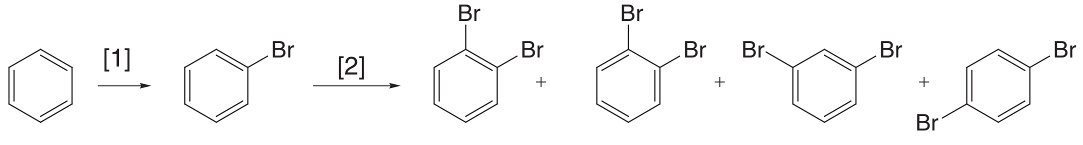
17.23

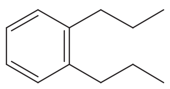
a. If benzene could be described by a single Kekulé structure, only one product would form in Reaction [1], but there would be four (not three) dibromobenzenes (**A**–**D**), because adjacent C–C bonds are different—one is single and one is double. Thus, compounds **A** and **B** would *not* be identical. **A** has two Br's bonded to the same double bond, but **B** has two Br's on different double bonds.

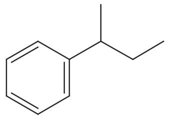
b. In the resonance description, only one product would form in Reaction [1], since all C's are identical, but only three dibromobenzenes (ortho, meta, and para isomers) are possible. **A** and **B** are identical because each C–C bond is identical and intermediate in bond length between a C–C single and C–C double bond.

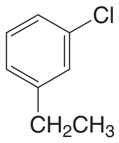


A **B** **C** **D**

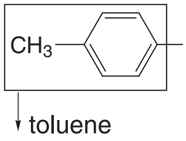
17.24 To name the compounds use the directions from Answer 17.3.

a.

o-dipropylbenzene

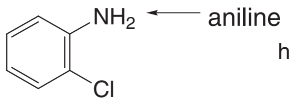
b.

sec-butylbenzene

c.


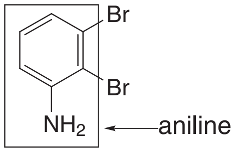
m-chloroethylbenzene

d.


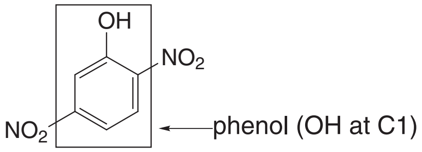
p-chlorotoluene

e.


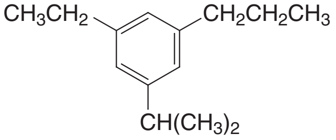
o-chloroaniline

f.


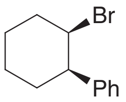
2,3-dibromoaniline

g.


2,5-dinitrophenol

h.


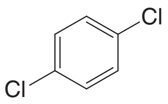
1-ethyl-3-isopropyl-5-propylbenzene

i.


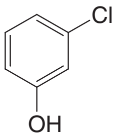
cis-1-bromo-2-phenylcyclohexane

17.25

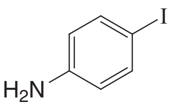
a. *p*-dichlorobenzene



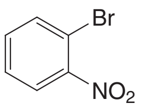
b. *m*-chlorophenol



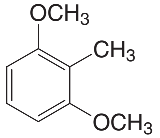
c. *p*-iodoaniline



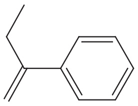
d. *o*-bromonitrobenzene



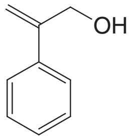
e. 2,6-dimethoxytoluene



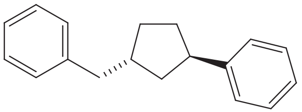
f. 2-phenyl-1-butene



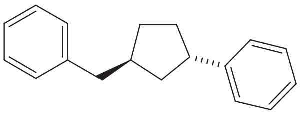
g. 2-phenyl-2-propen-1-ol



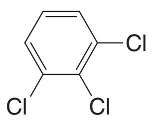
h. *trans*-1-benzyl-3-phenylcyclopentane



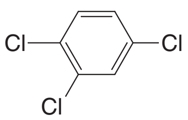
or



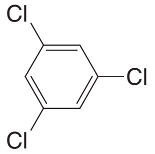
17.26



1,2,3-trichlorobenzene



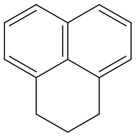
1,2,4-trichlorobenzene



1,3,5-trichlorobenzene

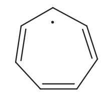
17.27 Count the electrons in the π bonds. Each π bond holds two electrons.

a.



