Chapter 17: Benzene and Aromatic Compounds

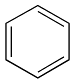
◆ Comparing aromatic, antiaromatic, and nonaromatic compounds (17.7)

Aromatic compound	A cyclic, planar, completely conjugated compound that contains $4n + 2$ π electrons ($n = 0, 1, 2, 3$, and so forth). An aromatic compound is more stable than a similar acyclic compound having the same number of π electrons.
Antiaromatic compound	A cyclic, planar, completely conjugated compound that contains $4n$ π electrons ($n = 0, 1, 2, 3$, and so forth). An antiaromatic compound is less stable than a similar acyclic compound having the same number of π electrons.
A compound that is not aromatic	A compound that lacks one (or more) of the requirements to be aromatic or antiaromatic.

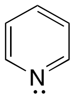
◆ Properties of aromatic compounds

- Every carbon has a *p* orbital to delocalize electron density (17.2).
- They are unusually stable. ΔH° for hydrogenation is much less than expected, given the number of degrees of unsaturation (17.6).
- They do not undergo the usual addition reactions of alkenes (17.6).
- ^{1}H NMR spectra show highly deshielded protons because of ring currents (17.4).

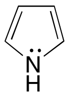
◆ Examples of aromatic compounds with 6 π electrons (17.8)



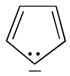
benzene



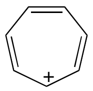
pyridine



pyrrole

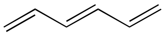


cyclopentadienyl anion

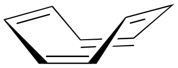


tropylium cation

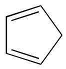
◆ Examples of compounds that are not aromatic (17.8)



not cyclic



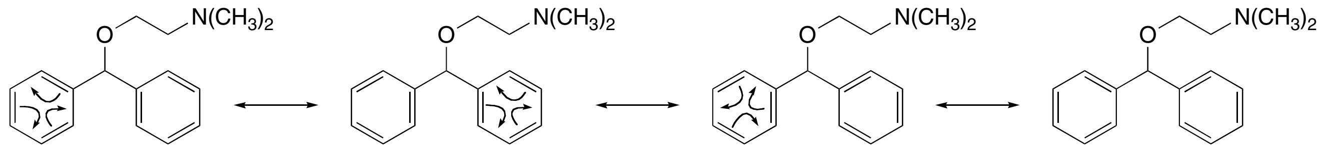
not planar



not completely conjugated

Chapter 17: Answers to Problems

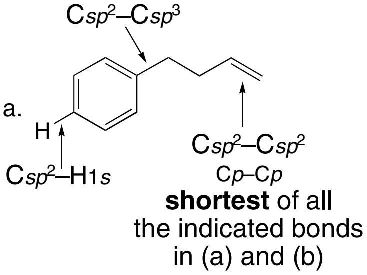
17.1 Move the electrons in the π bonds to draw all major resonance structures.



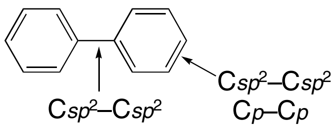
diphenhydramine

17.2 Look at the hybridization of the atoms involved in each bond. Carbons in a benzene ring are surrounded by three groups and are *sp*^{2} hybridized.

a.



b.



17.3

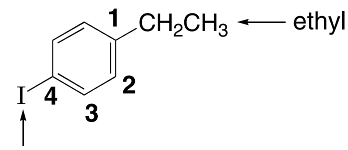
- To name a benzene ring with **one substituent**, name the substituent and add the word *benzene*.
- To name a **disubstituted ring**, select the correct prefix (ortho = 1,2; meta = 1,3; para = 1,4) and alphabetize the substituents. Use a common name if it is a derivative of that monosubstituted benzene.
- To name a **polysubstituted ring**, number the ring to give the lowest possible numbers and then follow other rules of nomenclature.

a. isopropyl group

$PhCH(CH_3)_2$

isopropylbenzene

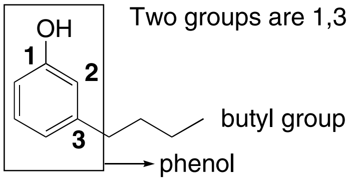
b.



iodo Two groups are 1,4 = para.

***p*-ethyliodobenzene**

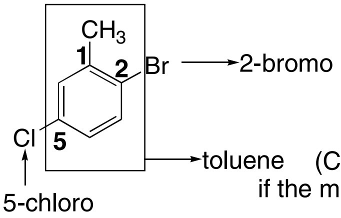
c.



Two groups are 1,3 = meta.

***m*-butylphenol**

d.

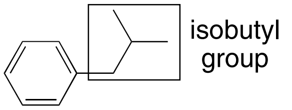


(CH$_3$ group must be at the "1" position, if the molecule is named as a toluene derivative.)

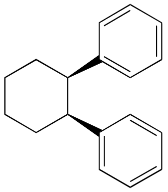
2-bromo-5-chlorotoluene

17.4 Work backwards to draw the structures from the names.

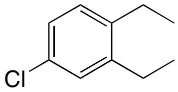
a. isobutylbenzene



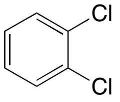
c. *cis*-1,2-diphenylcyclohexane



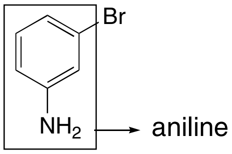
e. 4-chloro-1,2-diethylbenzene



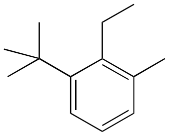
b. *o*-dichlorobenzene



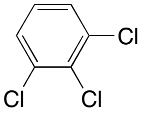
d. *m*-bromoaniline



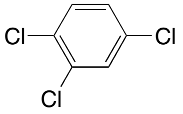
f. 3-*tert*-butyl-2-ethyltoluene



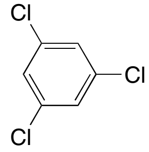
17.5



1,2,3-trichlorobenzene



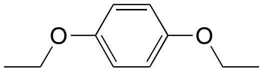
1,2,4-trichlorobenzene



1,3,5-trichlorobenzene

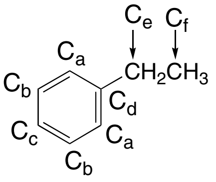
17.6

Molecular formula $C_{10}H_{14}O_2$: 4 degrees of unsaturation
IR absorption at 3150–2850 cm^{-1}: *sp*^{2} and *sp*^{3} hybridized C–H bonds
NMR absorptions (ppm):
- 1.4 (triplet, 6 H)
- 4.0 (quartet, 4 H)
- 6.8 (singlet, 4 H)



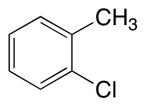
17.7 Count the different types of carbons to determine the number of ^{13}C NMR signals.

a.



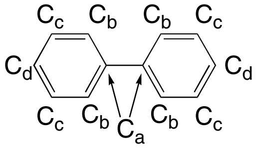
4 types of C's in the benzene ring
6 signals

b.



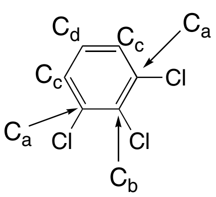
All C's are different.
7 signals

c.

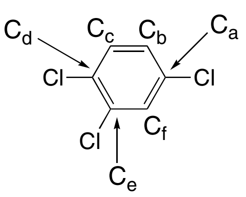


4 signals

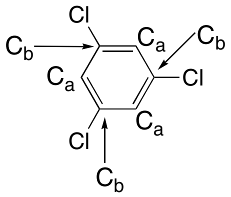
17.8 Each of the three isomeric trichlorobenzenes exhibits a different number of ^{13}C NMR signals.



