

CHEM 346 – Organic Chemistry I (for Majors)

Instructor: Paul J. Bracher

Hour Examination #1Wednesday, September 25th, 2013
6:30 p.m.

Student Name (Printed)	Solutions
Student Signature	

Please also write your name on the back of the exam

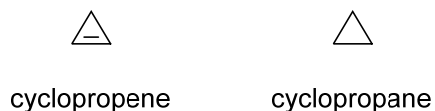
Scoring

Question	Points Earned	Points Available
1		15
2		25
3		20
4		20
5		20
TOTAL		100

Original Problems, **Required Information in Answers**, and **Supplementary Explanation**

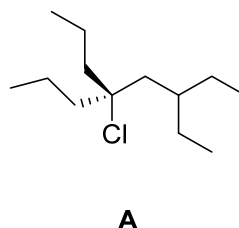
Problem 1. (15 points total, 3 points each) Determine whether the following five statements are true or false. Write out the full word “true” or “false” beside each statement; do not just write “T” or “F”. If any part of the statement is false, the entire statement is false.

- (i) TRUE Cyclopropene is more strained than cyclopropane.

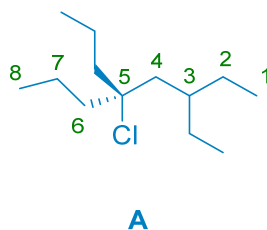


Cyclopropane is an especially strained compound because the sp^3 -hybridized carbons that prefer bond angles of 109.5° are forced into a geometry where they must assume 60° bond angles with the other carbons in the ring. The situation is worse for cyclopropene, as sp^2 -hybridized carbons prefer wider bond angles of 120° .

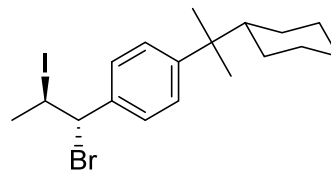
- (ii) FALSE The correct systematic name of compound **A** is 5-chloro-3-ethyloctane.



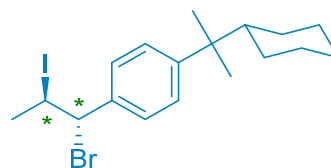
The name is partially correct in that the longest carbon chain in **A** is eight, and numbering the longest chain in the right-to-left direction gives the lowest-number to a substituent (3 for ethyl vs. 4 for chloro), but the name fails to include the propyl substituent at the 5 position). The correct IUPAC name for **A** is 5-chloro-3-ethyl-5-propyloctane. Note that the 5 position is not a stereogenic center because the carbon atom has two identical substituents (the propyl groups).



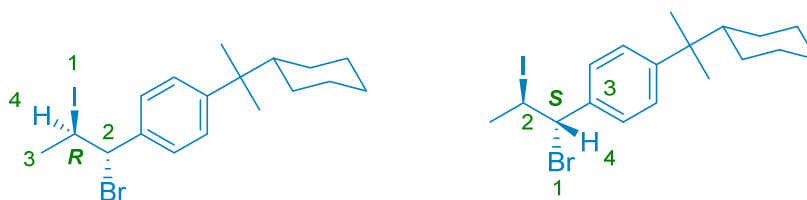
- (iii) TRUE Compound **B** has two stereogenic centers, only one of which is designated *R*.

**B**

Carbon atoms are stereogenic centers when they are sp^3 hybridized and have four different substituents. There are indeed two carbons in **B** that meet these criteria. Note that the substituted carbon on the cyclohexane ring is not a stereogenic center because each side of the ring is equivalent. If you are not convinced, try assigning priorities to the two sides—you won't be able to!



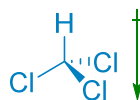
The next step is to assign *R* and *S* designations to the stereogenic centers. These designations and the priority assignments used to make them are below.



So, compound **B** has two stereogenic centers, one of which is *R* and one of which is *S*. The answer to the question is “true”.

- (iv) TRUE Chloroform (CHCl_3) is polar, achiral, and capable of serving as a Brønsted-Lowry acid.

