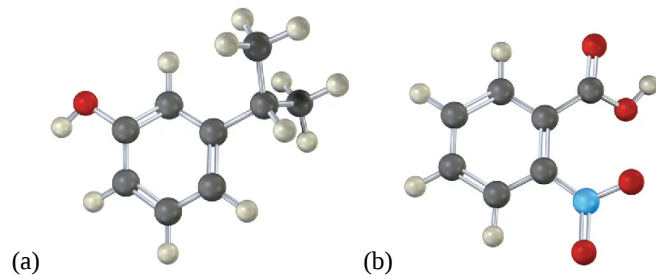


2.9: Additional Problems

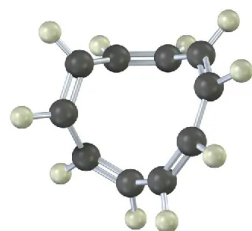
2 • Additional Problems

Visualizing Chemistry

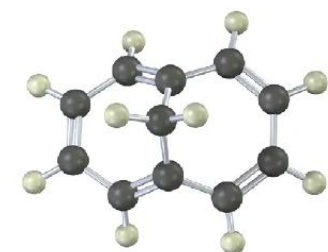
PROBLEM 2-13 Give IUPAC names for the following substances (red = O, blue = N):



PROBLEM 2-14 All-cis cyclodecapentaene is a stable molecule that shows a single absorption in its ^1H NMR spectrum at $5.67\ \delta$. Tell whether it is aromatic, and explain its NMR spectrum.

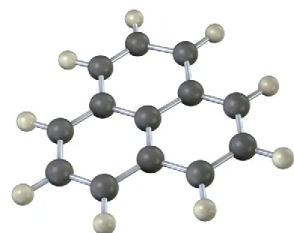


PROBLEM 2-15 1,6-Methanonaphthalene has an interesting ^1H NMR spectrum in which the eight hydrogens around the perimeter absorb at 6.9 to $7.3\ \delta$, while the two CH_2 protons absorb at $-0.5\ \delta$. Tell whether it is aromatic, and explain its NMR spectrum.

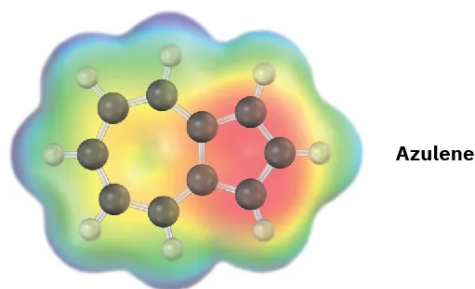


1,6-Methanonaphthalene

PROBLEM 2-16 The following molecular model is that of a carbocation. Draw two resonance structures for the carbocation, indicating the positions of the double bonds.

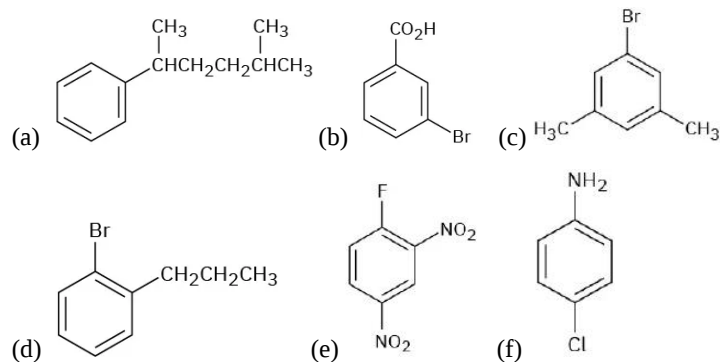


PROBLEM 2-17 Azulene, an isomer of naphthalene, has a remarkably large dipole moment for a hydrocarbon ($\mu = 1.0\ \text{D}$). Explain, using resonance structures.



Naming Aromatic Compounds

PROBLEM 2-18 Give IUPAC names for the following compounds:



PROBLEM 2-19 Draw structures corresponding to the following names:

- (a) 3-Methyl-1,2-benzenediamine (b) 1,3,5-Benzenetriol (c) 3-Methyl-2-phenylhexane
 (d) *o*-Aminobenzoic acid (e) *m*-Bromophenol (f) 2,4,6-Trinitrophenol (picric acid)

PROBLEM 2-20 Draw and name all possible isomers of the following:

- (a) Dinitrobenzene (b) Bromodimethylbenzene (c) Trinitrophenol

PROBLEM 2-21 Draw and name all possible aromatic compounds with the formula C_7H_7Cl .

