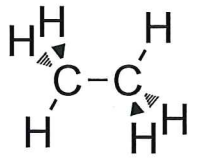
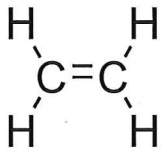
Problem Set 1 — *due MONDAY March 18th **IN CLASS*** — Chem 132
Dr. Fantini — March 4, 2013

Name: Key SB#: 007

Scaled w/ a total of 108 points. Does not include prob. 16

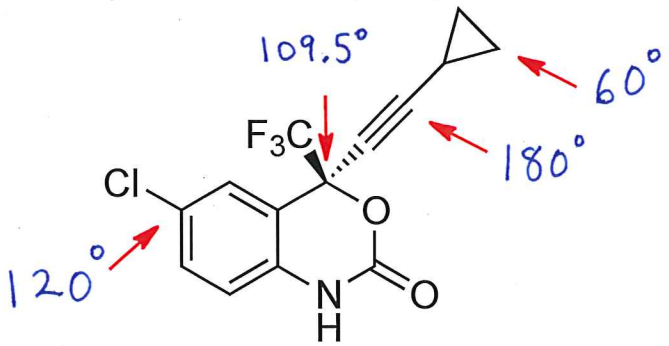
421

1. Please complete the following table:

property of molecule:			H–C≡C–H
name of shape at central atom	tetrahedral	trigonal planar	linear
hybrid orbital set	sp^3	sp^2	sp
# of left-over *p* orbitals	none	1 per carbon	2 per carbon
typical bond angles	109.5°	120°	180°
% *s*-character	25% s	33% s	50% s
C–H bond length (write "longest" and "shortest" at the correct ends of the arrow)	longest ←		shortest
C–H acidity (write "most acidic" and "least acidic" at the correct ends of the arrow)	least acidic ←		most acidic

Questions 2—11 refer to the following compound, which is efavirenz, a non-nucleoside reverse transcriptase inhibitor (antiviral used for the treatment of HIV).