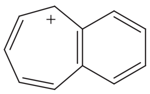
10 π electrons

b.



7 π electrons

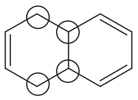
c.



10 π electrons

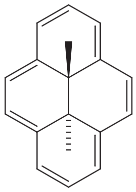
17.28 To be aromatic, the compounds must be cyclic, planar, completely conjugated, and have $4n + 2$ π electrons.

a.



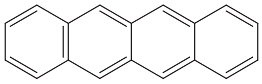
circled C's are not sp^2
not completely conjugated
not aromatic

b.



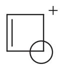
14 π electrons in outer ring
aromatic

c.



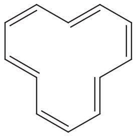
4 benzene rings
joined together
aromatic

d.



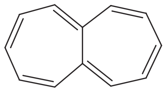
circled C's are not sp^2
not completely conjugated
not aromatic

e.



12 π electrons
does **not** have $4n + 2$
π electrons

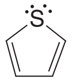
f.



12 π electrons
does **not** have $4n + 2$
π electrons

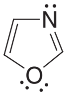
17.29 In determining if a heterocycle is aromatic, count a nonbonded electron pair if it makes the ring aromatic in calculating $4n + 2$.

a.



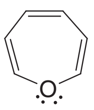
6 π electrons
counting a lone pair from S
4(1) + 2 = 6
aromatic

b.



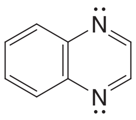
6 π electrons
counting a lone pair from O
4(1) + 2 = 6
aromatic

c.



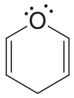
not aromatic

d.



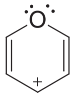
10 π electrons
4(2) + 2 = 10
aromatic

e.



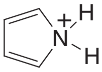
not aromatic

f.



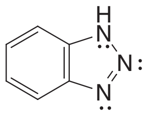
6 π electrons,
counting a lone pair from O
4(1) + 2 = 6
aromatic

g.



N is not sp^2 (no *p* orbital)
not aromatic

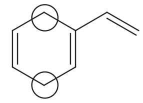
h.



10 π electrons
4(2) + 2 = 10
aromatic

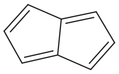
17.30

a.



circled C's are not sp^2
not aromatic

c.

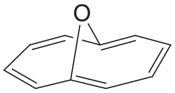


8 π electrons
4(2) = 8
antiaromatic

e.

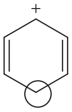
4 π electrons
4(1) = 4
antiaromatic

b.



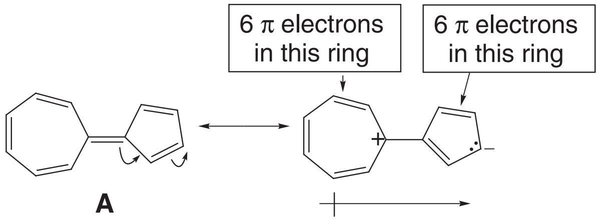
10 π electrons
in 10-membered ring
4(2) + 2 = 10
aromatic

d.