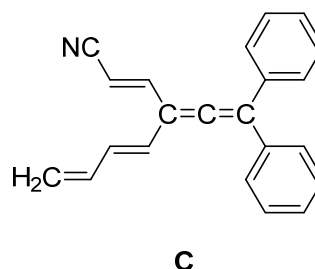
It is best to begin by quickly sketching out a Lewis structure for chloroform.



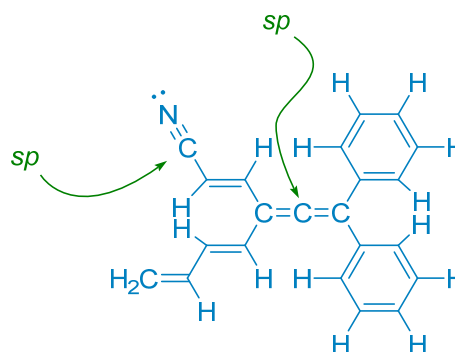
The molecule is polar because the dipole moments of the individual bonds—created by differences in electronegativity between C & H and C & Cl do not cancel exactly. The net dipole moment is drawn in green, above. The molecule is achiral because it is superposable with its mirror image. For a tetrahedral carbon to be a stereogenic

center, it must have four different substituents. The carbon in chloroform has only two different substituents. Finally, the molecule is capable of serving as a Brønsted–Lowry acid because it has a hydrogen that can be deprotonated, although chloroform is a relatively weak acid ($pK_a \approx 25$).

- (v) FALSE Every carbon atom in compound **C** is sp^2 hybridized except for one, which is sp hybridized.



A thorough approach to solving this problem begins by drawing a complete Lewis structure where all the bonds/groups are drawn explicitly:

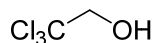
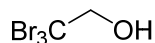
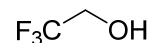
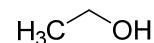


A carbon is typically sp hybridized when it is bonded to two groups (atoms or lone pairs), sp^2 hybridized when it is bonded to three groups, and sp^3 hybridized when it is bonded to four groups. Carbons that are sp hybridized have two unhybridized p orbitals available to participate in π bonds, while sp^2 carbons have one unhybridized p orbital and sp^3 carbons have zero.

Compound **C** has two carbons that are sp hybridized (so the answer is “false”). The first is a carbon in a cyano group that participates in a triple bond with nitrogen. The second is a carbon in an allene. Note that both of these carbons participate in two π bonds each (using their two unhybridized p orbitals).

Problem 2. (25 points total, 5 points each) For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided.

- (i) D Arrange the following four molecules in ascending order of pK_a (lowest pK_a to highest pK_a)

**D****E****F****G**

- (a) **G < E < D < F**
 (b) **G < F < E < D**
 (c) **G < D < E < F**
 (d) **F < D < E < G**
 (e) **F < E < D < G**

ref: Pocker, Y.; Page, J.D. *J. Biol. Chem.* **1990**, *265*, 22101–22108.

All of these molecules are substituted ethanols, and their most acidic protons are in the hydroxyl (–OH) groups. The order of acidity will depend on the relative stabilities of the alkoxide conjugate bases. The halogen atoms will help to stabilize the negative charge on the alkoxides by an inductive effect, and this effect will become more pronounced as the electronegativity of the halogens increases. The order of electronegativity is $\text{F} (4.0) > \text{Cl} (3.2) > \text{Br} (3.0) > \text{H} (2.2)$, so **F** should have the most stable conjugate base, and hence, the lowest pK_a . The correct final order is:

**F**

$$pK_a = 12.37$$

**D**

$$pK_a = 12.65$$

**E**

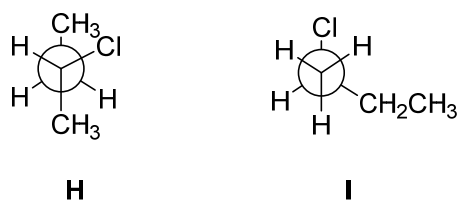
$$pK_a = 12.70$$

**G**

$$pK_a = 15.9$$

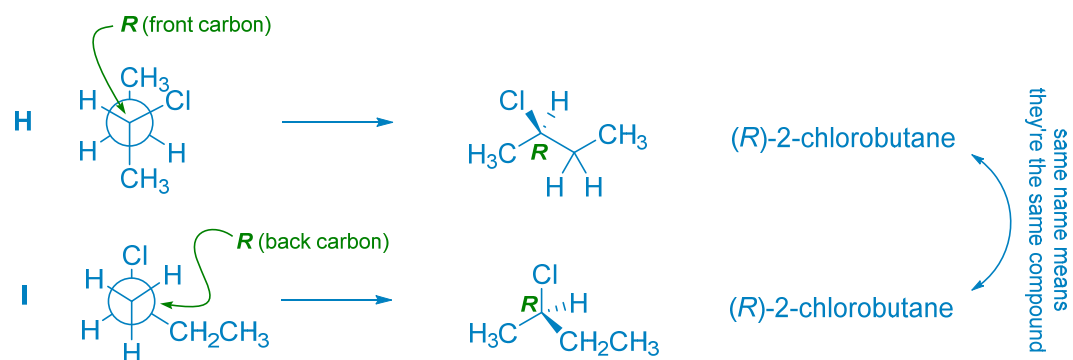
—————→
 decreasing acidity (increasing pK_a)

(ii) A The compounds represented by Newman projections **H** and **I** are:



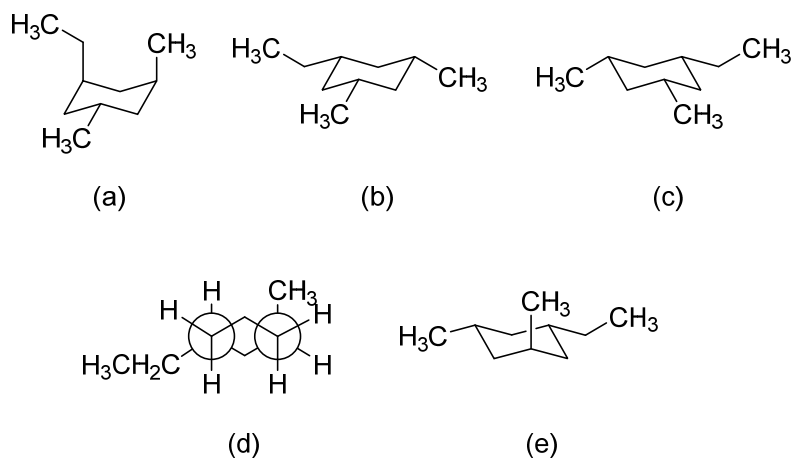
- (a) identical compounds
- (b) enantiomers
- (c) diastereomers
- (d) constitutional isomers
- (e) *cis* and *trans* compounds

A good approach here is to convert the Newman projections to skeletal Lewis structures that can be compared more easily. Be careful to assign *R* and *S* designations to the stereocenters correctly:

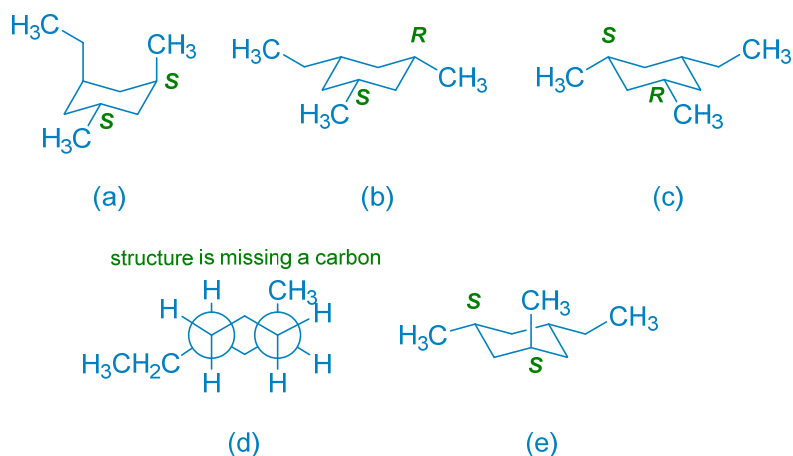


If you can't tell from the two structures that the compounds are identical, then trying naming them. You will come up with the same name.

(iii) E What is the most stable conformation of (3*S*,5*S*)-1-ethyl-3,5-dimethylcyclohexane?