4 signals

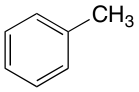


6 signals



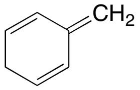
2 signals

17.9 The less stable compound has a larger heat of hydrogenation.



A

benzene ring, more stable
smaller $\Delta H°$

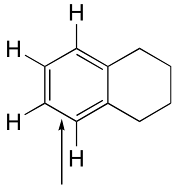


B

no benzene ring, less stable
larger $\Delta H°$

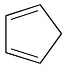
17.10 The protons on sp^2 hybridized carbons in aromatic hydrocarbons are highly deshielded and absorb at 6.5–8 ppm whereas hydrocarbons that are not aromatic show an absorption at 4.5–6 ppm, typical of protons bonded to the C=C of an alkene.

a.



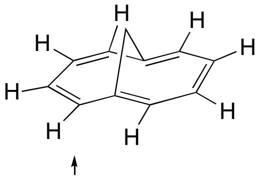
aromatic ring
H's ~ 6.5–8 ppm

b.



not aromatic
alkene H's ~ 4.5–6 ppm

c.



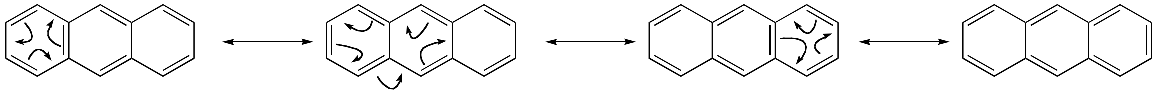
aromatic ring
H's ~ 6.5–8 ppm

17.11 To be aromatic, a ring must have $4n + 2$ π electrons.

$16\ \pi\ e^-$	$20\ \pi\ e^-$	$22\ \pi\ e^-$
$4n$	$4n$	$4n + 2$
$4(4) = 16$	$4(5) = 20$	$4(5) + 2 = 22$
antiaromatic	**antiaromatic**	**aromatic**

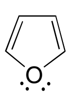
17.12 Annulenes have alternating double and single bonds. An odd number of carbon atoms in the ring would mean there would be two adjacent single bonds. Therefore an annulene having an odd number of carbon atoms cannot exist.

17.13



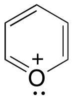
17.14 In determining if a heterocycle is aromatic, count a nonbonded electron pair if it makes the ring aromatic in calculating $4n + 2$. Lone pairs on atoms already part of a multiple bond cannot be delocalized in a ring, and so they are never counted in determining aromaticity.

a.



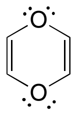
Count one lone pair from O.
$4n + 2 = 4(1) + 2 = 6$
aromatic

b.



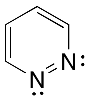
no lone pair from O
$4n + 2 = 4(1) + 2 = 6$
aromatic

c.



With one lone
pair from each O
there would be 8 electrons.
If O's are sp^3 hybridized, the
ring is not completely
conjugated.
not aromatic

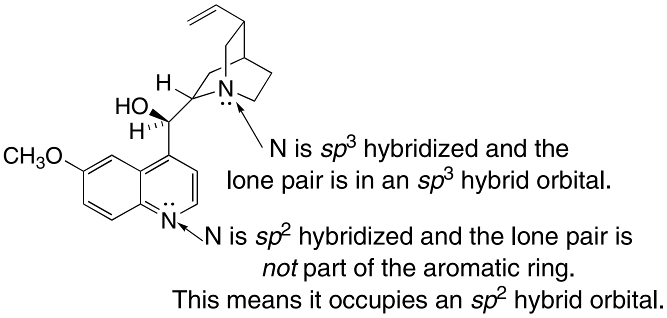
d.



Both N atoms are part of
a double bond, so the lone
pairs cannot be counted:
there are 6 electrons.
$4n + 2 = 4(1) + 2 = 6$
aromatic

17.15

quinine
(antimalarial drug)

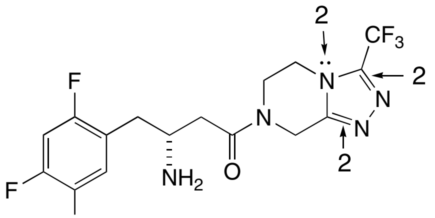


N is sp^3 hybridized and the lone pair is in an sp^3 hybrid orbital.

N is sp^2 hybridized and the lone pair is *not* part of the aromatic ring. This means it occupies an sp^2 hybrid orbital.

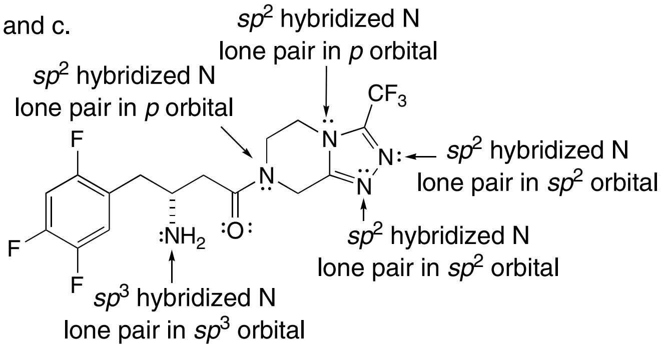
17.16

a. The five-membered ring is aromatic because it has 6 π electrons, two from each π bond and two from the N atom that is not part of a double bond.



sitagliptin

b. and c.



sp^2 hybridized N
lone pair in *p* orbital

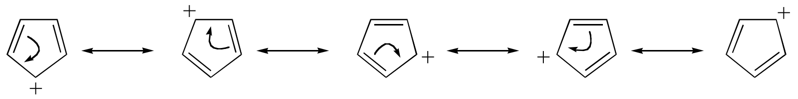
sp^2 hybridized N
lone pair in *p* orbital

sp^2 hybridized N
lone pair in sp^2 orbital

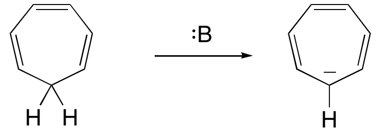
sp^2 hybridized N
lone pair in sp^2 orbital

sp^3 hybridized N
lone pair in sp^3 orbital

17.17



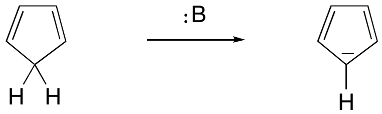
17.18 Compare the conjugate base of 1,3,5-cycloheptatriene with the conjugate base of cyclopentadiene. Remember that the compound with the more stable conjugate base will have a lower pK_a.



1,3,5-cycloheptatriene
pK_a = 39

8 π Electrons make this conjugate base especially unstable (**antiaromatic**).

Since the conjugate base is unstable, the pK_a of 1,3,5-cycloheptatriene is **high**.

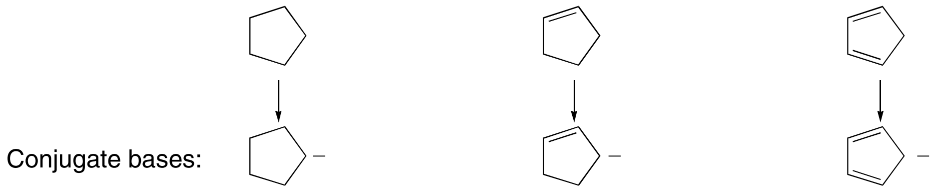


cyclopentadiene

6 π electrons
aromatic conjugate base
very stable anion

Since the conjugate base is very stable, the pK_a of cyclopentadiene is much **lower**.

17.19 The compound with the most stable conjugate base is the most acidic.



no resonance delocalization

most unstable base so **least acidic acid**

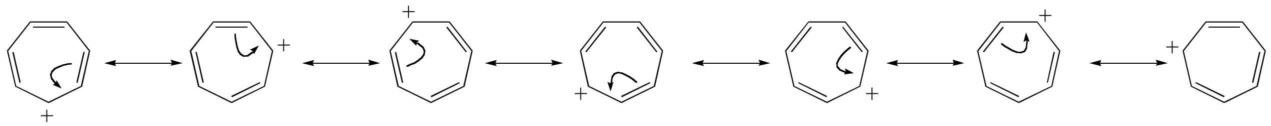
2 resonance structures

The acid is **intermediate in acidity.**

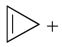
aromatic conjugate base most stable

The acid is the **most acidic.**

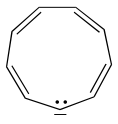
17.20



17.21 To be aromatic, the ions must have 4*n* + 2 π electrons. Ions in (b) and (c) do not have the right number of π electrons to be aromatic.