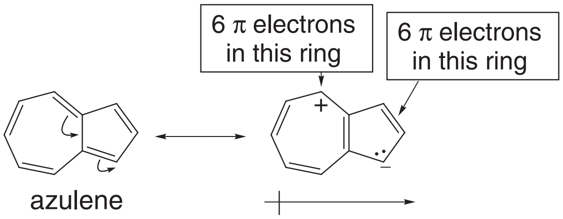


circled C is
not sp^2
not aromatic

17.31



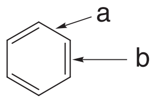
A



azulene
B

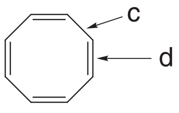
In both **A** and **B**, resonance structures can be drawn that place a negative charge in the five-membered ring and a positive charge in the seven-membered ring. These resonance structures show that each ring has 6 π electrons, making it aromatic. Each molecule possesses a dipole such that the seven-membered ring is electron deficient and the five-membered ring is electron rich.

17.32 Benzene has C–C bonds of equal length, intermediate between a C–C double and single bond. Cyclooctatetraene is not planar and not aromatic so its double bonds are localized.



6 electrons: aromatic
all bonds of equal length
intermediate

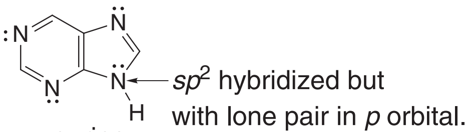
cyclooctatetraene



not aromatic
longer single bond
localized double bond: **shorter**

d < a = b < c

17.33



purine

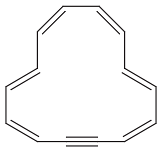
a. Each N atom is sp^2 hybridized.

b. The three unlabeled N atoms are sp^2 hybridized with lone pairs in one of the sp^2 hybrid orbitals. The labeled N has its lone pair in a p orbital.

c. 10 π electrons

d. Purine is cyclic, planar, completely conjugated, and has 10 π electrons [4(2) + 2] so it is aromatic.

17.34



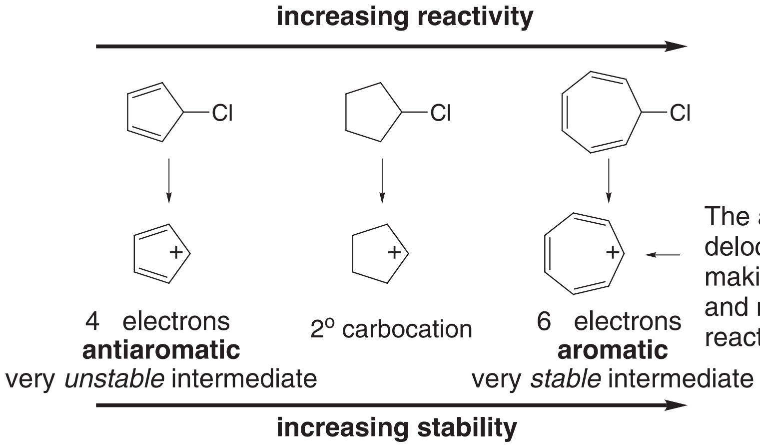
C

a. 16 total   electrons

b. 14   electrons delocalized in the ring. [Note: Two of the electrons in the triple bond are localized between two C's, perpendicular to the π electrons delocalized in the ring.]

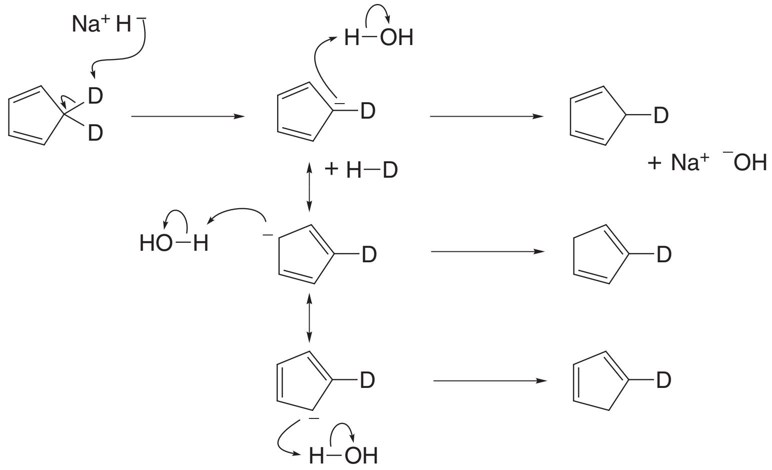
c. By having 2 of the *p* orbitals of the C–C triple bond co-planar with the *p* orbitals of all the C=C's, the total number of   electrons delocalized in the ring is 14. 4(3) + 2 = 14, giving it the right number of electrons to be **aromatic.**