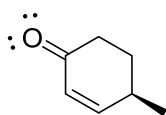
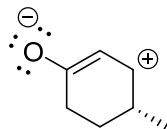
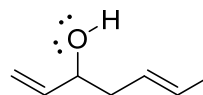


The easiest approach to solve this problem when it's presented as multiple choice is to check to see if the structures match the parent name given in the prompt, then assign *R* and *S* designations:



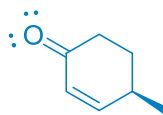
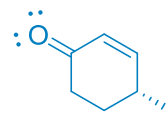
Only structures (a) and (e) match the compound named in the prompt—they must be the two chair conformations of the molecule. In both structures, there is one axial methyl group and one equatorial methyl group, but in (a) the ethyl group is axial while it is in an equatorial position in (e). Groups in equatorial positions experience less strain from electron cloud repulsions, so (e) is the more stable conformation.

- (iv) A Choose the most correct and complete statement about the following Lewis structures:

**J****K****L**

- (a) Structures **J** and **K** represent resonance forms of the same molecule
 (b) Structures **J** and **K** represent enantiomers
 (c) Structures **J** and **L** represent constitutional isomers
 (d) Statements (b) and (c) are both true
 (e) Statements (a), (b), and (c) are all false

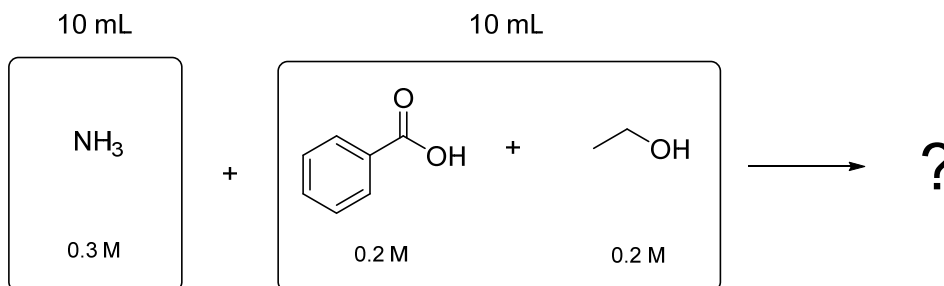
The best approach to this problem is to evaluate the veracity of statements (a), (b), and (c) individually. For statement (a), to judge whether the two structures are resonance forms, we should draw the most stable resonance form they correspond to:

**J****K'**

Structures **J** and **K'** are identical (just rotated 180° into the paper). Since statement (a) is true because **J** and **K** are resonance forms of the same molecule, they cannot be enantiomers. Try assigning *R* or *S* to the stereocenter—it's *R* for both—so statement (b) is false.

Structure **J** has a molecular formula of $C_7H_{10}O$, while **L** has a molecular formula of $C_7H_{12}O$, so they are not constitutional isomers and statement (c) is false. That leaves statement (a) is the only true statement.

- (v) E A 10 mL 0.3 M solution of ammonia is added to a 10 mL solution that is 0.2 M benzoic acid and 0.2 M ethanol. What percentage of the ethanol is deprotonated in the final reaction mixture? (Assume that the solvent does not play a role in the reaction.)



Compound	pK _a
ammonia (NH ₃)	38.0
ammonium (NH ₄ ⁺)	9.2
benzoic acid (C ₆ H ₅ COOH)	4.2
ethanol (CH ₃ CH ₂ OH)	15.9

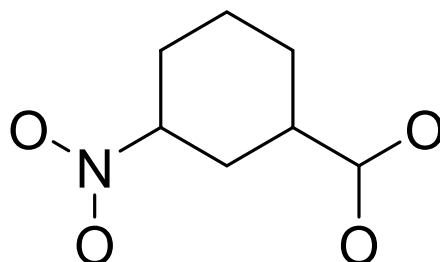
- (a) ≥99% deprotonated
 (b) 91% deprotonated
 (c) 50% deprotonated
 (d) 9% deprotonated
 (e) ≤1% deprotonated

This problem is deceptively easy. The first thing to recognize is that ammonia is the worst acid (pK_a = 38) and the strongest base (conj. acid pK_a = 9.2) present. Since 9.2 >> 4.2, the ammonia present will completely deprotonate the benzoic acid to produce 0.2 M deprotonated benzoic acid + 0.2 M ammonium + 0.1 M remaining ammonia.