PROBLEM 2-22 Draw and name all possible aromatic compounds with the formula C_8H_9Br . (There are 14.)

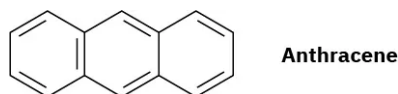
Structure of Aromatic Compounds

PROBLEM 2-23 Propose structures for aromatic hydrocarbons that meet the following descriptions:

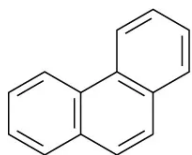
- (a) C_9H_{12} ; gives only one $C_9H_{11}Br$ product on substitution of a hydrogen on the aromatic ring with bromine
- (b) $C_{10}H_{14}$; gives only one $C_{10}H_{13}Cl$ product on substitution of a hydrogen on the aromatic ring with chlorine
- (c) C_8H_{10} ; gives three C_8H_9Br products on substitution of a hydrogen on the aromatic ring with bromine
- (d) $C_{10}H_{14}$; gives two $C_{10}H_{13}Cl$ products on substitution of a hydrogen on the aromatic ring with chlorine

PROBLEM 2-24 Look at the three resonance structures of naphthalene shown in Section 2.7, and account for the fact that not all carbon-carbon bonds have the same length. The C1-C2 bond is 136 pm long, whereas the C2-C3 bond is 139 pm long.

PROBLEM 2-25 Anthracene has four resonance structures, one of which is shown. Draw the other three.



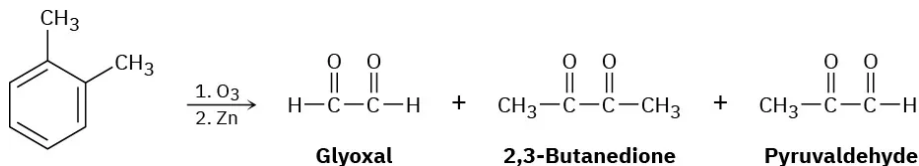
PROBLEM 2-26 Phenanthrene has five resonance structures, one of which is shown. Draw the other four.



Phenanthrene

PROBLEM 2-27 Look at the five resonance structures for phenanthrene (Problem 26), and predict which of its carbon–carbon bonds is shortest.

PROBLEM 2-28 In 1932, A. A. Levine and A. G. Cole studied the ozonolysis of *o*-xylene and isolated three products: glyoxal, 2,3-butanedione, and pyruvaldehyde:



In what ratio would you expect the three products to be formed if *o*-xylene is a resonance hybrid of two structures? The actual ratio found was 3 parts glyoxal, 1 part 2,3-butanedione, and 2 parts pyruvaldehyde. What conclusions can you draw about the structure of *o*-xylene?

Aromaticity and Hückel's Rule

PROBLEM 2-29 3-Chlorocyclopropene, on treatment with AgBF_4 , gives a precipitate of AgCl and a stable solution of a product that shows a single ^1H NMR absorption at 11.04 δ . What is a likely structure for the product, and what is its relation to Hückel's rule?



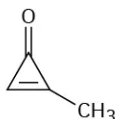
3-Chlorocyclopropene

PROBLEM 2-30 Draw an energy diagram for the three molecular orbitals of the cyclopropenyl system (C_3H_3). How are these three molecular orbitals occupied in the cyclopropenyl anion, cation, and radical? Which of the three substances is aromatic according to Hückel's rule?

PROBLEM 2-31 Cyclopropanone is highly reactive because of its large amount of angle strain. Methylcyclopropenone, although even more strained than cyclopropanone, is nevertheless quite stable and can even be distilled. Explain, taking the polarity of the carbonyl group into account.

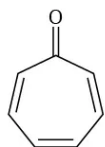


Cyclopropanone

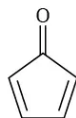


Methylcyclopropenone

PROBLEM 2-32 Cycloheptatrienone is stable, but cyclopentadienone is so reactive that it can't be isolated. Explain, taking the polarity of the carbonyl group into account.