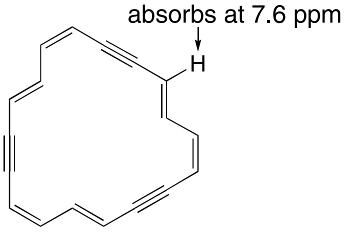
a. 

2 π electrons
4(0) + 2 = 2
aromatic

d. 

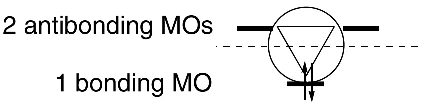
10 π electrons
4(2) + 2 = 10
aromatic

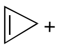
17.22

A = 

The NMR indicates that **A** is aromatic. The C's of the triple bond are *sp* hybridized. Each triple bond has one set of electrons in *p* orbitals that overlap with other *p* orbitals on adjacent atoms in the ring. This overlap allows electrons to delocalize. Each C of the triple bonds also has a *p* orbital in the plane of the ring. The electrons in these *p* orbitals are localized between the C's of the triple bond, and not delocalized in the ring. Although **A** has 24 π e$^-$ total, only 18 e$^-$ are delocalized around the ring.

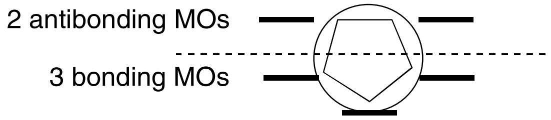
17.23 In using the inscribed polygon method, always draw the vertex pointing down.



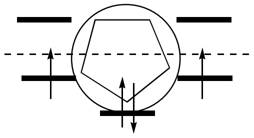


2 π electrons
All bonding MOs are filled.
aromatic

17.24 Draw the inscribed pentagons with the vertex pointing down. Then draw the molecular orbitals (MOs) and add the electrons.

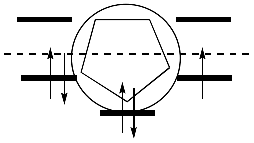


Cation:



4 π electrons
Not all bonding MOs are filled.
not aromatic

Radical:



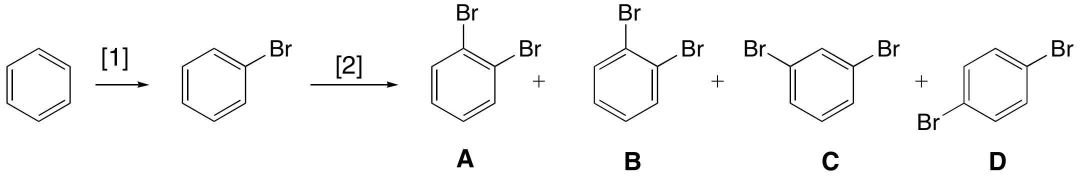
5 π electrons
Not all bonding MOs are filled.
not aromatic

17.25 C_{60} would exhibit only one ^{13}C NMR signal because all the carbons are identical.

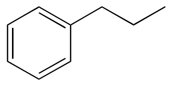
17.26

a. If the Kekulé description of benzene was accurate, 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.

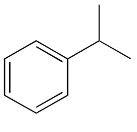
b. In the resonance description, only one product would form in Reaction [1], since all C's are identical, but only three dibromobenzenes (ortho, meta, and para isomers) are possible. **A** and **B** are identical because each C–C bond is identical and intermediate in bond length between a C–C single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



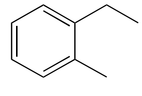
17.27



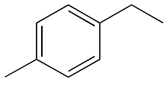
propylbenzene



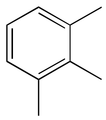
isopropylbenzene



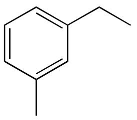
o-ethyltoluene



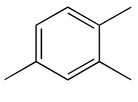
p-ethyltoluene



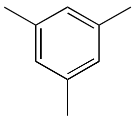
1,2,3-trimethylbenzene



m-ethyltoluene

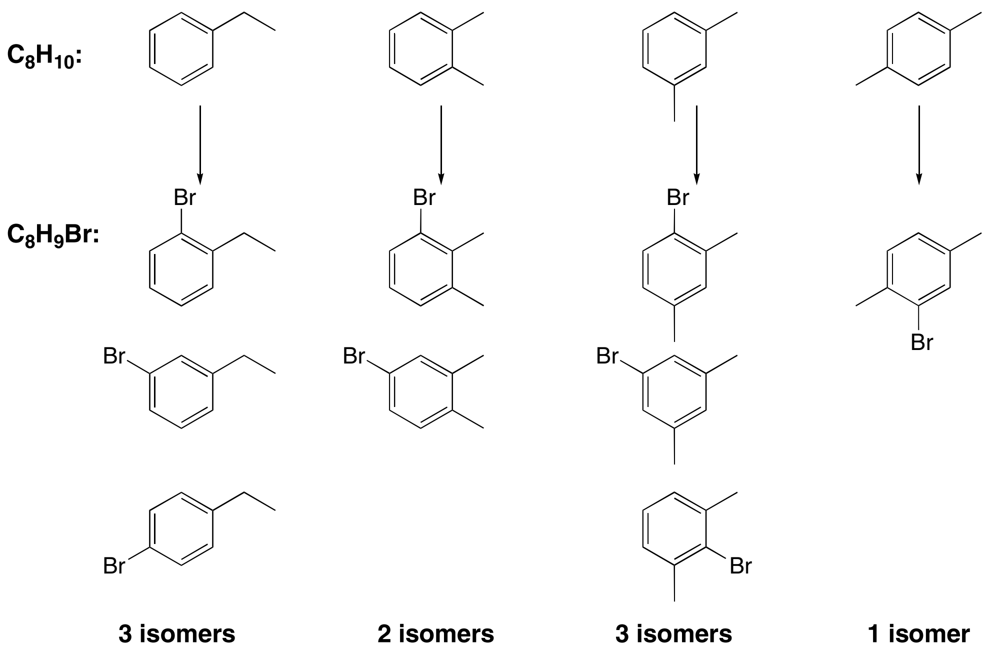


1,2,4-trimethylbenzene



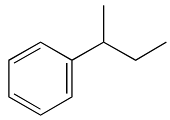
1,3,5-trimethylbenzene

17.28



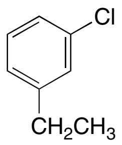
17.29 To name the compounds use the directions from Answer 17.3.

a.



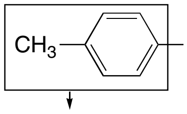
sec-butylbenzene

b.



m-chloroethylbenzene

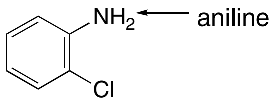
c.



toluene

p-chlorotoluene

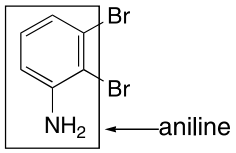
d.



aniline

o-chloroaniline

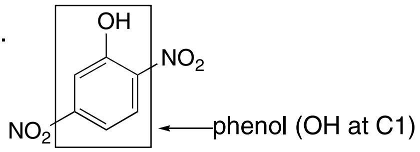
e.



aniline

2,3-dibromoaniline

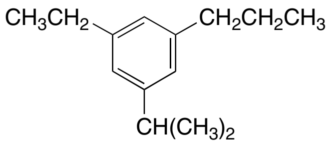
f.



phenol (OH at C1)

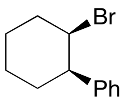
2,5-dinitrophenol

g.