C 14
H 9
N 1
O 2
Cl 1
F 3



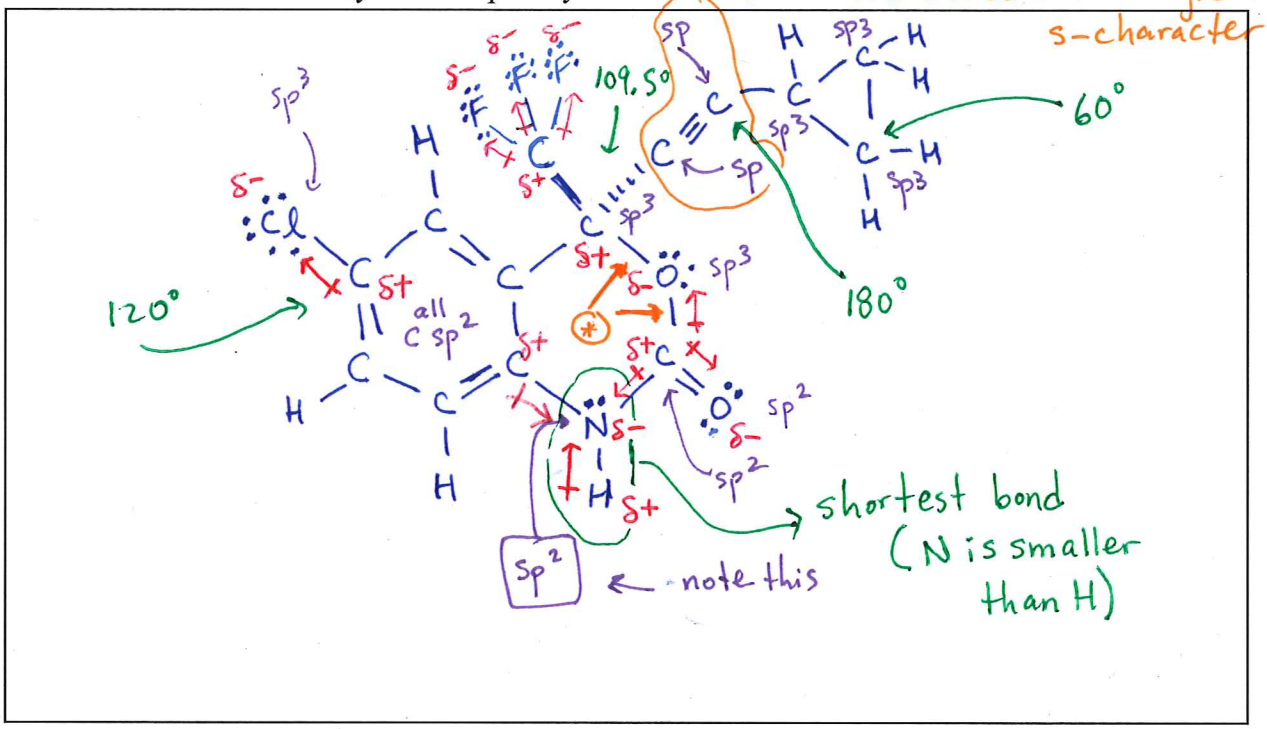
C then H then alphabetical

2

2. What is the molecular formula of this drug? $C_{14}H_9ClF_3NO_2$

3

3. Draw a "regular" Lewis structure for this molecule (make it big). A "regular" Lewis structure is one that has all element symbols explicitly shown.



5

4. Mark up the large drawing of the molecule with δ+ and δ- as appropriate to show polar bonds. Also draw the bond dipole symbol in the proper manner at each polar bond.

7

5. Identify the hybridization at each carbon atom. (did the heteroatoms for your info)

3

6. Write the bond angles around the atoms marked with red arrows.

3

7. Identify the carbon atom (or atoms) where there is the greatest *s*-character in the hybrid orbital.

3

8. Which bond do you expect to be the shortest in the molecule? (It is from H to another atom.) Why?

There are C–H and N–H bonds. N is smaller than C so the N–H bond is shorter than the C–H bond.

3

9. Which bond from a carbon atom to a halogen is longer? Why? (The halogens are the elements of group 17.)

C–Cl bond longer than C–F bond because Cl is larger than F.

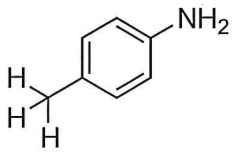
3

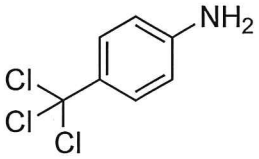
10. Which is the longest C—O single-bond in the molecule? Why?

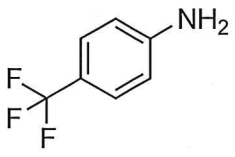
See ⊛ in diagram. There are two C—O bonds. The one to an sp^3 carbon is longer because sp^3 orbital is longer than sp^2.

11. The following amines are ordered according to base strength:

most basic







least basic

/10

Explain, using resonance and inductive effects, the trend in base strength for these three compounds.

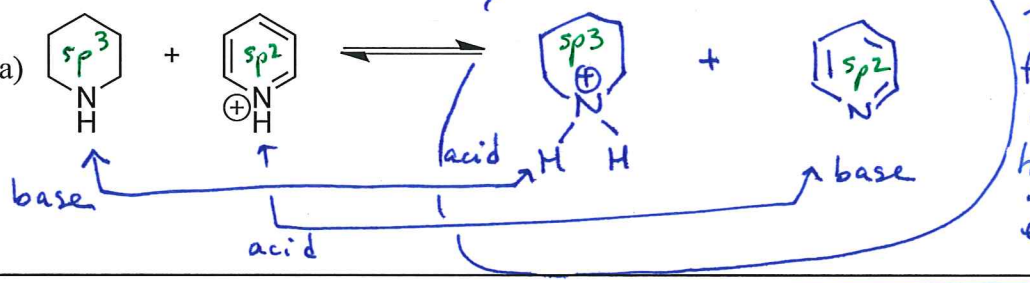
Resonance through the aromatic ring is what lets the group across from the NH_2 affect it from so far away.

The more electron-withdrawing X is, the better it stabilizes the negative charge. The more stabilization of the second resonance structure, the less available the lone pair of electrons on N is to act as a base.

12. Draw products, label conjugate acid-base pairs, and predict which side of the reaction is favored. Under each reaction, briefly explain if you used element, inductive, resonance, or hybridization trends in your reasoning.

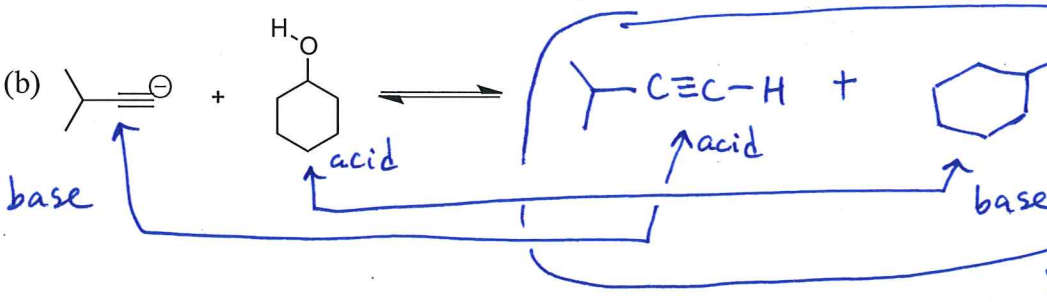
/3 ea

(a)



This side favored by the hybridization effect.

