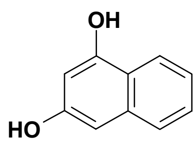
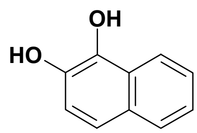
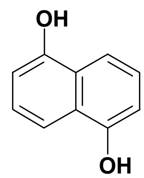
1. Rank the molecules according to their expected mp/bp. Use 1 for least and 3 for highest mp/bp. (3 pts)







2 **1** **3**

2. In few sentences, explain why I has lower pKa than II. (4 pts)

ClN $(CH_3)_3CH_2CH_2NH_2$ — **I**

$(CH_3)_2NCH_2CH_2NH_2$ — **II**

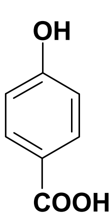
I has lower pKa than II because the β-carbon of ethylamine bears a positively charged group which is electron withdrawing, thus reducing the availability of the lone pair on the amine nitrogen in comparison to that in II. In other words, the acid ←→ conjugate base equilibrium favors the base in I while it favors the acid in II. Thus, more acid will be needed to shift the equilibrium towards acid in I or more base will be needed to shift the equilibrium to acid in II. This means that the pKa will be lower for I and higher for II.

3. Rank the molecules/ions in each series according to their pKa values. If more than one pKa values exist for a molecule/ion, use the lower pKa value for comparison. Use 1 for the least pKa value, 2 for the next higher and so on. (12 pts)

a)

$O_2N-CH_2-CH_2-COOH$	$CH_3-CH(NO_2)-COOH$	$CH_3-CH(COOH)-COOH$
3	**1**	**2**

b)



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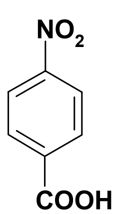

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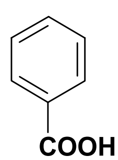

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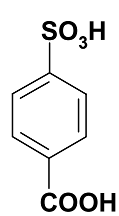


1

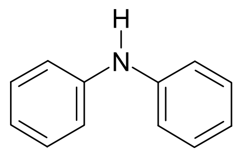
c)

H_2N-CH_2-COOH	CH_3-COOH	$HO-CH_2-COOH$
1	**3**	**2**

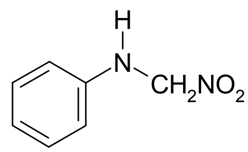
4. Rank the molecules/ions in each series according to their basicity. Use 1 for the most basic, 2 for the next most basic and so on. (12 pts)

	Ethylamine	Asparagine (HOOCCH(CONH$_2$)NH$_2$)	Alanine (HOOCCH(CH$_3$)NH$_2$)
a)	1	3	2

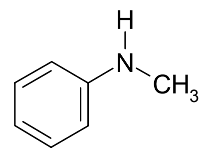
b)



3

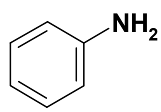


1



2

c)



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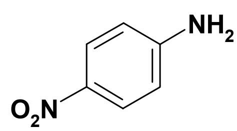
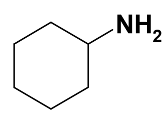
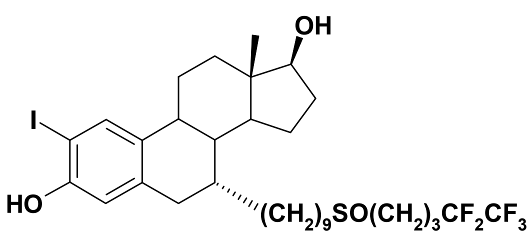


3



1

5. The molecule underneath is potential diagnostic marker for an anti-estrogenic agent. Indicate the Kier-Hall electronegativity values of the following atoms. (4 pts)



Kier-Hall eN Value

-O- of phenolic OH = 1.0

I- = 6/25 or 0.24

S = 3/9 or 0.33

F of CF$_2$ = 6/4 or 1.5

6. Heparin is a sulfated polysaccharide used in anti-coagulation therapy. A typical chain of heparin polysaccharide has an average of some 50 sulfate groups (-OSO$_3$H). Each sulfate group has a pKa of 0.2. Heparin sometimes causes bleeding, which is the direct result of its high activity as a anti-clotting agent. This bleeding can be stopped using a chemical antidote to heparin. _Using the understanding gained in the class on bonds, types of bonds involved, and ability to groups to form specific types of bonds_, circle the **structure(s)** from below, which would work as **plausible** antidote(s) under physiological conditions (pH ~7.2 – 7.4). (5 pts)