

3) What is suggested by the fact that benzene's molar heat of hydrogenation is 36 kcal less than three times the molar heat of hydrogenation of cyclohexene?

Answer: This suggests that the type of π bonding in benzene lends special stability to the molecule.

Diff: 2

5) In the molecular orbital representation of benzene, how many π molecular orbitals are present?

A) 1

B) 2

C) 4

D) 6

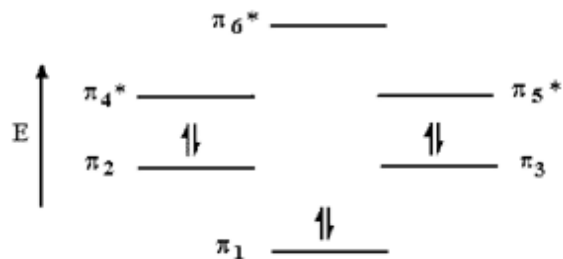
E) 8

Answer: D

Diff: 1

7) Provide a diagram which depicts the relative energies of the π molecular orbitals of benzene. Show which molecular orbitals are filled in benzene's ground state.

Answer:



Diff: 3

8) How many pairs of degenerate π molecular orbitals are found in benzene?

- A) 6
- B) 5
- C) 4
- D) 3
- E) 2

Answer: E

Diff: 2

10) List the criteria which compounds must meet in order to be considered aromatic.

Answer: 1. The structure must be cyclic.

2. Each atom in the ring must have an unhybridized p orbital.

3. The structure must be planar or nearly planar so that overlap of these p orbitals is effective.

4. The π network must contain $4n + 2$ electrons (where n is a whole number), so that delocalization of the π electrons results in a lowering of the molecule's electronic energy.

Diff: 2

11) Which is more stable, cyclobutadiene or 1,3-butadiene? Explain.

Answer: 1,3-Butadiene is more stable. Cyclobutadiene is antiaromatic since it contains 4 (i.e., $4n$) π electrons.

Antiaromatic systems are less stable than their open-chain counterparts.

Diff: 2

12) Aromatic molecules contain _____ π electrons.

- A) no
- B) $4n + 1$ (with n an integer)
- C) $4n + 2$ (with n an integer)
- D) $4n$ (with n an integer)
- E) unpaired

Answer: C

Diff: 1

13) Is cyclooctatetraene a planar molecule? Explain.

Answer: No. In addition to increasing other forms of strain, a planar conformation would make this molecule antiaromatic.

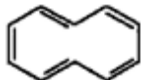
Diff: 2

14) Is the all-cis form of [10]annulene aromatic? Explain.

Answer: No. Planarity, which is required for aromaticity, is precluded due to excessive angle strain.

Diff: 3

15) Is the [10]annulene shown below aromatic? Explain.

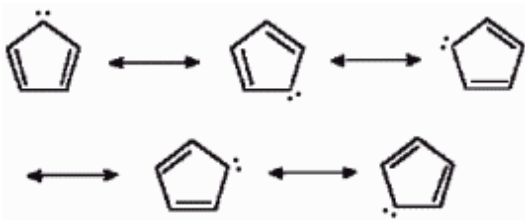


Answer: No. The ring cannot achieve a planar conformation since such a conformation would result in severe and unfavorable steric interactions between the two H's oriented inside the ring.

Diff: 3

16) Provide the major resonance structures of the ion which results when the most acidic hydrogen of cyclopentadiene is lost.

Answer:



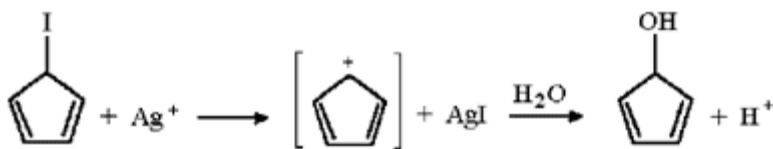
Diff: 2

17) Explain the relative acidities of cyclohexene (pK_a of 46) and cyclopentadiene (pK_a of 16).

Answer: The conjugate base of cyclopentadiene is aromatic.

Diff: 2

18) Why would the reaction below proceed at an extremely slow rate if at all?



Answer: The carbocation intermediate involved in this reaction is antiaromatic. Based on Hammond's Postulate, one can surmise that the activation energy required to produce this intermediate would be very high.