(b)



This side favored by the element effect

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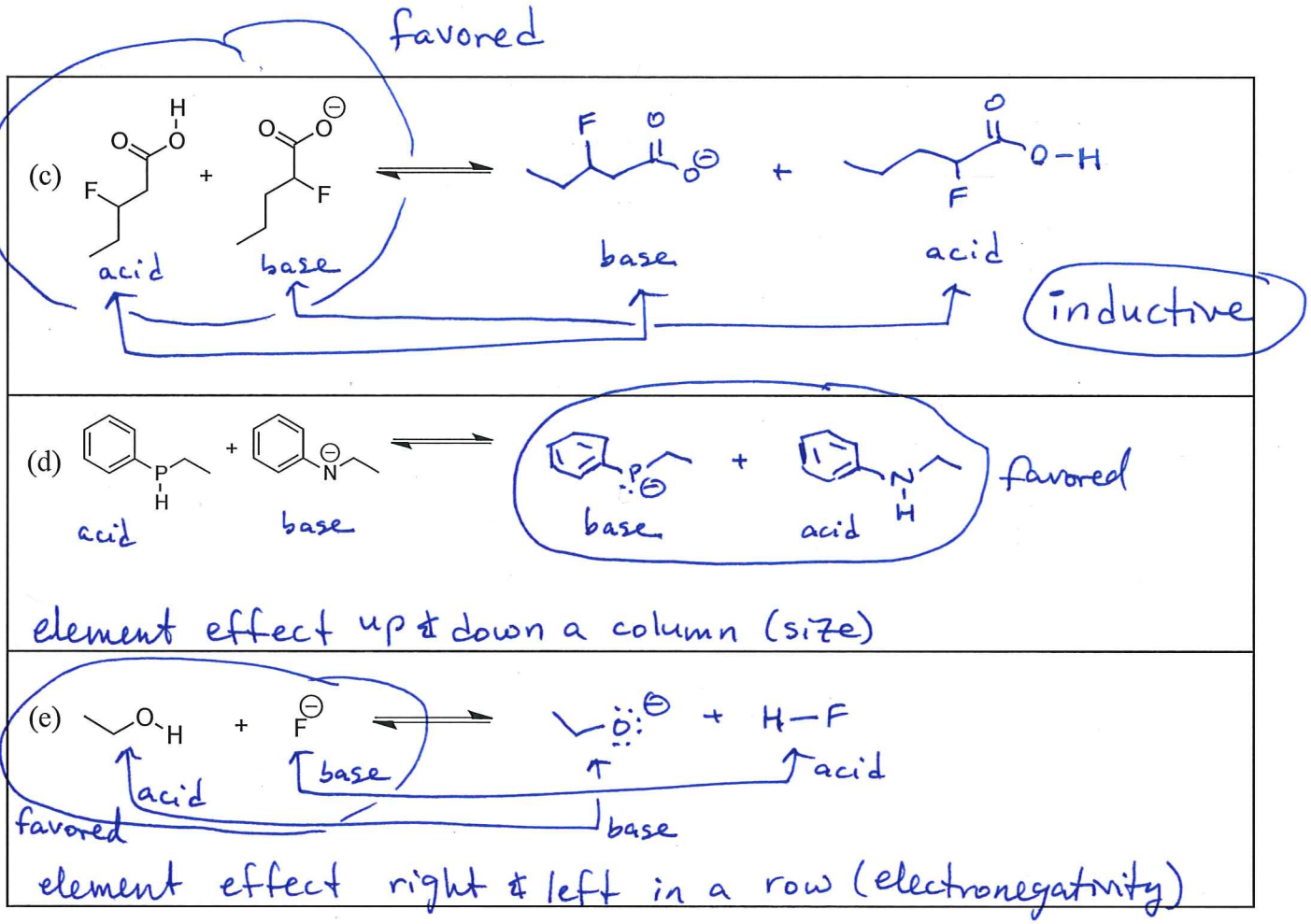
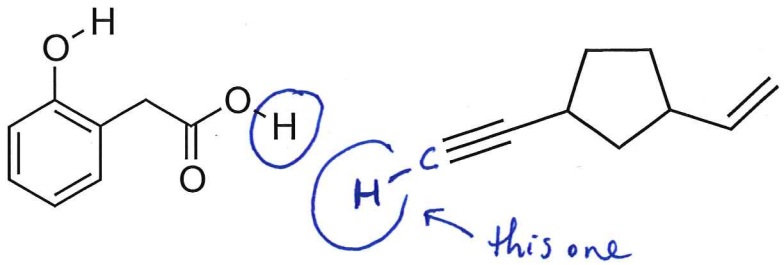
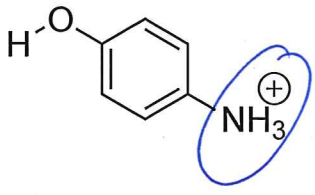