17.35 The rate of an S_N1 reaction increases with increasing stability of the intermediate carbocation.

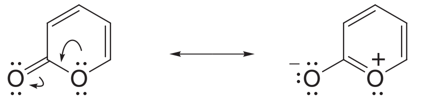


The aromatic carbocation is delocalized over the whole ring making it a very stable intermediate and most easily formed in an S_N1 reaction.

17.36



17.37 α-Pyrone reacts like benzene because it is aromatic. A second resonance structure can be drawn showing how the ring has six π electrons. Thus, α-pyrone undergoes reactions characteristic of aromatic compounds; that is, substitution rather than addition.



α-pyrone

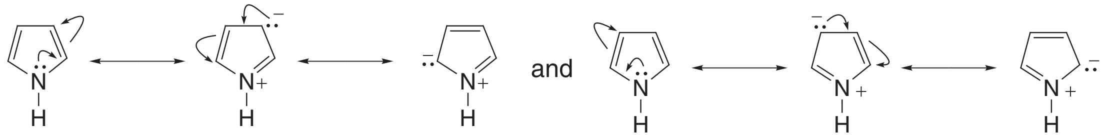
6 π electrons

17.38

a.

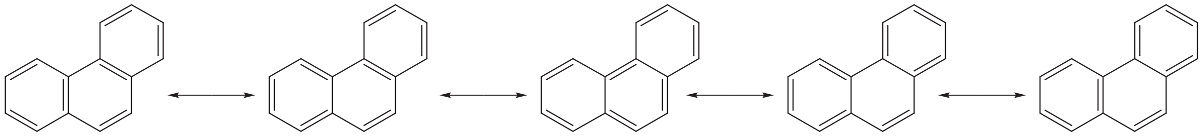
cyclopropenyl radical

b.



pyrrole

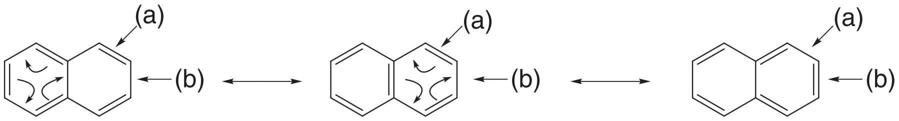
c.



phenanthrene

17.39

Naphthalene can be drawn as three resonance structures:

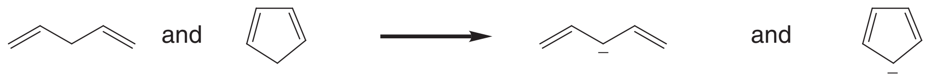


In two of the resonance structures bond (a) is a double bond, and bond (b) is a single bond. Therefore, bond (b) has more single bond character, making it longer.

17.40 The compound with the more stable conjugate base is the stronger acid. Draw and compare the conjugate bases of each pair of compounds.

conjugate bases

a.

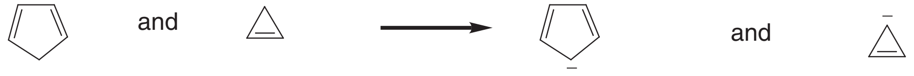


more acidic

resonance-stabilized
but not aromatic

6 electrons, aromatic
more stable conjugate base
Its acid is more acidic.

b.