Cycloheptatrienone

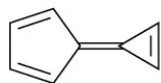


Cyclopentadienone

PROBLEM 2-33 Which would you expect to be most stable, cyclononatetraenyl radical, cation, or anion? (Cyclononatetraene has a ring of nine carbons and four double bonds.)

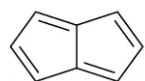
PROBLEM 2-34 How might you convert 1,3,5,7-cyclononatetraene to an aromatic substance?

PROBLEM 2-35 Calicene, like azulene (Problem 17), has an unusually large dipole moment for a hydrocarbon. Explain, using resonance structures.

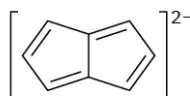


Calicene

PROBLEM 2-36 Pentalene is a most elusive molecule that has been isolated only at liquid-nitrogen temperature. The pentalene dianion, however, is well known and quite stable. Explain.



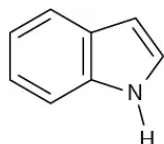
Pentalene



Pentalene dianion

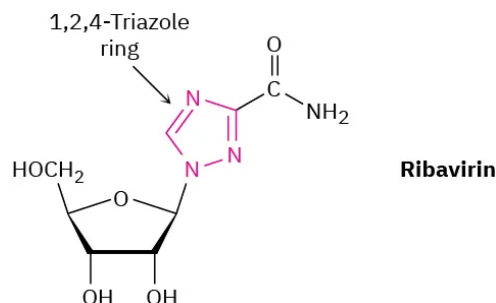
PROBLEM 2-37 Indole is an aromatic heterocycle that has a benzene ring fused to a pyrrole ring. Draw an orbital picture of indole.

- (a) How many π electrons does indole have?
- (b) What is the electronic relationship of indole to naphthalene?



Indole

PROBLEM 2-38 Ribavirin, an antiviral agent used against hepatitis C and viral pneumonia, contains a 1,2,4-triazole ring. Why is the ring aromatic?



Ribavirin

Spectroscopy

PROBLEM 2-39 Compound A, C_8H_{10} , yields three substitution products, C_8H_9Br , on reaction with Br_2 . Propose two possible structures for A. The 1H NMR spectrum of A shows a complex four-proton multiplet at 7.0δ and a six-proton singlet at 2.30δ . What is the structure of A?

PROBLEM 2-40 What is the structure of a hydrocarbon that has $M^+ = 120$ in its mass spectrum and has the following 1H NMR spectrum?

7.25δ (5 H, broad singlet); 2.90δ (1 H, septet, $J = 7$ Hz); 1.22δ (6 H, doublet, $J = 7$ Hz)

PROBLEM 2-41 Propose structures for compounds that fit the following descriptions:

(a) $C_{10}H_{14}$

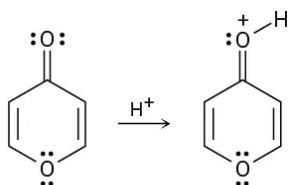
- 1H NMR: 7.18δ (4 H, broad singlet); 2.70δ (4 H, quartet, $J = 7$ Hz); 1.20δ (6 H, triplet, $J = 7$ Hz)
- IR absorption at 745 cm^{-1}

(b) $C_{10}H_{14}$

- 1H NMR: 7.0δ (4 H, broad singlet); 2.85δ (1 H, septet, $J = 8$ Hz); 2.28δ (3 H, singlet); 1.20δ (6 H, doublet, $J = 8$ Hz)
- IR absorption at 825 cm^{-1}

General Problems

PROBLEM 2-42 On reaction with acid, 4-pyrone is protonated on the carbonyl-group oxygen to give a stable cationic product. Using resonance structures and the Hückel $4n + 2$ rule, explain why the protonated product is so stable.

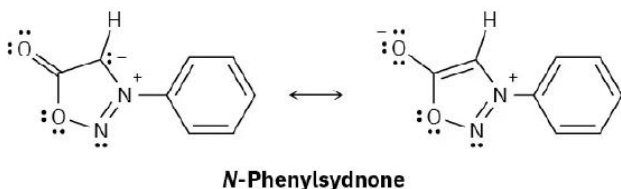


4-Pyrone

PROBLEM 2-43 Bextra, a COX-2 inhibitor once used in the treatment of arthritis, contains an isoxazole ring. Why is the ring aromatic?



