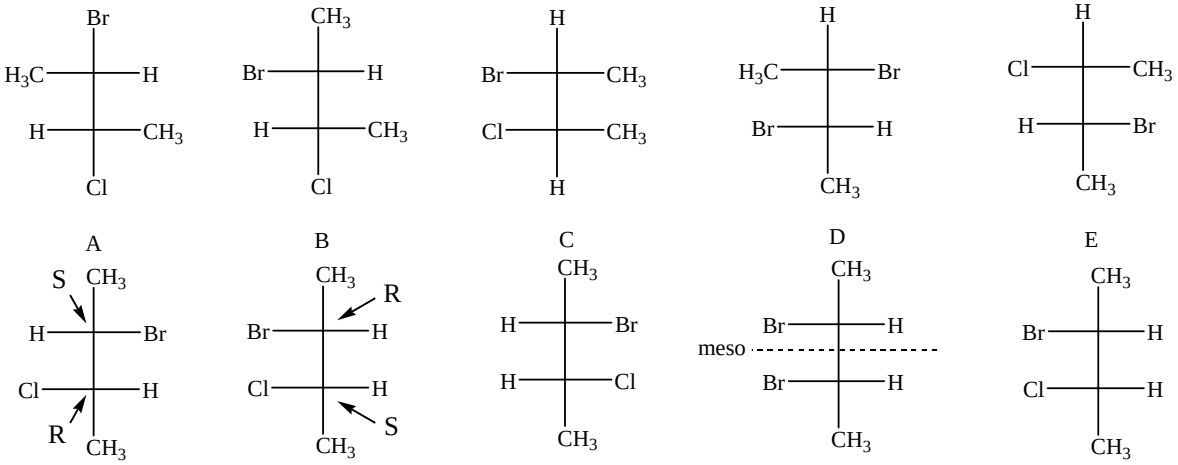
$= 10^{-0.29} = \frac{1}{2} = \frac{\text{isomer 3}}{\text{isomer 1}}$



1	2	3	4	5	6
0.2	1.7	0.2	8.1	2.1	1.7
0.1	1.5	0.1	1.5	1.6	4.5
1.6	1.6	0.1	1.0	0.1	1.0
0.2	4.8	0.0	10.6	0.0	7.2
0.0		0.2		0.0	
0.2		2.1		0.2	
2.3		2.7		4.0	



13. For the following set of Fischer projections answer each of the questions below by circling the appropriate letter(s) or letter combination(s). Hint: Redraw the Fischer projections with the longest carbon chain in the vertical direction and having similar atoms in the top and bottom portion. Classify all chiral centers in the first structure as R or S absolute configuration and write an acceptable name for that isomer.



a. Which are optically active? (A) (B) (C) D (E)

b. Which are meso? A B C (D) E

c. Which is not an isomer with the others? A B C (D) E

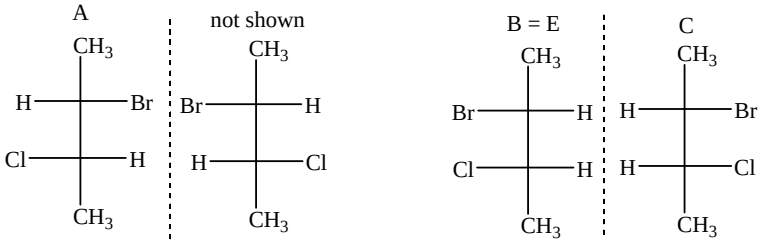
d. Which pairs are enantiomers? AB AC ~~AD~~ AE (BC) ~~BD~~ ~~BE~~ ~~CD~~ (CE) ~~DE~~

e. Which pairs are identical? AB AC AD AE BC ~~BD~~ (BE) CD CE DE

f. Which pairs are diastereomers? (AB) (AC) AD (AE) BC BD BE CD CE DE

g. Which pairs, when mixed in equal amounts will not rotate plane polarized light? AB AC ~~AD~~ AE (BC) BD BE CD (CE) DE

h. Draw any stereoisomers of 2-bromo-3-chlorobutane as Fischer projections, which are not shown above. If there are none, indicate this.

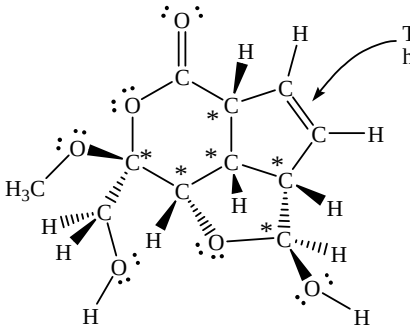


i. Would anything change if, in compound D, the Br was replaced with a Cl group? How about compound A?

Compound D would not be meso and become chiral.
Compound A is chiral and would still be chiral.

j. The structure of lucknolide B was recently determined (and the absolute configuration of all chiral centers!). It was isolated from the terrestrial bacteria, Streptomyces sp. ANK-289, in screenings for new medicinal lead compounds (Org. Lett. p.3800, 2010). Circle all chiral centers and any other stereochemical features, and calculate the maximum number of stereoisomers possible.

lucknolide B
one of two
related compounds



This ring is too small to have a trans double bond.

* = chiral center

7 chiral centers

possible stereoisomers = $2^7 = 128$