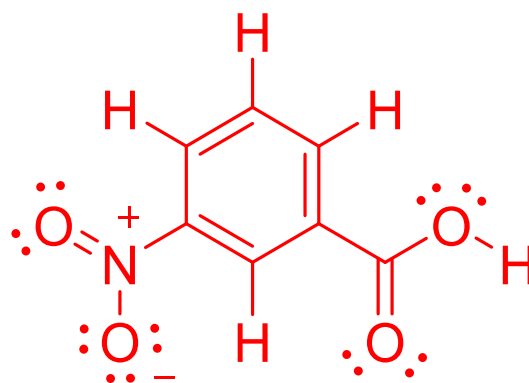
The pK_a of ethanol is 15.9, which makes the conjugate base of ethanol over 100,000 times (10^{15.9-9.2}) stronger of a base than ammonia. The remaining ammonia will not substantially deprotonate ethanol at a relative concentration of 1:2; you needn't even bother running calculations with equilibrium constants.

Problem 3. (20 points total) Short answers.

(i) (12 points) Complete the following Lewis structure for 3-nitrobenzoic acid, which has the structural formula $O_2NC_6H_4COOH$. The molecule has a carboxylic acid functional group, an aromatic ring, and a nitro group. Draw the most stable resonance form and explicitly include all hydrogens, bonding pairs, lone pairs, and formal charges on your Lewis structure.



You can begin by adding up valence electrons (1 for hydrogen, 4 for carbon, 5 for nitrogen, 6 for oxygen) to get $5(1)+7(4)+1(5)+4(6)=62$ electrons. Your final answer must account for 31 pairs of electrons. Next, you can see that the formula written in the prompt gives you some clues about what functional groups are present and how the atoms are bonded (see chapter 3). There's a nitro group, an aromatic ring, and a carboxylic acid. You can start filling out electrons accordingly to arrive at the following answer. You should try to give a full octet to every 2p-block atom, and try to minimize the magnitude and number of formal charges. You know from experience with homework problems that nitro groups have two adjacent formal charges. Formal charges are calculated by assigning to each atom one of the two electrons in a bonding pair and both electrons in each lone pair, then subtracting this count from the number of valence electrons expected of that element. For the nitrogen in the nitro group, this calculation is $5 - [4(1)+0(2)] = +1$.



(ii) (8 points) Draw the most acidic optically-active isomer of C₆H₁₀.

When asked to provide a structure for an organic compound of a particular molecular formula, it is usually best to begin by figuring out the degree of unsaturation in the molecule:

$$\Omega = \frac{2 + 2 (\# \text{ of C's}) + (\# \text{ of N's}) - (\# \text{ of H's}) - (\# \text{ of X's})}{2}$$

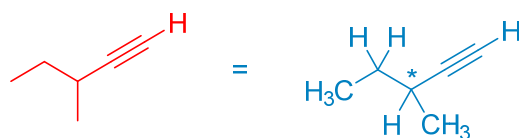
$$\Omega \text{ for C}_6\text{H}_{10} = 2$$

So, we are looking for a molecule where the sum of the rings and π bonds is 2. Next, we know that the molecule is a hydrocarbon (made of only carbon and hydrogen atoms) and that the most acidic hydrocarbons are typically those where you can generate a conjugate base that is stabilized in orbitals with high s character. This means we are probably looking for a molecule with a terminal alkyne: $-\text{C}\equiv\text{C}-\text{H}$ ($\text{p}K_a \approx 25$). (Incidentally, there are hydrocarbons that are stronger Brønsted–Lowry acids than terminal alkynes. We will discuss those when we cover aromaticity, but aromaticity does not come into play in this problem.)