Diff: 2

20) 3-Chlorocyclopropene is solvolyzed in methanol at a much higher rate than is chlorocyclopropane. Offer an explanation.

Answer: Cyclopropenyl cation, the carbocationic intermediate in the case of 3-chlorocyclopropene, is aromatic and via Hammond's Postulate we can say that the activation energy required to form it is lower.

Diff: 2

21) Classify 1,3,5-heptatriene as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: nonaromatic

Diff: 1

22) Classify cyclopentadienyl cation as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: antiaromatic

Diff: 2

23) Classify cyclopropenyl cation as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: aromatic

Diff: 2

24) Classify cycloheptatrienyl cation as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: aromatic

Diff: 2

25) Classify naphthalene as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: aromatic

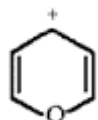
Diff: 1

26) Classify pyridine as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: aromatic

Diff: 2

27) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: aromatic

Diff: 3

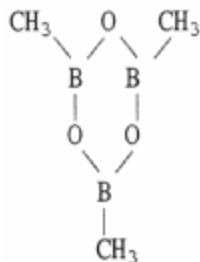
28) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: aromatic

Diff: 3

29) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: aromatic

Diff: 3

30) Classify cycloheptatriene as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: nonaromatic

Diff: 2

31) Classify cyclopentadiene as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: nonaromatic

Diff: 2

32) Which is more basic, pyridine or pyrrole? Explain.

Answer: Pyrrole is a much weaker base than pyridine. When pyrrole is protonated, the system's aromaticity is destroyed.

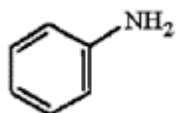
Diff: 2

33) Why are researchers interested in the properties of large polynuclear aromatic hydrocarbons?

Answer: These compounds are formed to some extent in nearly all combustion reactions of organic compounds and are known to be potent carcinogens.

Diff: 2

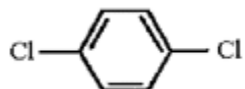
35) Provide an acceptable name for the compound below.



Answer: aniline or aminobenzene or benzeneamine

Diff: 2

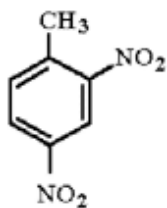
36) Provide an acceptable name for the compound below.



Answer: *para*-dichlorobenzene or 1,4-dichlorobenzene

Diff: 1

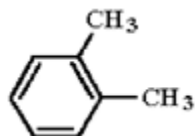
37) Provide an acceptable name for the compound below.



Answer: 2,4-dinitrotoluene

Diff: 2

39) Provide an acceptable name for the compound below.

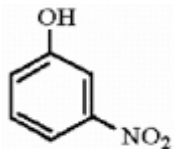


Answer: *ortho*-xylene or 1,2-dimethylbenzene

Diff: 1

40) Provide the structure of *m*-nitrophenol.

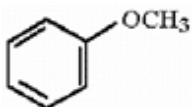
Answer:



Diff: 2

41) Provide the structure of anisole.

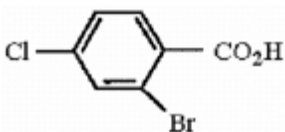
Answer:



Diff: 2

44) Provide the structure of 2-bromo-4-chlorobenzoic acid.

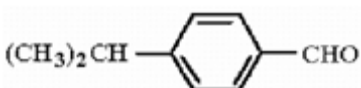
Answer:



Diff: 2

45) Provide the structure of 4-isopropylbenzaldehyde.

Answer:



Diff: 2

46) Which of the following compounds has the lowest boiling point?

- A) 1,2,3-trichlorobenzene
- B) 1,2,4-trichlorobenzene
- C) *p*-dichlorobenzene
- D) *m*-dichlorobenzene
- E) *o*-dichlorobenzene

Answer: C

Diff: 2

47) Which of the following compound has the highest melting point?

- A) benzene
- B) toluene
- C) *o*-dichlorobenzene
- D) *m*-dichlorobenzene
- E) *p*-dichlorobenzene

Answer: E

Diff: 2

48) The IR spectrum of *m*-xylene contains stretches which are characteristic of most aromatic hydrocarbons. List the peaks (in cm^{-1}) associated with the aromatic C=C stretch and the aromatic C-H stretch.