PROBLEM 2-44 *N*-Phenylsydnone, so-named because it was first studied at the University of Sydney, Australia, behaves like a typical aromatic molecule. Explain, using the Hückel $4n + 2$ rule.

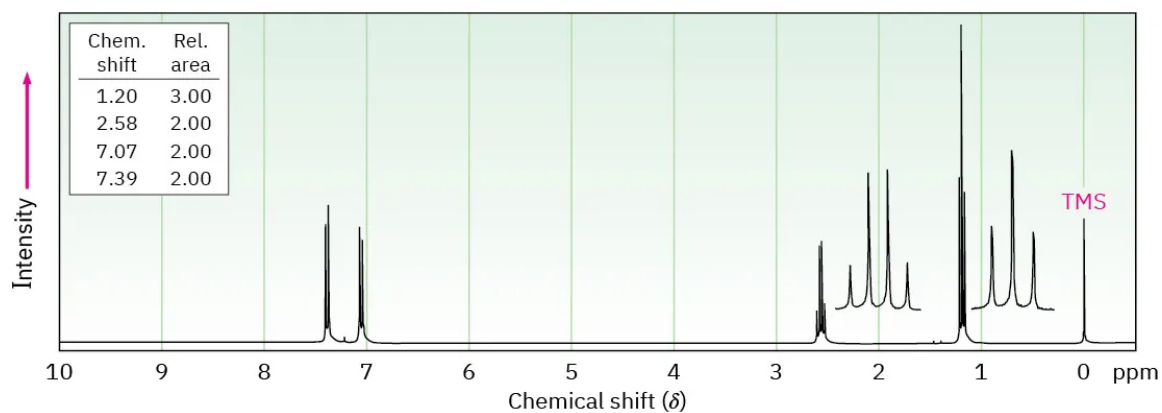


PROBLEM 2-45 Show the relative energy levels of the seven π molecular orbitals of the cycloheptatrienyl system. Tell which of the seven orbitals are filled in the cation, radical, and anion, and account for the aromaticity of the cycloheptatrienyl cation.

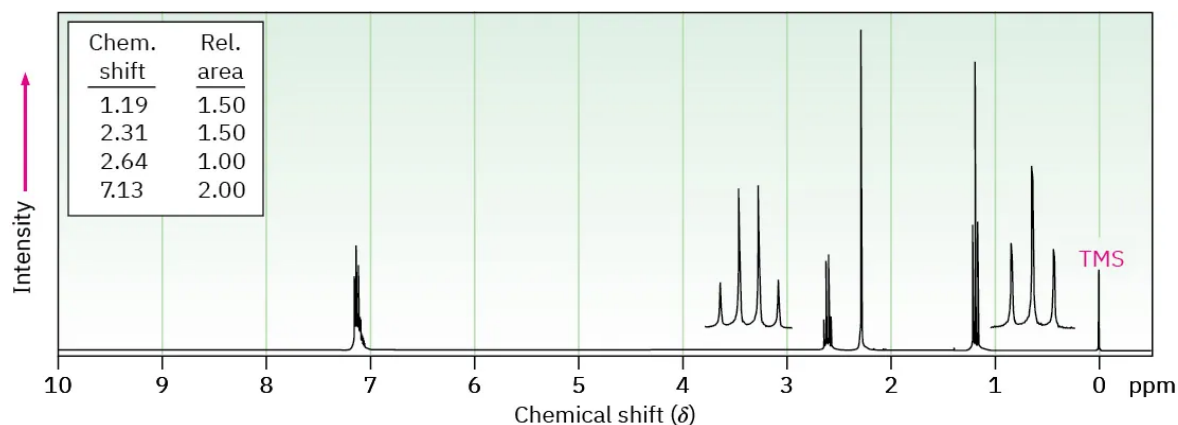
PROBLEM 2-46 1-Phenyl-2-butene has an ultraviolet absorption at $\lambda_{\max} = 208 \text{ nm}$ ($\epsilon = 8000$). On treatment with a small amount of strong acid, isomerization occurs and a new substance with $\lambda_{\max} = 250 \text{ nm}$ ($\epsilon = 15,800$) is formed. Propose a structure for this isomer, and suggest a mechanism for its formation.