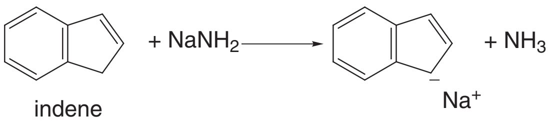


more acidic

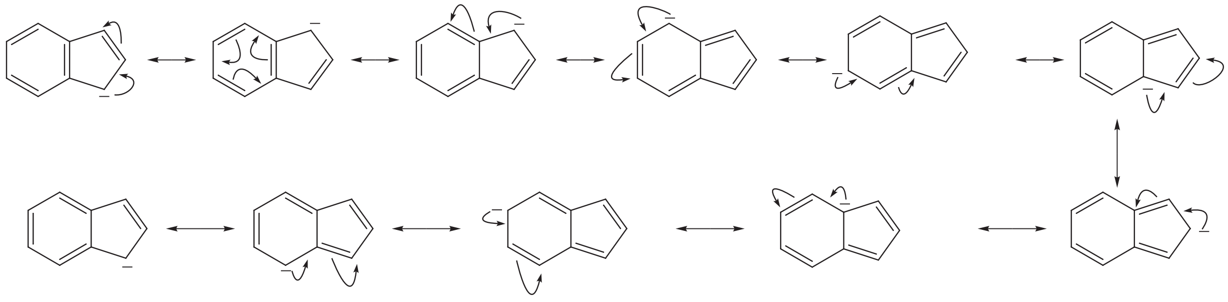
6 electrons, aromatic
more stable conjugate base
Its acid is more acidic.

antiaromatic
highly destabilized
conjugate base

17.41

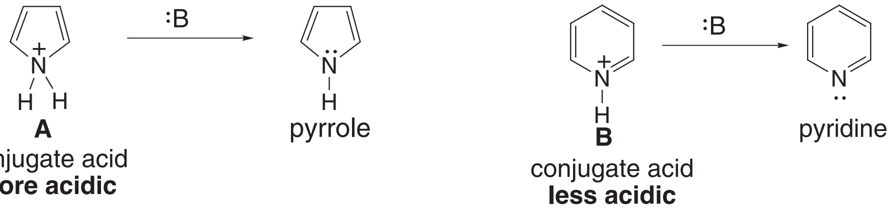


indene



The conjugate base of indene has 10   electrons making it aromatic and very stable. Therefore, indene is more acidic than many hydrocarbons.

17.42



A
conjugate acid
more acidic

pyrrole

B
conjugate acid
less acidic

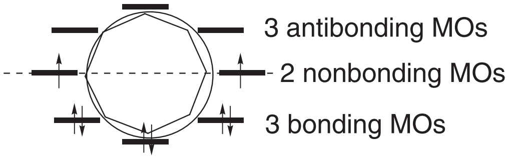
pyridine

Loss of a proton from **A** (which is not aromatic) gives two electrons to N, so pyrrole has six π electrons that can then delocalize in the five-membered ring, making it aromatic. This makes deprotonation a highly favorable process.

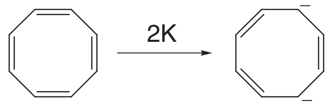
Both **B** and its conjugate base (pyridine) are aromatic. Since **B** has six π electrons, it is already aromatic to begin with, so there is less to be gained by deprotonation, and **B** is thus less acidic than **A**.

17.43

a.



cyclooctatetraene and its 8 π electrons

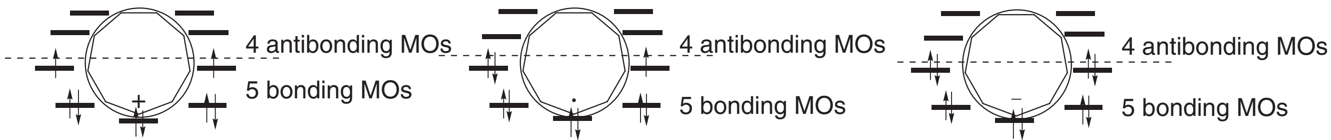


cyclooctatetraene

dianion of cyclooctatetraene

b. Even if cyclooctatetraene were flat, it has two unpaired electrons in it HOMOs (nonbonding MOs) so it cannot be aromatic.
c. The dianion has 10   electrons.
d. The two additional electrons fill the nonbonding MOs; that is, all the bonding and nonbonding MOs are filled with electrons in the dianion.
e. The dianion is aromatic since its HOMOs are completely filled, and it has no electrons in antibonding MOs.