Answer: C=C: around 1600 cm^{-1}

C-H: just above 3000 cm^{-1} (usually around 3030 cm^{-1})

Diff: 2

49) In the proton NMR, in what region of the spectrum does one typically observe hydrogens bound to the aromatic ring?

- A) 1.0-1.5 ppm
- B) 2.0-3.0 ppm
- C) 4.5-5.5 ppm
- D) 7.0-8.0 ppm
- E) 9.0-10.0 ppm

Answer: D

Diff: 2

50) In the carbon NMR, in what region of the spectrum does one typically observe carbons which are part of the aromatic ring?

- A) -10-0 ppm
- B) 40-60 ppm
- C) 80-100 ppm
- D) 120-150 ppm
- E) 200-220 ppm

Answer: D

Diff: 2

56) How many distinct trichlorobenzene isomers are possible?

- A) 2
- B) 3
- C) 4
- D) 5
- E) 6

Answer: B

Diff: 1

58) Which of the following undergoes S_N2 reaction with sodium methoxide most rapidly?

- A) PhCH₂Br
- B) Ph₃CBr
- C) PhCH₂CH₂Br
- D) PhBr
- E) PhCH₂CH₂CH₂Br

Answer: A

Diff: 2

59) Which of the following undergoes solvolysis in methanol most rapidly?

- A) PhCH₂Br
- B) Ph₃CBr
- C) PhCH₂CH₂Br
- D) PhBr
- E) PhCH₂CH₂CH₂Br

Answer: B

Diff: 2

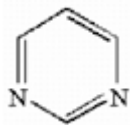
63) Classify pyrrole as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.

Answer: aromatic

Diff: 2

64) Provide the structure of pyrimidine.

Answer:



Diff: 2

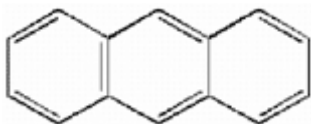
65) _____ is similar to furan, with a sulfur atom in place of the oxygen.

Answer: Thiophene

Diff: 2

66) Provide the structure of anthracene.

Answer:



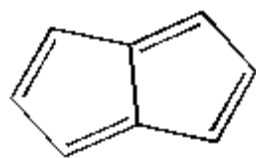
Diff: 2

67) Provide an acceptable name for PhSO_3H .

Answer: benzenesulfonic acid

Diff: 2

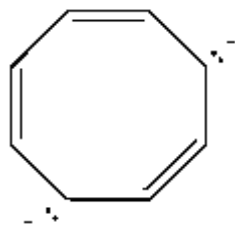
71) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: antiaromatic

Diff: 2

72) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: aromatic

Diff: 1

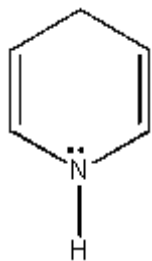
73) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: nonaromatic

Diff: 2

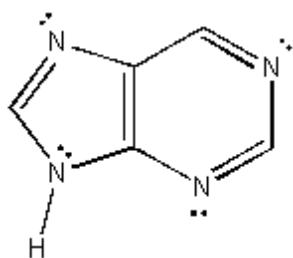
74) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: nonaromatic

Diff: 2

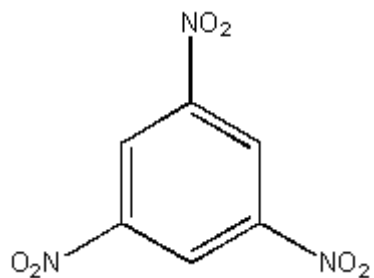
75) Classify the compound below as aromatic, antiaromatic, or nonaromatic. Assume planarity of the π network.



Answer: aromatic

Diff: 2

76) Provide an acceptable name for the compound below.

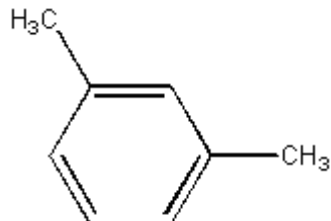


Answer: 1,3,5-trinitrobenzene

Diff: 1

77) Provide the structure of *m*-xylene.

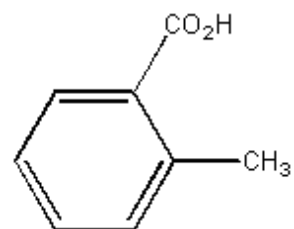
Answer:



Diff: 2

78) Provide the structure of *o*-toluic acid.

