

Chemistry 30A Exam 1 Solutions Summer 2003

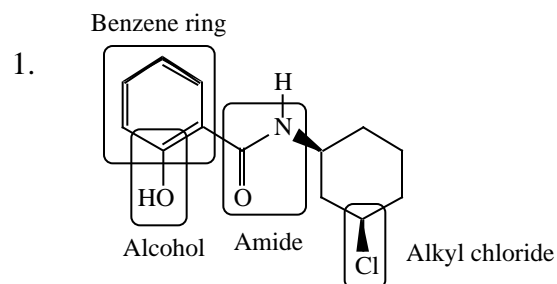
Statistics: High score = 94 Average score = 65.3 Low score = 17

Standard Deviation = irrelevant as it does not control grade distribution in this class.

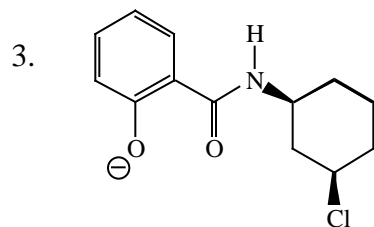
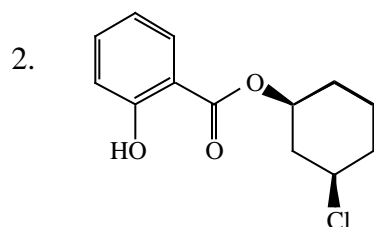
A note about exam keys: The answers presented here are usually significantly longer than expected from a student taking the exam. An exam key serves not only to reveal what was expected, but to instruct you as well.

Exam key posted 11 AM, Monday, July 7, 2003

To see the current course grade cutoffs, consult "If Grades Were Assigned Today" at the Chem 30A Home Page.

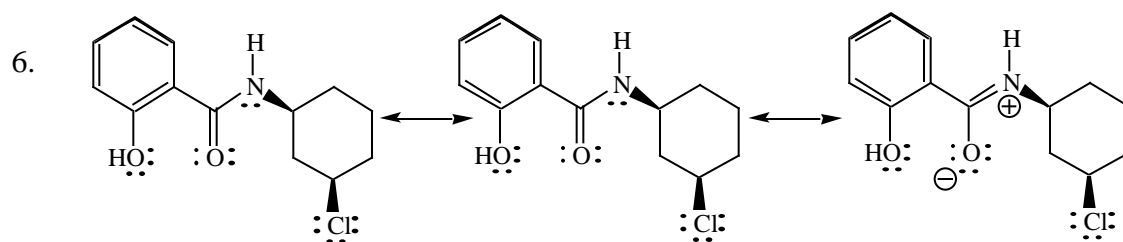


An OH attached to a benzene ring is also called a phenol group.



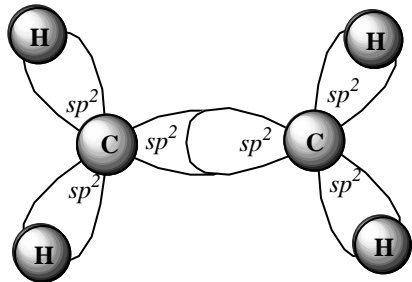
4. The Cl-C-C bond angle of (+)-Squirrelbesmart is **a bit greater than 109.5°**.

5. (+)-Squirrelbesmart has **8** lone pairs, **8** sp^2 atoms and **16** hydrogen atoms.



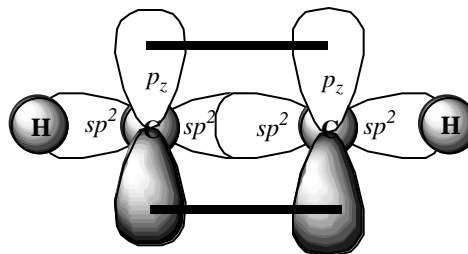
7. An “ sp^2 atom” is one whose orbital contributions to its bonds can be thought of as a mathematical hybrid of one part s orbital and two parts p orbital. The resulting bond geometry is trigonal planar with bond angles close to 120° .

8. Top view:



C p_z orbitals not shown.

Side view:

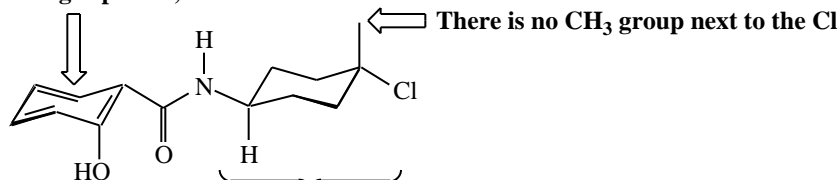


H uses $1s$ orbitals in both views.

9. Cl = 3.0; C = 2.5.

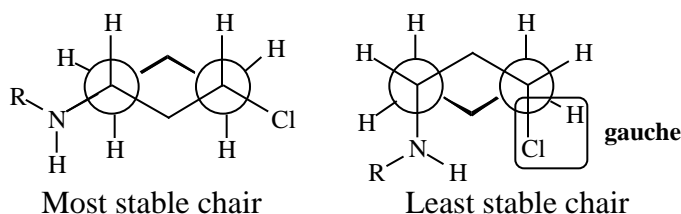
10. C—O—H
+ - +

11. Benzene ring is planar, not chair



- (a) The amide and chloride are incorrectly shown in a 1,4-relationship
(b) The amide and chloride are cis, not trans

12. (a) and (b)