17.44



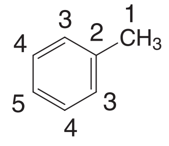
cyclononatetraenyl cation
8 electrons
antiaromatic

cyclononatetraenyl radical
9 electrons
not aromatic

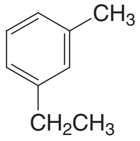
cyclononatetraenyl anion
10 electrons
aromatic

All bonding MOs are filled.

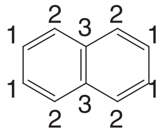
17.45 Use the directions from Answer 17.6.

a.


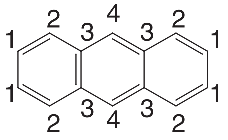
5 different C's

b.


all unique
9 different C's

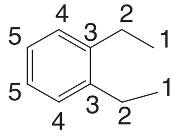
c.


3 different C's

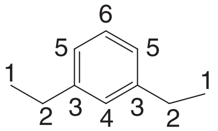
d.


4 different C's

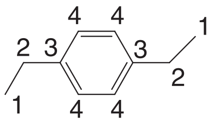
17.46 Draw the three isomers and count the different types of carbon in each. Then match the structures with the data.



ortho isomer
5 types of C
5 lines in spectrum
Spectrum [B]



meta isomer
6 types of C
6 lines in spectrum
Spectrum [A]



para isomer
4 types of C
4 lines in spectrum
Spectrum [C]

17.47

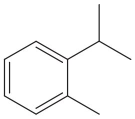
a. $C_{10}H_{14}$: IR absorptions at 3150–2850 (sp^2 and sp^3 hybridized C–H), 1600, and 1500 (due to a benzene ring) cm^{-1}.

^{1}H NMR data:

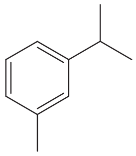
Absorption	**ppm**	**# of H's**	**Explanation**
doublet	1.2	6	6H's adjacent to 1H
singlet	2.3	3	CH_3
septet	3.1	1	1H adjacent to 6H's
multiplet	7–7.4	4	a disubstituted benzene ring

$(CH_3)_2CH$ group

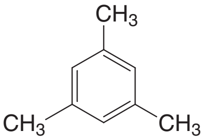
You can't tell from these data where the two groups are on the benzene ring. They are not para. That usually gives two sets of distinct peaks (resembling two doublets) so there are two possible structures—ortho and meta isomers.



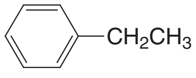
or



b. C_9H_{12}: ^{13}C NMR signals at 21, 127, and 138 ppm → means three different types of C's.
^1H NMR shows 2 types of H's: 9H's probably means 3 CH_3 groups; the other 3 H's are very deshielded so they are bonded to a benzene ring.
Only one possible structure fits:

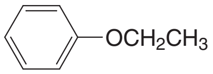


c. C_8H_{10}:IR absorptions at 3108–2875 (sp^2 and sp^3 hybridized C–H), 1606, and 1496 (due to a benzene ring) cm^{-1}.
^1H NMR data:

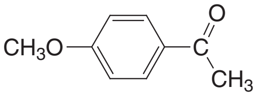
Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
triplet	1.3	3	3H's adjacent to 2H's	
quartet	2.7	2	2H's adjacent to 3H's	
multiplet	7.3	5	a monosubstituted benzene ring	