So, we can start by drawing out a terminal alkyne, and fortunately, we have just the degree of unsaturation (2) to get the job done:

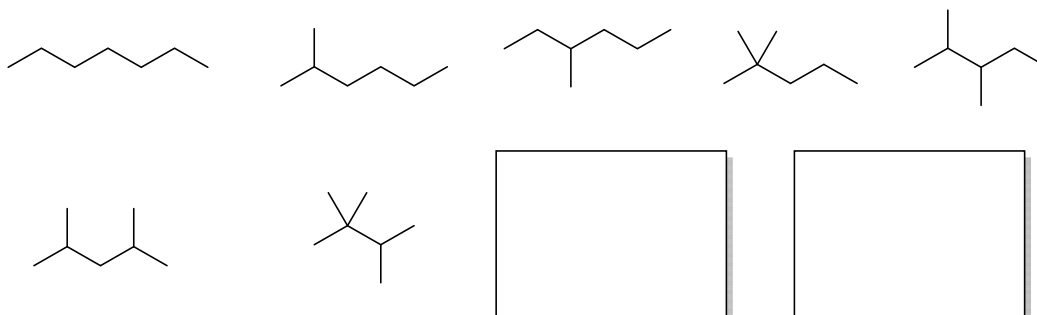


That structure uses three carbons and one hydrogen, so we need to add three more carbons and 9 more hydrogens. Fortunately, we need only worry about the three carbons, because completing their valences with bonds to hydrogen must give us a formula of C₆H₁₀. (That follows automatically from the degree of unsaturation we calculated.) To generate a stereogenic center that will make the molecule optically active (chiral), we need to have a tetrahedral carbon with four different substituents. The two carbons in the triple bond cannot be tetrahedral, but the one adjacent to it can be. Now, can we assign the remaining atoms to make it a stereocenter? Yes, the molecule is 3-methyl-1-pentyne.



Problem 4. (20 points total) Isomers of C_7H_{16} .

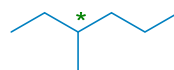
(i) (8 points) Draw in the two missing structures from the set of constitutional isomers with the molecular formula C_7H_{16} .



n-heptane

m.p. = $-91\text{ }^{\circ}\text{C}$; b.p. = $98\text{ }^{\circ}\text{C}$ 

2-methylhexane

m.p. = $-119\text{ }^{\circ}\text{C}$; b.p. = $90\text{ }^{\circ}\text{C}$ 

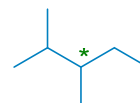
3-methylhexane

m.p. = $-119\text{ }^{\circ}\text{C}$; b.p. = $92\text{ }^{\circ}\text{C}$ 

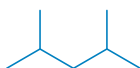
2,2-dimethylpentane

b.p. = $78\text{ }^{\circ}\text{C}$ 

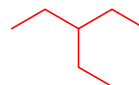
3,3-dimethylpentane

m.p. = $-135\text{ }^{\circ}\text{C}$; b.p. = $86\text{ }^{\circ}\text{C}$ 

2,3-dimethylpentane

b.p. = $89\text{ }^{\circ}\text{C}$ 

2,4-dimethylpentane

m.p. = $-123\text{ }^{\circ}\text{C}$; b.p. = $80\text{ }^{\circ}\text{C}$ 

3-ethylpentane

m.p. = $-119\text{ }^{\circ}\text{C}$; b.p. = $93\text{ }^{\circ}\text{C}$ 

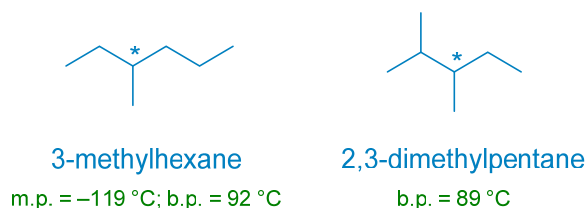
2,2,3-trimethylbutane

m.p. = $-26\text{ }^{\circ}\text{C}$; b.p. = $81\text{ }^{\circ}\text{C}$

The best way to draw isomers is to develop a methodical system. Start with the one heptane isomer, then try to move a methyl group around to make the hexane isomers...

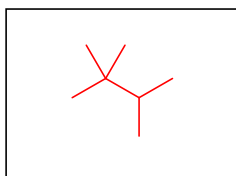
(ii) (4 points) How many of the nine constitutional isomers of C_7H_{16} are chiral?

Carbons atoms are stereogenic centers when they are bonded to four different groups. There are two isomers with stereogenic centers, labeled above with asterisks (*). Since each isomer only has one stereocenter, the possibility that either of these isomers is an achiral meso compound is absent. So, there are **two** chiral molecules:



(iii) (8 points) Triptane is the isomer of C_7H_{16} with the highest melting point. What is its structure and systematic IUPAC name?