PROBLEM 2-47 Propose structures for aromatic compounds that have the following 1H NMR spectra:

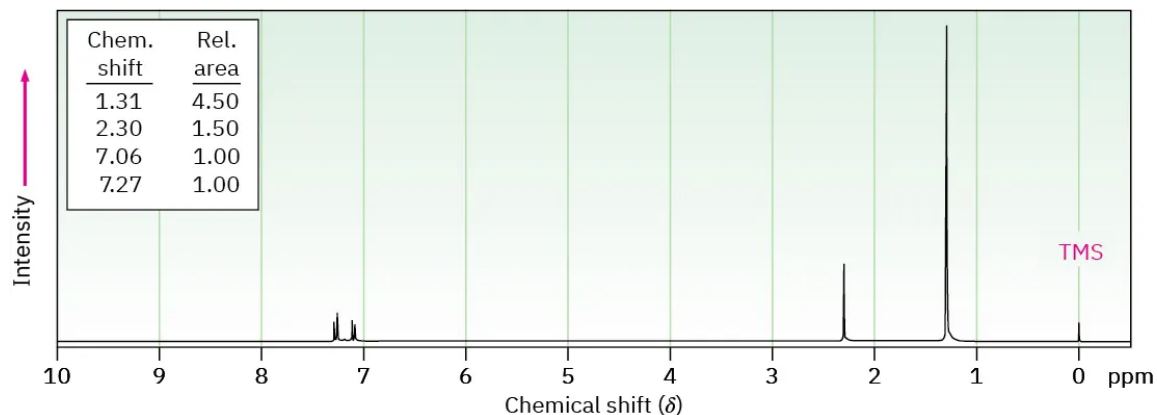
(a) C_8H_9Br - IR absorption at 820 cm^{-1}



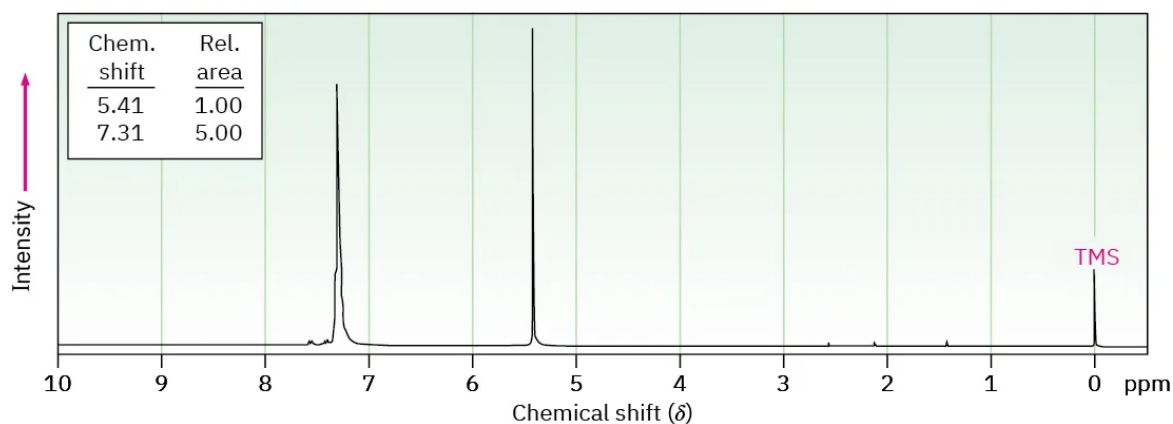
(b) C_9H_{12} - IR absorption at 750 cm^{-1}