17.48

a. Compound **A**: Molecular formula $C_8H_{10}O$.
IR absorption at 3150–2850 (sp^2 and sp^3 hybridized C–H) cm^{-1}.
^1H NMR data:

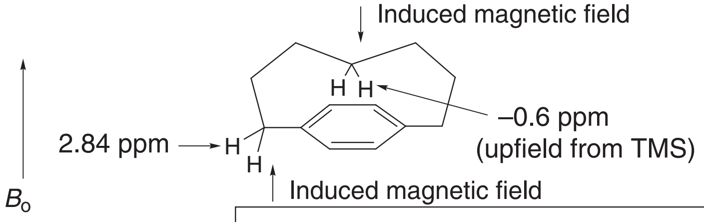
Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
triplet	1.4	3	3H's adjacent to 2H's	
quartet	3.95	2	2H's adjacent to 3H's	
multiplet	6.8–7.3	5	a monosubstituted benzene ring	

b. Compound **B**: Molecular formula $C_9H_{10}O_2$.
IR absorption at 1669 (C=O) cm^{-1}.
^1H NMR data:

Absorption	**ppm**	**# of H's**	**Explanation**	**Structure:**
singlet	2.5	3	CH_3 group	
singlet	3.8	3	CH_3 group	
doublet	6.9	2	2H's on a benzene ring	
doublet	7.9	2	2H's on a benzene ring	

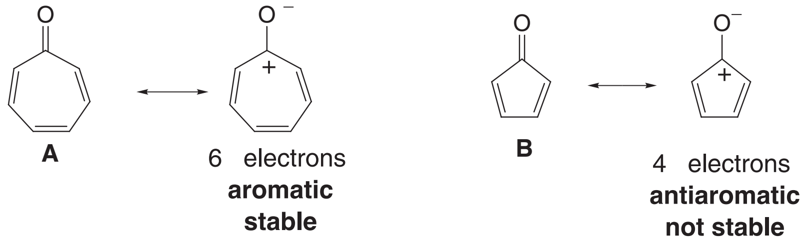
17.49

The induced magnetic field by the circulating π electrons opposes the applied field in this vicinity, shifting the absorption upfield to a lower chemical shift than other sp^3 C–H protons.
In this case the protons absorb upfield from TMS, an unusual phenomenon for C–H protons.

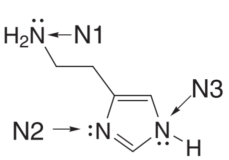


The induced magnetic field by the circulating π electrons reinforces the applied field in this vicinity, shifting the absorption downfield to a higher chemical shift.

17.50 A second resonance structure for **A** shows that the ring is completely conjugated and has 6 π electrons, making it aromatic and especially stable. A similar charge-separated resonance structure for **B** makes the ring completely conjugated, but gives the ring 4 π electrons, making it antiaromatic and especially unstable.