Structure

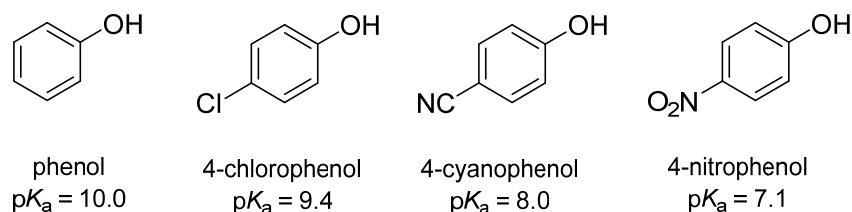


Name

2,2,3-trimethylbutane

For similar molecules (in terms of size and functional groups), the most branched and symmetrical compound usually has the highest melting point. Here, that's the isomer with the shortest chain length, 2,2,3-trimethylbutane.

Problem 5. (20 points total) Consider the following four molecules and their pK_a values in water.

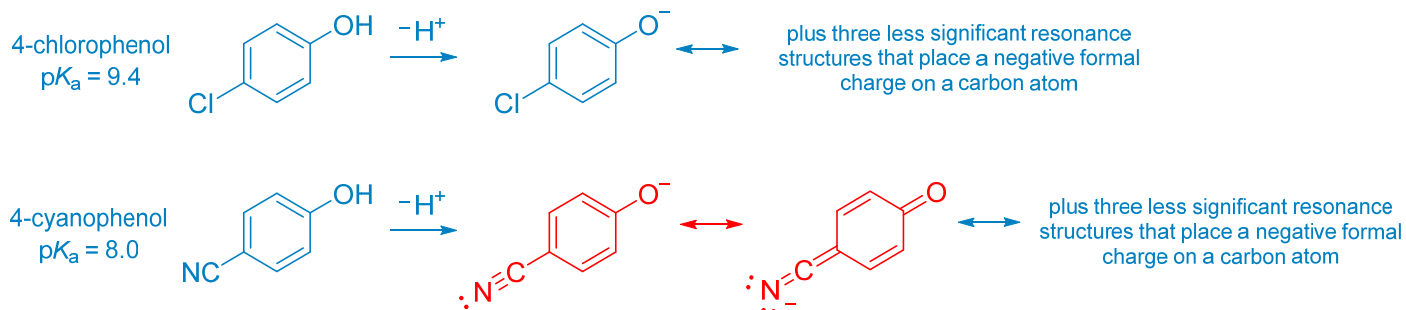


(i) (5 points) In one or two sentences, explain why 4-chlorophenol is a stronger acid than phenol.

The chlorine atom in 4-chlorophenol is more electronegative than the hydrogen in phenol that it replaced, and as such, the Cl is electron withdrawing by an inductive effect. This property helps stabilize the conjugate base of 4-chlorophenol, making it a stronger acid than phenol.