1-ethyl-3-isopropyl-5-propylbenzene

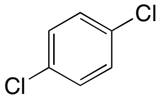
h.



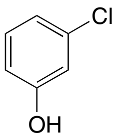
cis-1-bromo-2-phenylcyclohexane

17.30

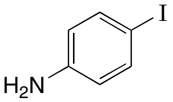
a. *p*-dichlorobenzene



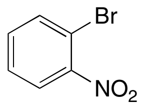
b. *m*-chlorophenol



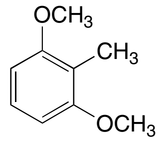
c. *p*-iodoaniline



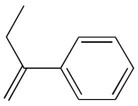
d. *o*-bromonitrobenzene



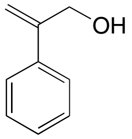
e. 2,6-dimethoxytoluene



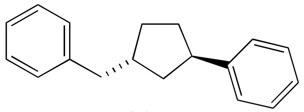
f. 2-phenyl-1-butene



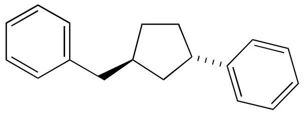
g. 2-phenyl-2-propen-1-ol



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

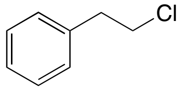


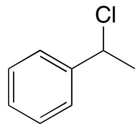
or



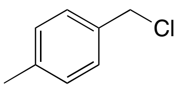
17.31

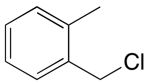
a. constitutional isomers of molecular formula **C_8H_9Cl**, and b. names of the trisubstituted benzenes

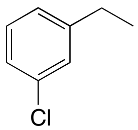


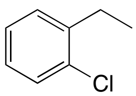


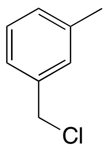
stereoisomers
for this isomer

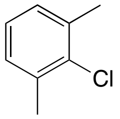




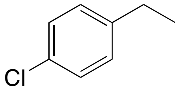


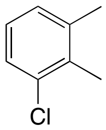




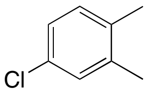


2-chloro-1,3-dimethylbenzene

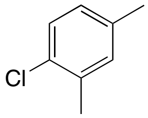




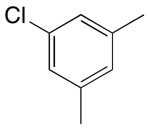
1-chloro-2,3-dimethylbenzene



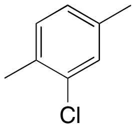
4-chloro-1,2-dimethylbenzene



1-chloro-2,4-dimethylbenzene

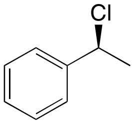


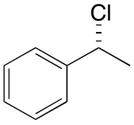
1-chloro-3,5-dimethylbenzene



2-chloro-1,4-dimethylbenzene

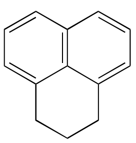
c. stereoisomers





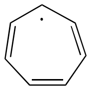
17.32 Count the electrons in the π bonds. Each π bond holds two electrons.

a.



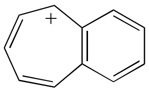
10 π electrons

b.



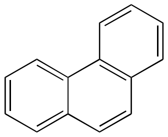
7 π electrons

c.



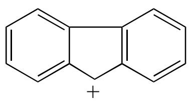
10 π electrons

d.



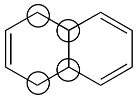
14 π electrons

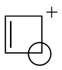
e.

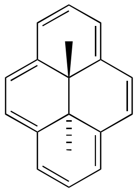


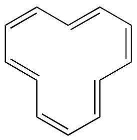
12 π electrons

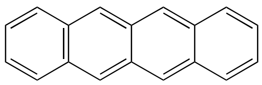
17.33 To be aromatic, the compounds must be cyclic, planar, completely conjugated, and have $4n + 2$ π electrons.

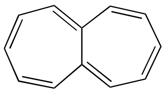
a.

Circled C's are not sp^2.
not completely conjugated
not aromatic

d.

Circled C is not sp^2.
not completely conjugated
not aromatic

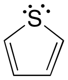
b.

14 π electrons in outer ring
aromatic

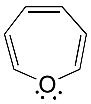
e.

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

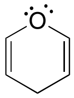
c.

4 benzene rings
joined together
aromatic

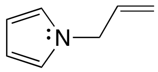
f.

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

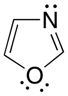
17.34 In determining if a heterocycle is aromatic, count a nonbonded electron pair if it makes the ring aromatic in calculating $4n + 2$. Lone pairs on atoms already part of a multiple bond cannot be delocalized in a ring, and so they are never counted in determining aromaticity.

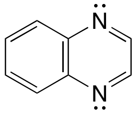
a.

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

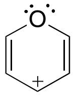
c.

not aromatic

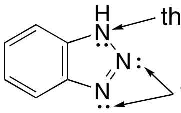
e.

not aromatic

g.

6 π electrons
counting the lone
pair from N
4(1) + 2 = 6
aromatic

b.

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

d.

10 π electrons
4(2) + 2 = 10
aromatic

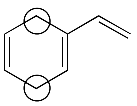
f.

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

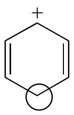
h.

Count
these 2e⁻.

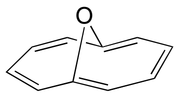
These lone
pairs are on
doubly
bonded N
atoms, so they
can't be
counted.

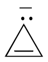
10 π electrons
4(2) + 2 = 10
aromatic

17.35

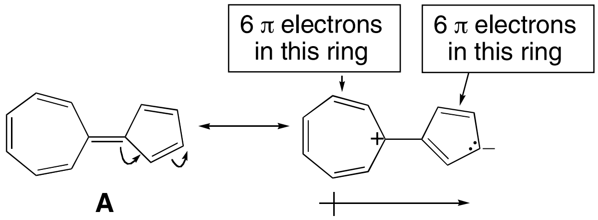
a.

Circled C's are
not sp^2.
not aromatic

c.

Circled C is
not sp^2.
not aromatic

b.

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

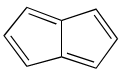
d.

4 π electrons
4(1) = 4
antiaromatic

17.36



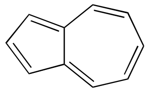
A resonance structure can be drawn for **A** that places a negative charge in the five-membered ring and a positive charge in the seven-membered ring. This resonance structure shows that each ring has 6 π electrons, making it aromatic. The molecule possesses a dipole such that the seven-membered ring is electron deficient and the five-membered ring is electron rich.

17.37 Each compound is completely conjugated. A compound with 4*n* + 2 π electrons is especially stable, while a compound with 4*n* π electrons is especially unstable.



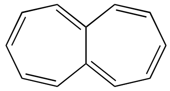
pentalene

8 π electrons
4(2) = 8
antiaromatic
unstable



azulene

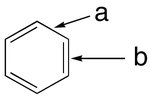
10 π electrons
4(2) + 2 = 10
aromatic
very stable



heptalene

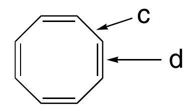
12 π electrons
6(2) = 12
antiaromatic
unstable

17.38 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 π electrons: aromatic
all bonds of equal length
intermediate

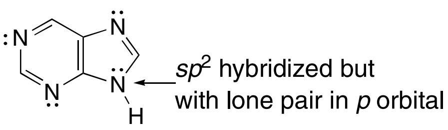
cyclooctatetraene



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

d < a = b < c

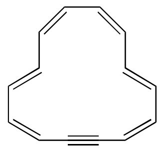
17.39



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.