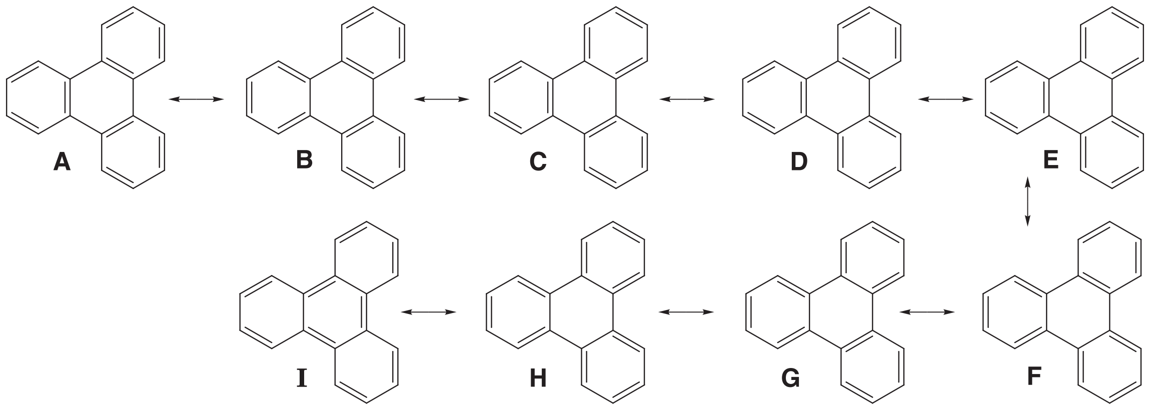
17.51



N1: The electron pair occupies an sp^3 hybrid orbital on the N atom.
N2: The electron pair is contained in an sp^2 hybrid orbital and is not delocalized over the five-membered ring.
N3: The electron pair is in a *p* orbital, delocalized on the five-membered ring to make it aromatic.

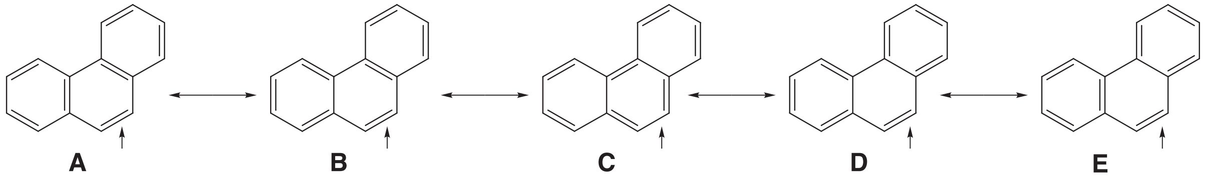
Basicity depends on the ability of an atom to donate an electron pair. Electron pairs that are delocalized in a π system to make it aromatic are less available for electron donation, making them less basic. Basicity is also affected by percent *s*-character. The higher the percent *s*-character, the weaker the base. Electrons are held closer to the nucleus so they are less available for electron donation. Thus, in order of increasing basicity: N3 < N2 < N1.

17.52 Resonance structures for triphenylene:



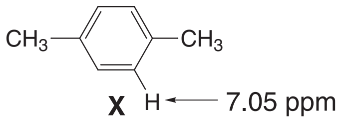
Resonance structures **A–H** all keep three double and three single bonds in the three six-membered rings on the periphery of the molecule. This means that each ring behaves like an isolated benzene ring undergoing substitution rather than addition because the π electron density is delocalized within each six-membered ring. Only resonance structure **I** does not have this form. Each C–C bond of triphenylene has four (or five) resonance structures in which it is a single bond and four (or five) resonance structures in which it is a double bond.

Resonance structures for phenanthrene:



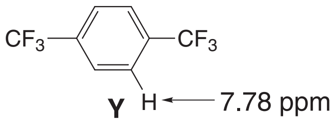
With phenanthrene, however, four of the five resonance structures keep a double bond at the labeled C's. (Only **C** does not.) This means that these two C's have more double bond character than other C–C bonds in phenanthrene, making them more susceptible to addition rather than substitution.

17.53



X

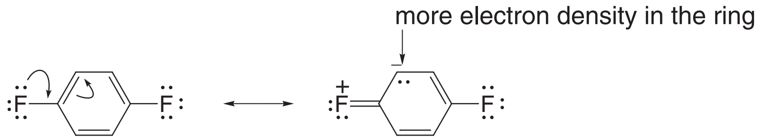
CH_3 groups are electron donating. Increasing the electron density of the ring shields the protons and shifts the absorption slightly upfield.



Y

The 3 electronegative F's make CF_3 an electron withdrawing group. Decreasing the electron density of the ring deshields the protons and the absorption goes slightly downfield.

When F's are directly bonded to the benzene ring, two conflicting factors come into play. Since F is very electronegative, it withdraws electron density from the ring. But, F atoms also contain lone pairs of electrons that can be donated to the ring by resonance. For example:



This increases the electron density of the ring. On balance, these factors just about cancel, so the absorption occurs at ~7 ppm.