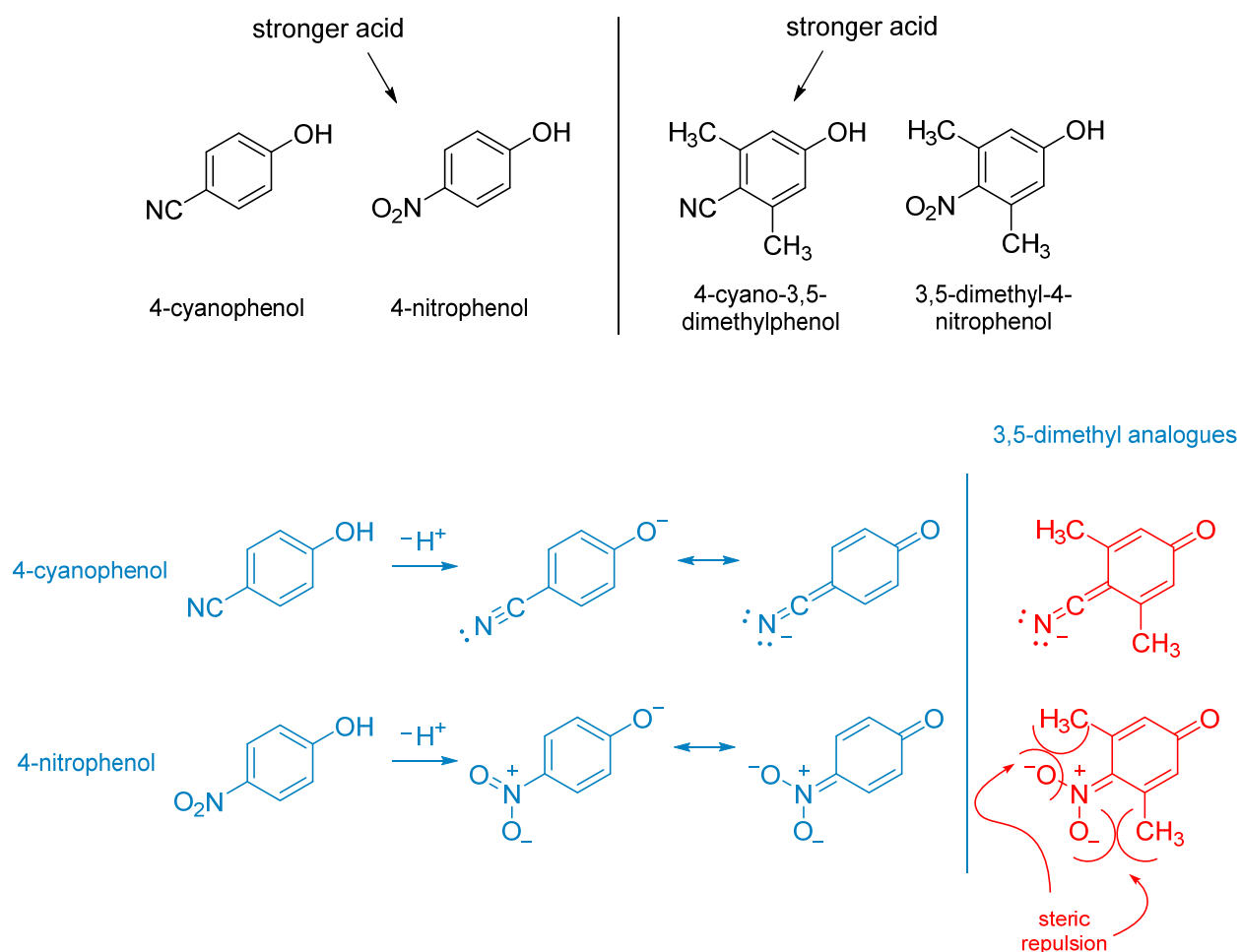
(ii) (8 points) Explain why 4-cyanophenol is a much stronger acid than 4-chlorophenol. You will want to draw something here.

Again, to judge the relative acidities of the two compounds, we will have to analyze the stability of their conjugate bases:



The cyano group ($-C\equiv N$) is electron withdrawing by a resonance effect, which allows more extensive delocalization of the negative charge on the conjugate base of 4-cyanophenol. This helps stabilize the conjugate base of 4-cyanophenol relative to 4-chlorophenol, rendering the former compound a much stronger acid.

(iii) (7 points) Explain why when methyl groups are added to the 3 and 5 positions of the ring, the relative strength of acidity of the 4-cyano and 4-nitro phenols switches (see below).



The conjugate bases of 4-cyanophenol and 4-nitrophenol are both stabilized by a resonance effect. 4-nitrophenol is the stronger acid because the nitro group is more electron withdrawing (delocalizing the negative charge onto an oxygen atom vs. a nitrogen atom, which is less electronegative). Adding the two methyl groups to the adjacent positions of the ring does little to change the resonance stabilization provided by the cyano group, which sticks straight out. The nitro group, however, juts out to the sides and experiences a repulsive steric interaction with the electron cloud of the methyl groups. To relieve this strain, the nitro group must tilt out of planarity with the π system of the ring. This ruins the overlap of p orbitals, and as such, partially spoils the resonance stabilization of the anion in the conjugate base of 3,5-dimethyl-4-nitrophenol.