17.40



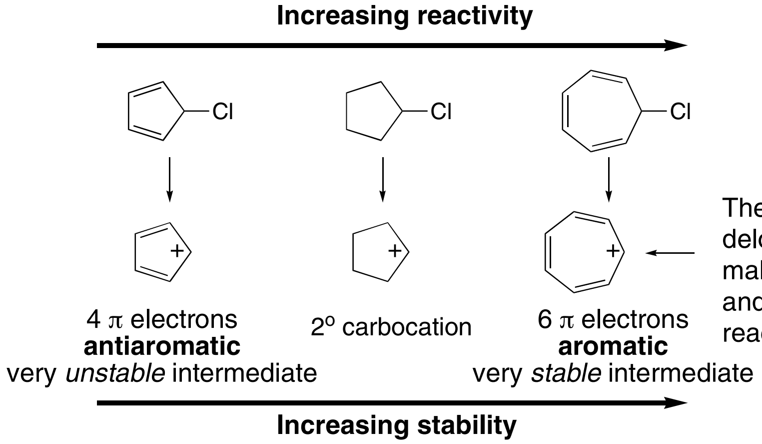
C

a. 16 total π electrons

b. 14 π 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.]

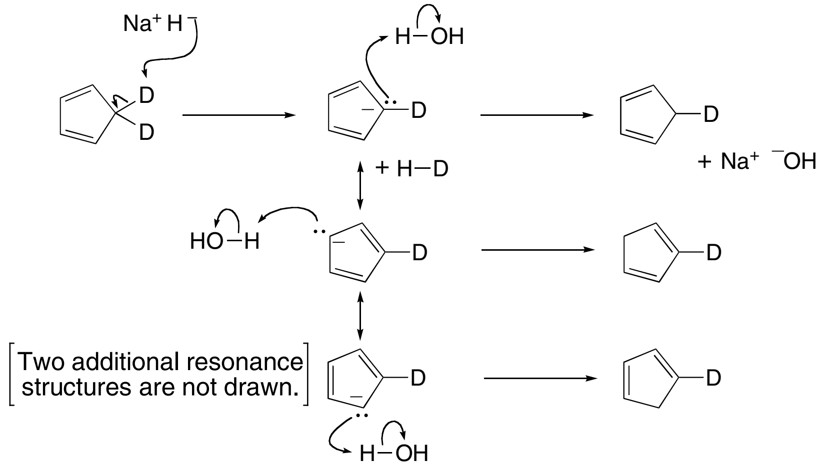
c. By having two of the *p* orbitals of the C–C triple bond co-planar with the *p* orbitals of all the C=C's, the total number of π electrons delocalized in the ring is 14. 4(3) + 2 = 14, so the ring is **aromatic.**

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



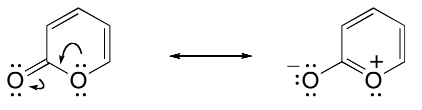
The aromatic carbocation is delocalized over the whole ring, making it a very stable intermediate and most easily formed in an S_N1 reaction.

17.42



[Two additional resonance structures are not drawn.]

17.43 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

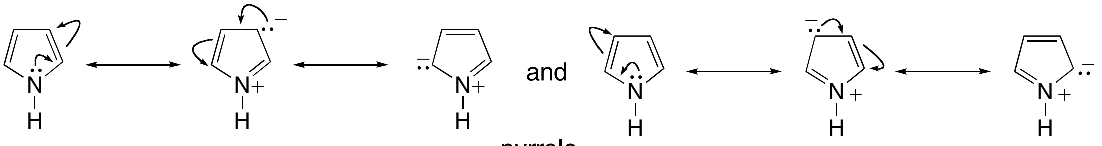
6 π electrons

17.44

a.

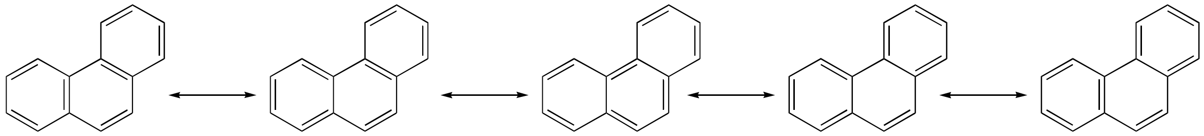
cyclopropenyl radical

b.



pyrrole

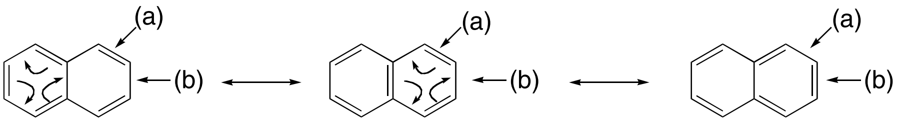
c.



phenanthrene

17.45

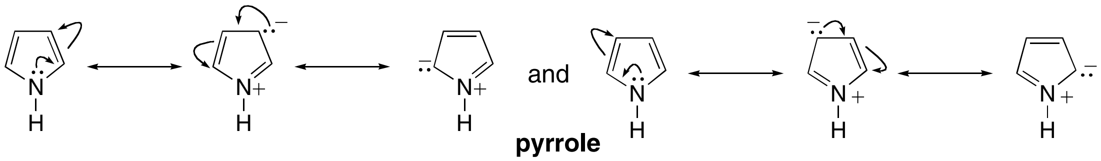
Naphthalene can be drawn as three resonance structures:



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.

17.46

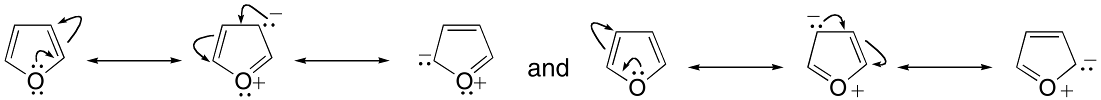
a.



pyrrole

Pyrrole is less resonance stabilized than benzene because four of the resonance structures have charges, making them less good.

b.



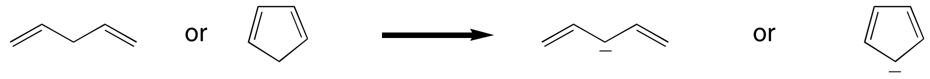
furan

Furan is less resonance stabilized than pyrrole because its O atom is less basic, so it donates electron density less "willingly." Thus, charge-separated resonance forms are more minor contributors to the hybrid than the charge-separated resonance forms of pyrrole.

17.47 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.

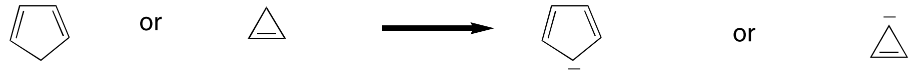


more acidic

resonance-stabilized
but not aromatic

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

b.

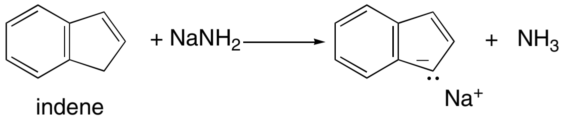


more acidic

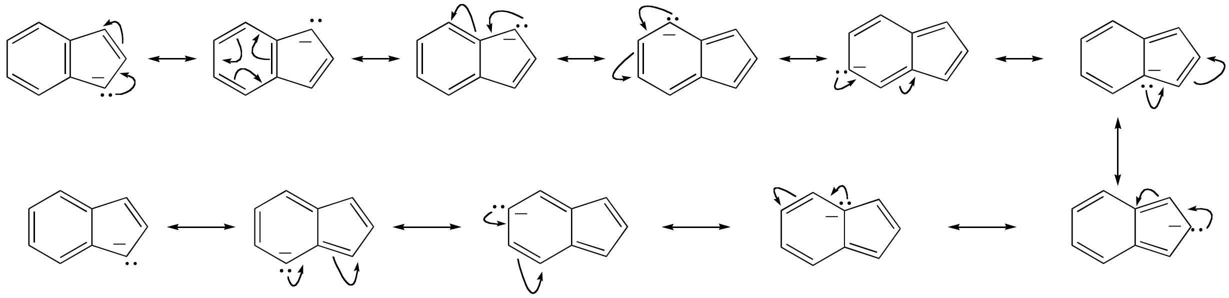
6 π electrons, aromatic
more stable conjugate base
Its acid is more acidic.

antiaromatic
highly destabilized
conjugate base

17.48

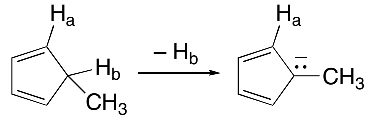


indene



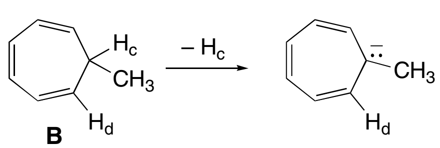
The conjugate base of indene has 10 π electrons making it aromatic and very stable. Therefore, indene is more acidic than many hydrocarbons.