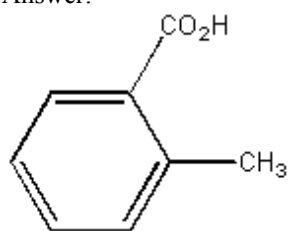
Answer:



Diff: 2

79) Provide the structure of 2,5-dichlorophenol.

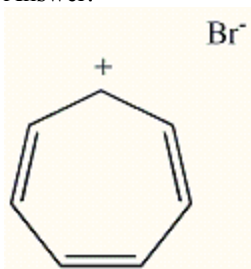
Answer:



Diff: 2

86) Provide the structure of tropylium bromide.

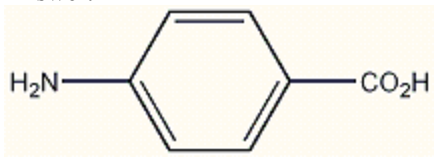
Answer:



Diff: 2

87) Provide the structure of p-aminobenzoic acid.

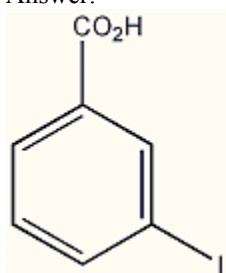
Answer:



Diff: 2

90) Provide the structure of m-iodobenzoic acid.

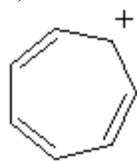
Answer:



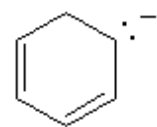
Diff: 2

92) Which of the following structures is aromatic?

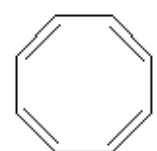
A)



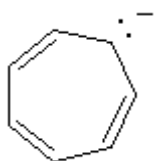
B)



C)



D)



E)

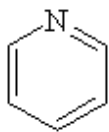


Answer: A

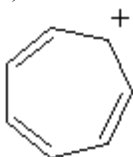
Diff: 2

93) Which of the following structures, if flat, would be classified as antiaromatic?

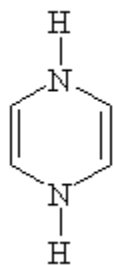
A)



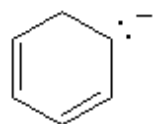
B)



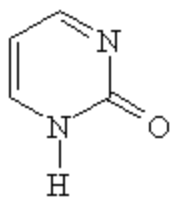
C)



D)

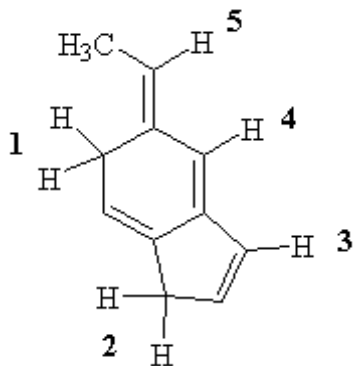


E)



Answer: C
Diff: 2

94) Which of the labeled H atoms (1 -5) in the following molecule would be predicted to be the most acidic?

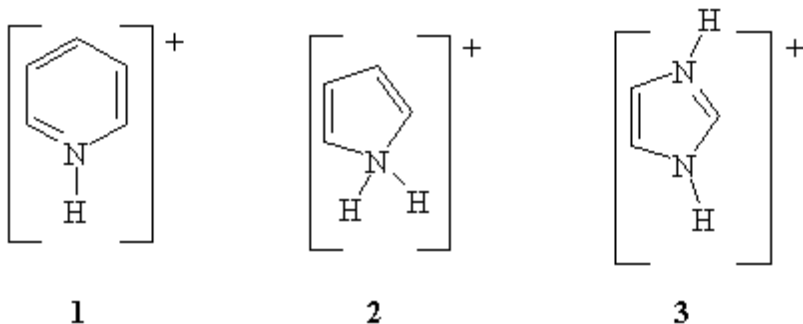


- A) 1
- B) 2
- C) 3
- D) 4
- E) 5

Answer: A

Diff: 3

95) Rank the following in order of increasing pKa (from lowest to highest pKa)



- A) 1 < 2 < 3
- B) 3 < 2 < 1
- C) 2 < 1 < 3
- D) 3 < 1 < 2
- E) 2 < 3 < 1

Answer: C

Diff: 3