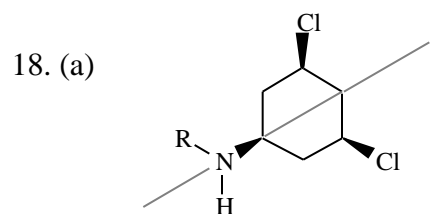
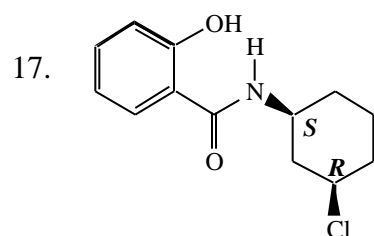
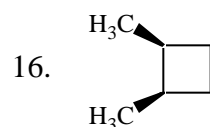
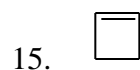
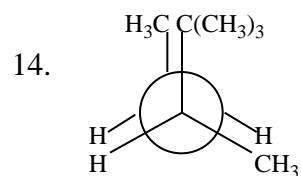


(c) The least stable chair is less stable as it has greater torsional strain due to more severe gauche interactions. In the most stable conformation, the chlorine atom and amide groups are gauche to hydrogens, whereas in the least stable conformation these same groups are gauche to CH_2 (methylene) groups of the cyclohexane ring. (In a substituted cyclohexane, these are also called 1,3-diaxial interactions.) Methylene groups are larger than hydrogen atoms, so the amide- CH_2 and chlorine- CH_2 gauche interactions cause more electron repulsion than the amide-hydrogen and chlorine-hydrogen interactions. Greater repulsion results in more torsional strain and less stability.

13. (a) The conformation with the least torsional strain is **B**.

(b) The conformation with the most torsional strain is **A**.

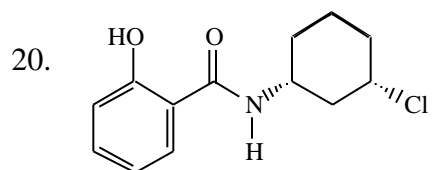
(c) When the *tert*-butyl group of conformation **A** is replaced with a chlorine atom, the torsional strain **decreases**.

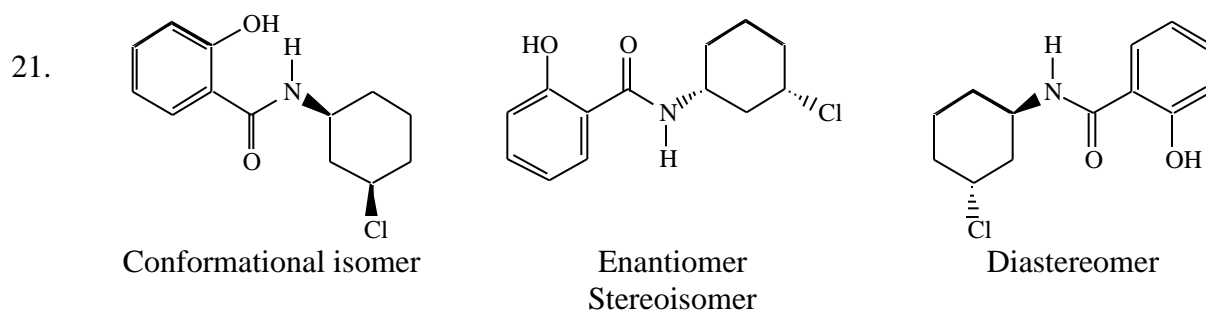


(b) This new structure is meso because it has stereocenters (the carbons bearing the chlorine atoms) but is achiral (it has an internal mirror plane of symmetry as shown with the dotted line above).

19. (a) Cis

(b) Switch between axial and equatorial



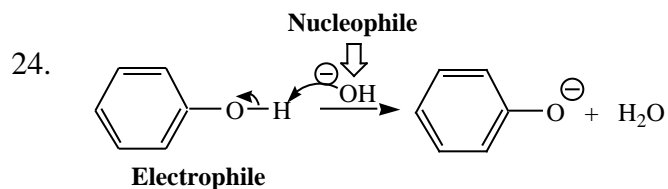


22. (a) The optical rotation of the enantiomer is **levorotatory**.

(b) The enantiomer is **optically active**.

(c) The enantiomer's biological effect on squirrels **cannot be guessed**.

23. Resolution: Separation of enantiomers.



25. Resonance: Molecules **E** and **G**.

Explanation: Resonance may delocalize the negative charge of the conjugate base, making it more stable. This delocalization also dilutes the negative charge on any given atom thus reducing the base's drive to share electron density with a proton to regain neutrality. A more stable base is a weaker base, and corresponds to a stronger acid. In this case, the conjugate base of phenol (PhOH) has significant resonance stabilization whereas the conjugate base of cyclohexanol does not, so pK_a phenol (10) < pK_a cyclohexanol (18).

Atomic size: Molecules **C** and **E**.

Explanation: Consider the atomic radius of the atom of the base that shares an electron pair with a hydrogen atom to form a new bond. The larger this atom is the greater volume of space occupied by the valence shell electrons. Spreading this electron density over a larger area means less charge concentration and thus less drive to share electron density. Sulfur has a larger atomic radius than oxygen, so PhS^- is a weaker base than PhO^- . Therefore PhSH is a stronger acid (pK_a 7.8) than PhOH (pK_a 10).

Inductive effect: Molecules **D** and **E**.

Explanation: The effect of atoms in one portion of the molecule on the electron density elsewhere in the molecule is termed the inductive effect. If these remote atoms are highly

electronegative, they will draw electron density towards themselves from elsewhere in the molecule. If electron density is removed from a base's atom that would share electron density with a hydrogen atom, then the base strength is weakened. In the case of the conjugate base of molecule **D**, the chlorine has high electronegativity (3.0) so it removes electron density from the oxygen atom. Thus the conjugate base of **D** (2-chlorophenol) is weaker than the conjugate base of **E** (phenol), and therefore 2-chlorophenol is a stronger acid (pK_a 8.1) than phenol (pK_a 10).