(c) $C_{11}H_{16}$ - IR absorption at 820 cm^{-1}

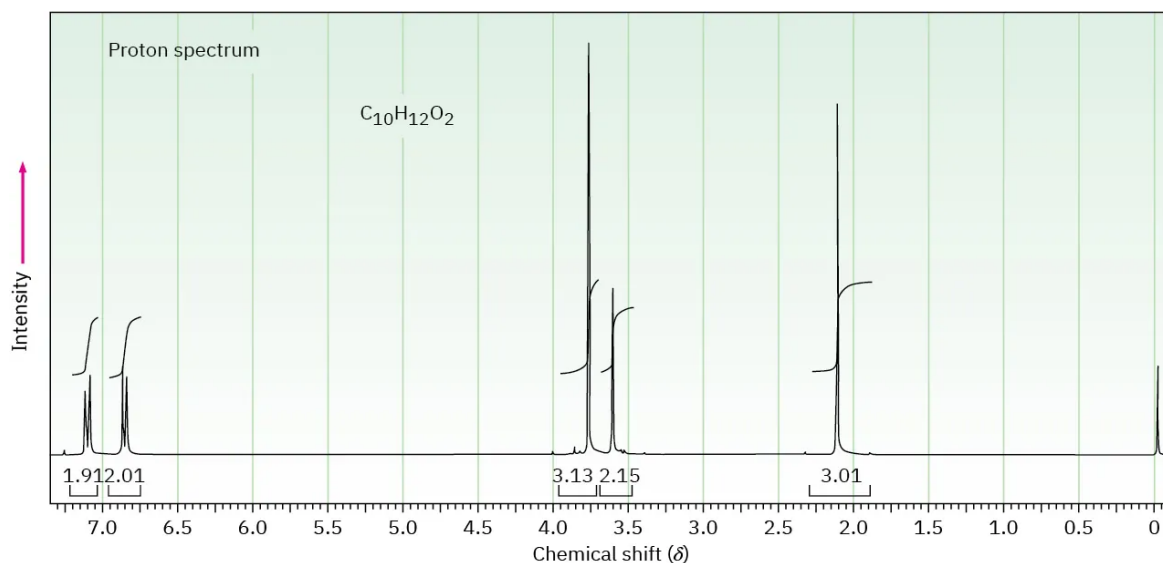


PROBLEM 2-48 Propose a structure for a molecule $C_{14}H_{12}$ that has the following 1H NMR spectrum and has IR absorptions at 700 , 740 , and 890 cm^{-1} :



PROBLEM 2-49 The proton NMR spectrum for a compound with formula $C_{10}H_{12}O_2$ is shown. The infrared spectrum has a strong band at 1711 cm^{-1} . The normal carbon-13 NMR spectral results are tabulated along with the DEPT-135 and DEPT-90 information. Draw the structure of this compound.

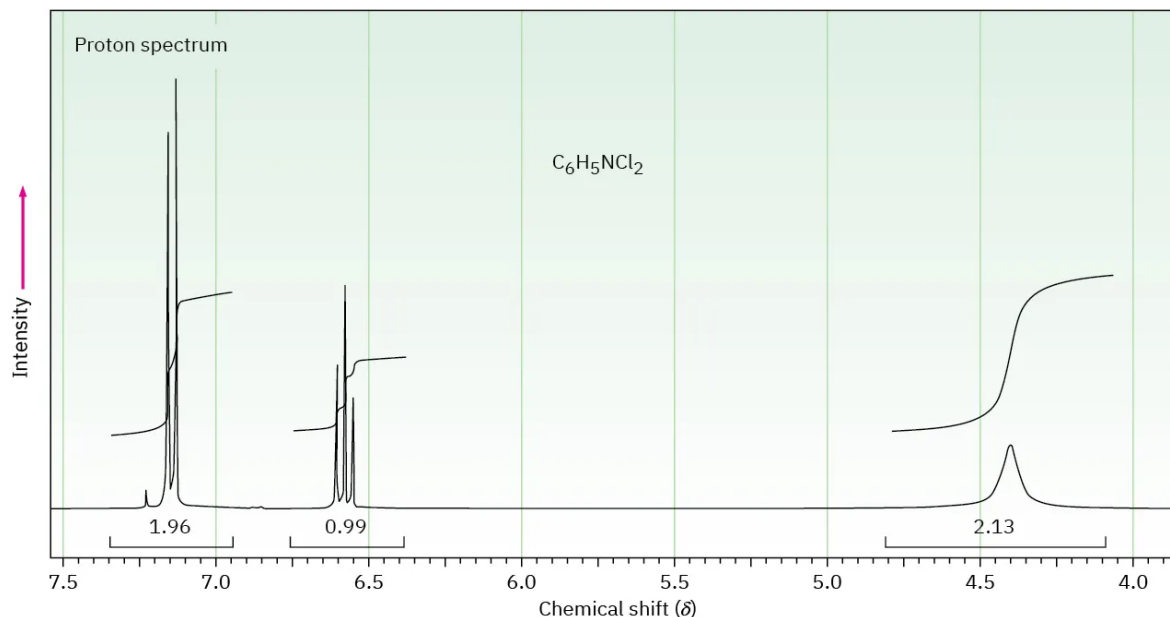
Normal Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50 ppm	Negative	No peak
55 ppm	Positive	No peak
114 ppm	Positive	Positive
126 ppm	No peak	No peak
130 ppm	Positive	Positive
159 ppm	No peak	No peak
207 ppm	No peak	No peak



PROBLEM 2-50 The proton NMR spectrum of a compound with formula $C_6H_5NCl_2$ is shown. The normal carbon-13 and DEPT experimental results are tabulated. The infrared spectrum shows peaks at 3432 and 3313 cm^{-1} and a series of medium-sized peaks between 1618 and 1466 cm^{-1} . Draw the structure of this compound.