17.49



A

H_b is most acidic because its conjugate base is aromatic (6 π electrons).

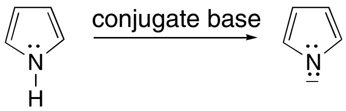


B

H_c is least acidic because its conjugate base has 8 π electrons, making it antiaromatic.

17.50

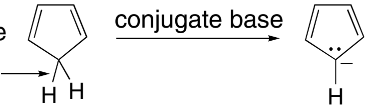
pyrrole



Both pyrrole and the conjugate base of pyrrole have 6 π electrons in the ring, making them both aromatic. Thus, deprotonation of pyrrole does not result in a gain of aromaticity since the starting material is aromatic to begin with.

cyclopentadiene

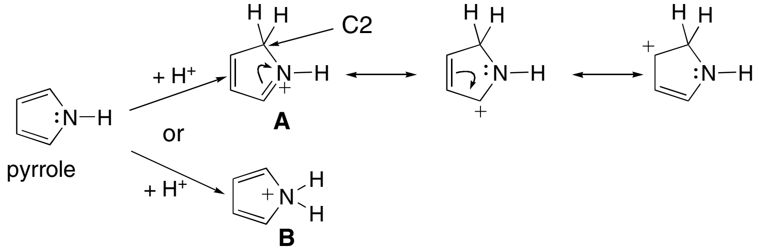
more acidic



Cyclopentadiene is not aromatic, but the conjugate base has 6 π electrons and is therefore aromatic. This makes the C–H bond in cyclopentadiene more acidic than the N–H bond in pyrrole, since deprotonation of cyclopentadiene forms an aromatic conjugate base.

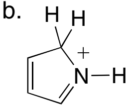
17.51

a.



Protonation at C2 forms conjugate acid **A** because the positive charge can be delocalized by resonance. There is no resonance stabilization of the positive charge in **B**.

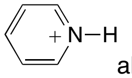
b.



A

pK_a = 0.4

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



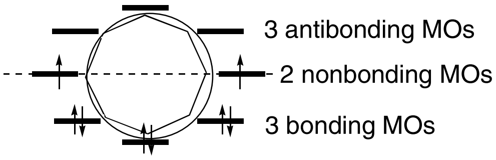
pK_a = 5.2

C

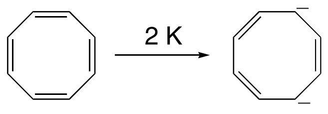
Both **C** and its conjugate base pyridine are aromatic. Since **C** has six π electrons, it is already aromatic to begin with, so there is less to be gained by deprotonation, and **C** is thus less acidic than **A**.

17.52

a.



cyclooctatetraene and its 8 π electrons



cyclooctatetraene

dianion of cyclooctatetraene

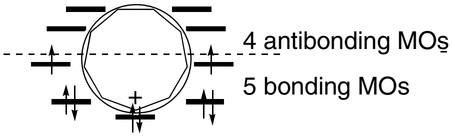
b. Even if cyclooctatetraene were flat, it has two unpaired electrons in its HOMOs (nonbonding MOs) so it cannot be aromatic.

c. The dianion has 10 π 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.

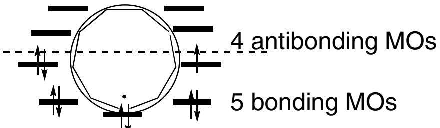
e. The dianion is aromatic since its HOMOs are completely filled, and it has no electrons in antibonding MOs.

17.53



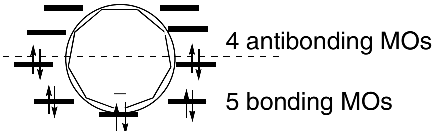
cyclononatetraenyl cation

8 π electrons
antiaromatic



cyclononatetraenyl radical

9 π electrons
not aromatic

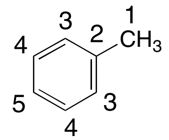


cyclononatetraenyl anion

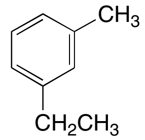
10 π electrons
aromatic

All bonding MOs are filled.

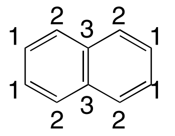
17.54 The number of different types of C's = the number of signals.

a.


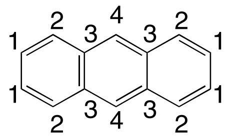
5 different C's

b.


all unique
9 different C's

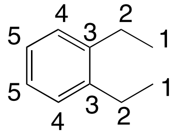
c.


3 different C's

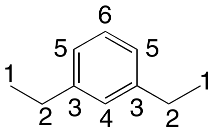
d.


4 different C's

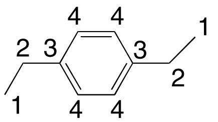
17.55 Draw the three isomers and count the different types of carbons in each. Then match the structures with the data.



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]

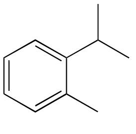
17.56

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}

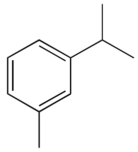
^1H NMR data:

Absorption	**ppm**	**# of H's**	**Explanation**	
doublet	1.2	6	6 H's adjacent to 1 H	$(CH_3)_2CH$ group
singlet	2.3	3	CH_3	
septet	3.1	1	1 H adjacent to 6 H's	
multiplet	7–7.4	4	a disubstituted benzene ring	

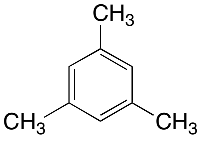
You can't tell from these data where the two groups are on the benzene ring. They are not para, since the para arrangement usually gives two sets of distinct peaks (resembling two doublets) so there are two possible structures—ortho and meta isomers.



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: 9 H'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:

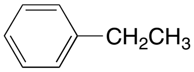


c. C_8H_{10}: IR absorptions at 3108–2875 (sp^2 and sp^3 hybridized C–H), 1606, and 1496 (due to a benzene ring) cm^{-1}

^1H NMR data:

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

Structure:



17.57

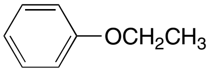
a. Compound **A**: Molecular formula $C_8H_{10}O$

IR absorption at 3150–2850 (sp^2 and sp^3 hybridized C–H) cm^{-1}

^1H NMR data:

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

Structure:



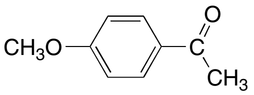
b. Compound **B**: Molecular formula $C_9H_{10}O_2$

IR absorption at 1669 (C=O) cm^{-1}

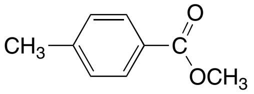
^1H NMR data:

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

Structure:



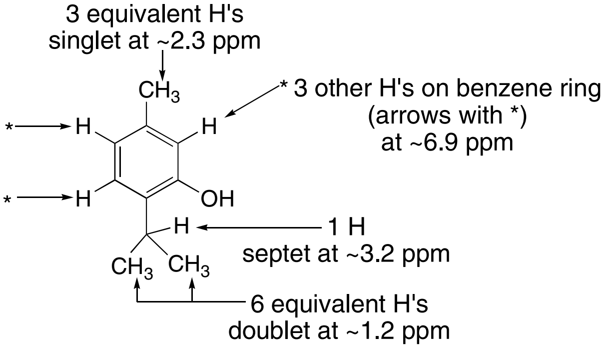
or



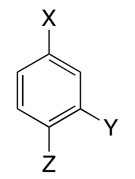
It would be hard to distinguish these two compounds with the given data.