13. Circle the most acidic H in each molecule or ion. (Draw in the H if necessary.)

/9





C N O F
Si P S Cl
Br
I

14. Arrange these compounds in order of increasing acidity.

all seem to be element effect, but mixing row & column

in between

CH_3SH CH_3OH HI NH_3

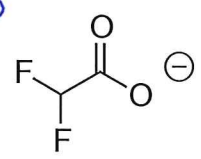
stronger weaker strongest weakest

6

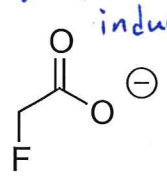
$NH_3 < CH_3OH < CH_3SH < HI$

15. Arrange the bases in order of increasing basicity. (Redraw in order in the box.)

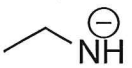
weaker (more inductive)



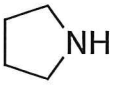
stronger (less inductive)



strongest (element)



weakest b/c neutral (others are anionic)



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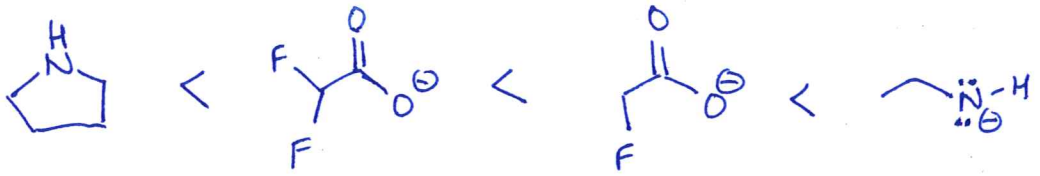
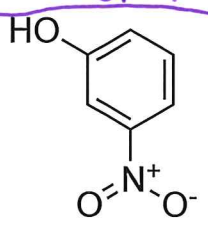
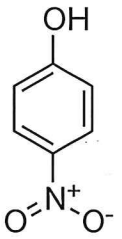


16. Explain and justify that 4-nitrophenol is a stronger acid than 3-nitrophenol. (Invoke resonance effects in your answer.) The H on the oxygen is the acidic H.

8 NOT GRADED

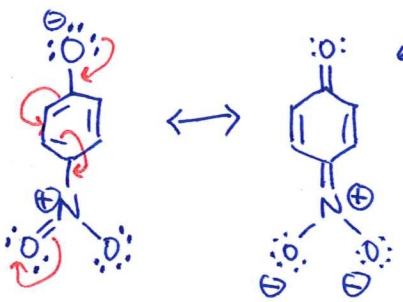


3-nitrophenol



4-nitrophenol

look at the conjugate bases. The given information means the anion of 4-nitrophenol is more stable than that of 3-nitrophenol. Can you find the distinction?



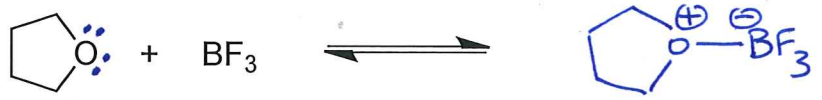
this is a good resonance structure, it delocalizes the charge onto the nitro group.

No matter how you shift the electrons of 3-nitrophenolate you can't get an equivalent delocalization onto the nitro group.

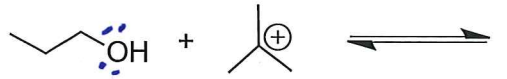
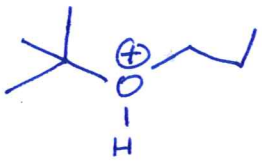
/9 3 eq

2 pieces becoming one

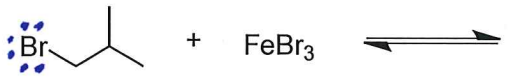
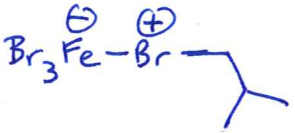
17. Identify the Lewis acid and Lewis base in each reaction. Draw the Lewis acid–base adduct as the product. (For (c), there are two bonds to Br in the product.)

(a)  + BF_3

Lewis base Lewis acid

(b)  

Lewis base Lewis acid

(c)  + $FeBr_3$ 

Lewis base Lewis acid