Normal Carbon	DEPT-135	DEPT-90

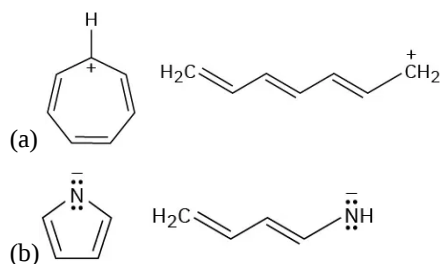
118.0 ppm	Positive	Positive
119.5 ppm	No peak	No peak
128.0 ppm	Positive	Positive
140.0 ppm	No peak	No peak



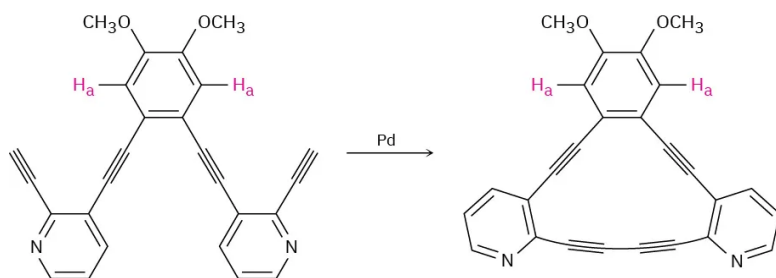
PROBLEM 2-51 Aromatic substitution reactions occur by the addition of an electrophile such as Br^+ to an aromatic ring to yield an allylic carbocation intermediate, followed by loss of H^+ . Show the structure of the intermediate formed by the reaction of benzene with Br^+ .

PROBLEM 2-52 The substitution reaction of toluene with Br_2 can, in principle, lead to the formation of three isomeric bromotoluene products. In practice, however, only *o*- and *p*-bromotoluene are formed in substantial amounts. The meta isomer is not formed. Draw the structures of the three possible carbocation intermediates (Problem 51), and explain why ortho and para products predominate over meta products.

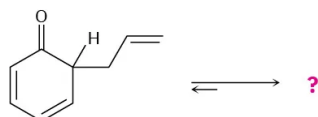
PROBLEM 2-53 Look at the following aromatic anions and their linear counterparts, and draw all of the resonance forms for each. What patterns emerge?



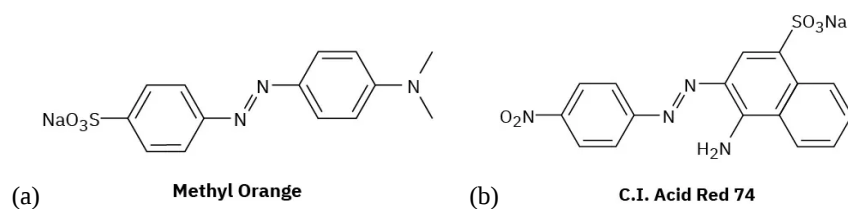
PROBLEM 2-54 After the following reaction, the chemical shift of H_a moves downfield from 6.98 ppm to 7.30 ppm. Explain.



PROBLEM 2-55 The following compound is the product initially formed in a Claisen rearrangement, which we'll see in Section 4.5. This product is not isolated, but tautomerizes to its enol form. Give the structure of the enol and provide an explanation as to why the enol tautomer is favored.



PROBLEM 2-56 Compounds called azo dyes are the major source of artificial color in textiles and food. Part of the reason for their intense coloring is the conjugation from an electron-donating group through the diazo bridge ($-N=N-$) to an electron-withdrawing group on the other side. For the following azo dyes, draw a resonance form that shows how the electron-donating group is related to the electron-withdrawing group on the other side of the diazo bridge. Used curved arrows to show how the electrons are reorganized.



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