17.58

thymol



IR absorptions:
3500–3200 cm^{-1} (O–H)
3150–2850 cm^{-1} (C–H bonds)
1621 and 1585 cm^{-1} (benzene ring)

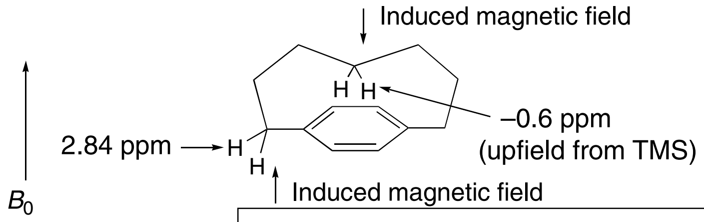


basic structure of thymol

Thymol must have this basic structure given the NMR and IR data since it is a trisubstituted benzene ring with one singlet and two doublets in the NMR at ~6.9 ppm. However, which group [OH, CH_3, or $CH(CH_3)_2$] corresponds to X, Y, and Z is not readily distinguished with the given data. The correct structure for thymol is given.

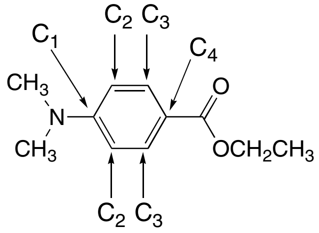
17.59

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 somewhat higher chemical shift.

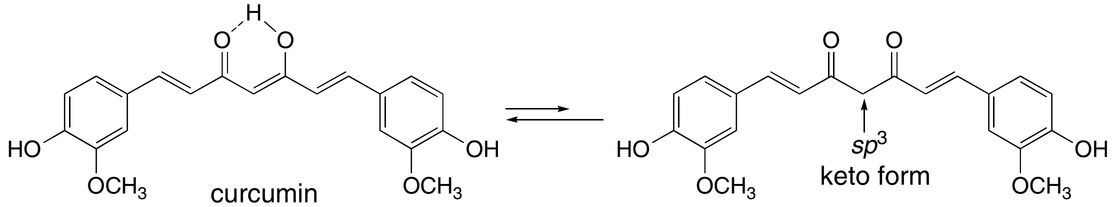
17.60



^{13}C NMR has four lines that are located in the aromatic region (~110–155 ppm), corresponding to the four different types of carbons in the aromatic ring of the para isomer. The ortho and meta isomers have six different C's, and so six lines would be expected for each of them.

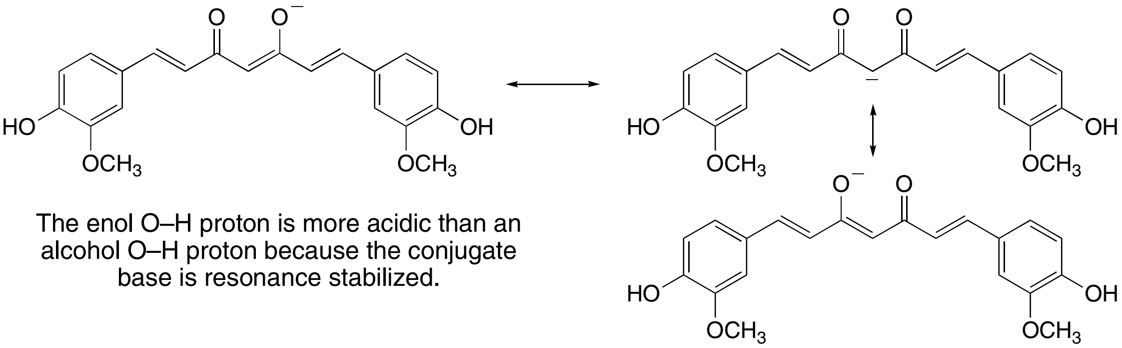
17.61

a.



The enol form is more stable because the enol double bond makes a highly conjugated system. The enol OH can also intramolecularly hydrogen bond to the nearby carbonyl O atom.

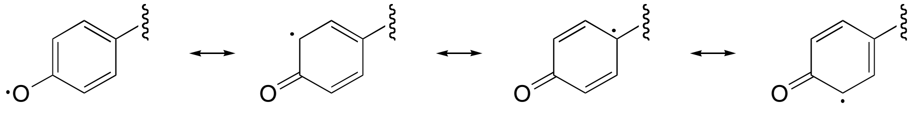
b.



The enol O–H proton is more acidic than an alcohol O–H proton because the conjugate base is resonance stabilized.

c. Curcumin is colored because it has many conjugated π electrons, which shift absorption of light from the UV to the visible region.

d. Curcumin is an antioxidant because it contains a phenol. Homolytic cleavage affords a resonance-stabilized phenoxy radical, which can inhibit oxidation from occurring, much like vitamin E and BHT in Chapter 15.



(+ other resonance structures)

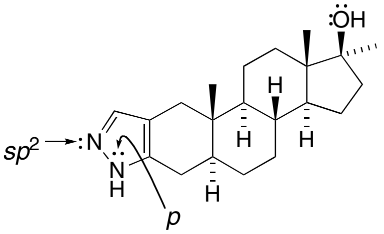
phenoxy radical

Resonance delocalizes the radical on the ring and C chain of curcumin.

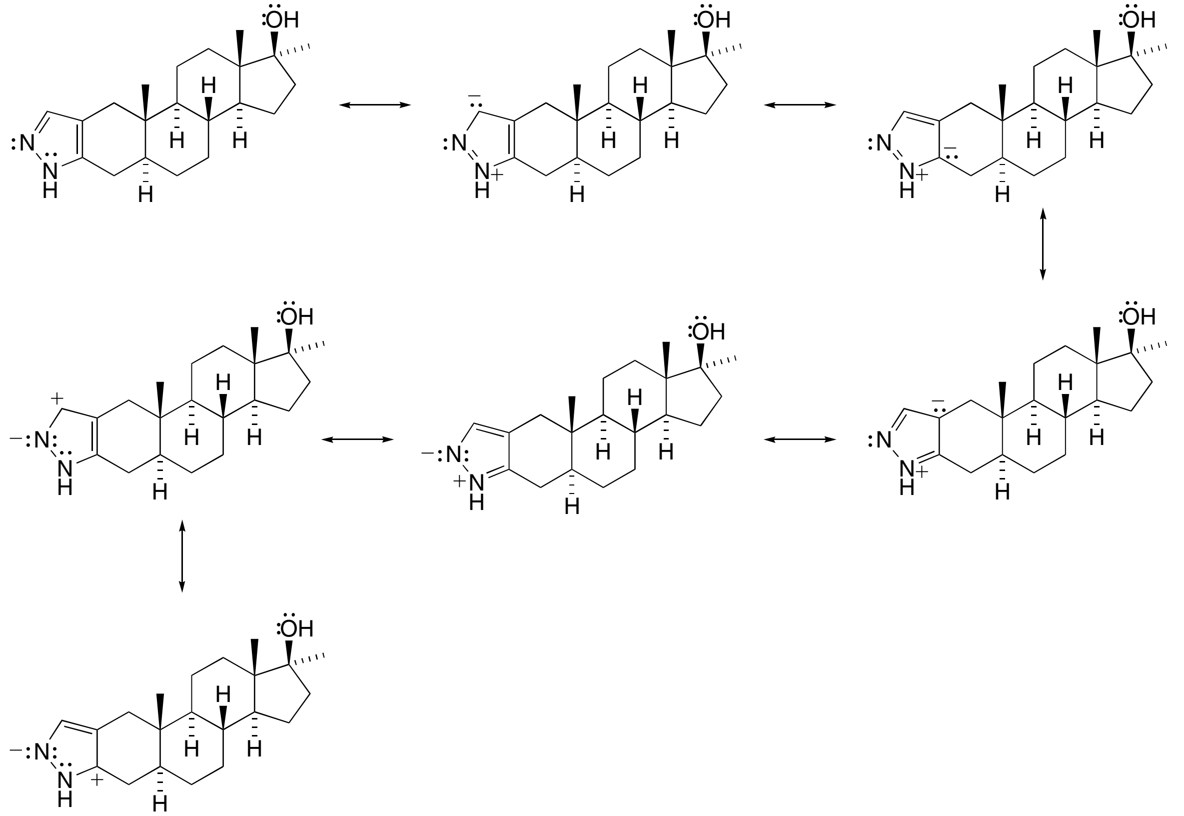
17.62

a. Pyrazole rings are aromatic because they have 6 π electrons—two from the lone pair on the N atom that is not part of the double bond, and four from the double bonds.

b.

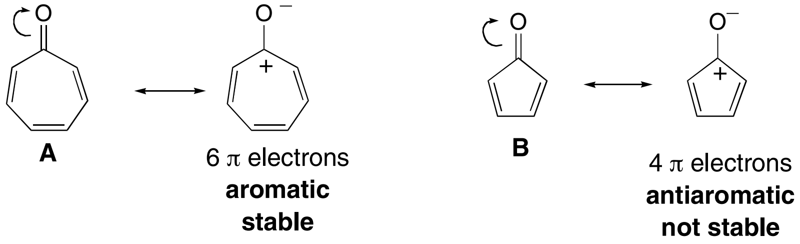


c.

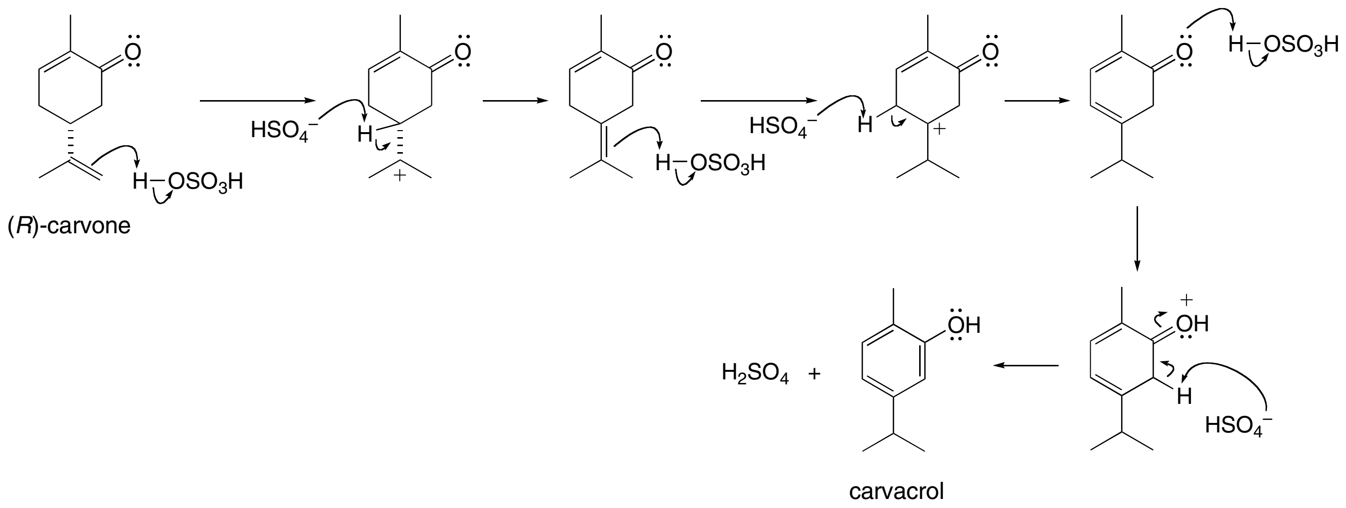


d. The N atom in the NH bond in the pyrazole ring is sp^2 hybridized with 33% *s*-character, increasing the acidity of the N–H bond. The N–H bond of CH_3NH_2 contains an sp^3 hybridized N atom.

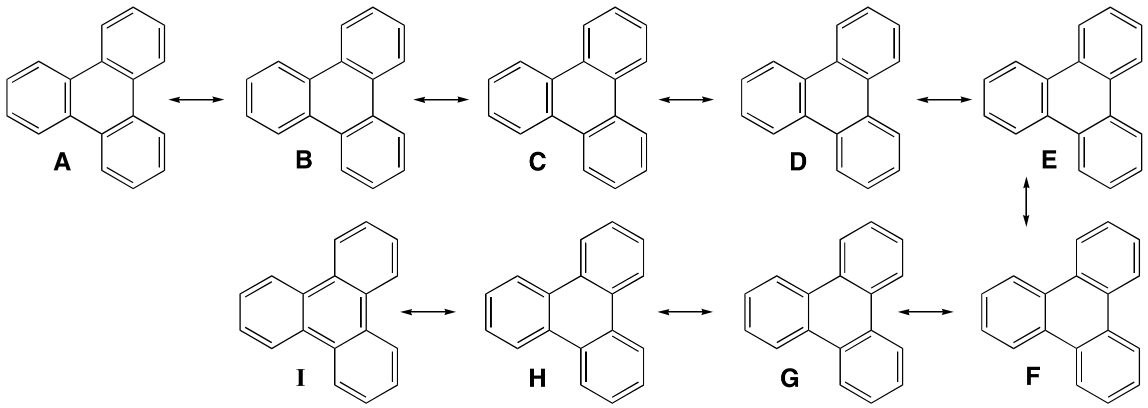
17.63 A second resonance structure for **A** shows that the ring is completely conjugated and has 6 π electrons, making it aromatic and especially stable. A similar charge-separated resonance structure for **B** makes the ring completely conjugated, but gives the ring 4 π electrons, making it antiaromatic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



17.64 The conversion of carvone to carvacrol involves acid-catalyzed isomerization of two double bonds and tautomerization of a ketone to an enol tautomer. In this case the enol form is part of an aromatic phenol. Each isomerization of a C=C involves Markovnikov addition of a proton, followed by deprotonation.

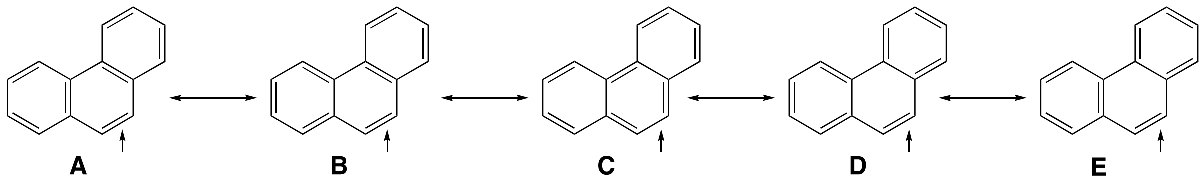


17.65 Resonance structures for triphenylene:



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.

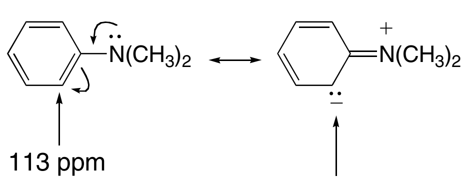
Resonance structures for phenanthrene:



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.

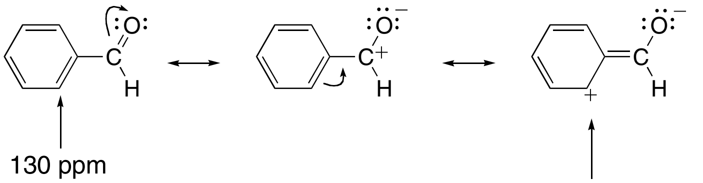
17.66

X



The negative charge and increased electron density make the carbon more shielded and shift the absorption upfield.

Y



The positive charge and decreased electron density make the carbon deshielded and shift the absorption downfield.