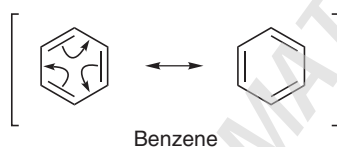


AROMATICITY

If you are using this book, then you have likely begun the second half of your organic chemistry course. By now, you have certainly encountered aromatic rings, such as benzene. In this chapter, we will explore the criteria for aromaticity, and we will discover many compounds (other than benzene) that are also classified as aromatic.

1.1 INTRODUCTION TO AROMATIC COMPOUNDS

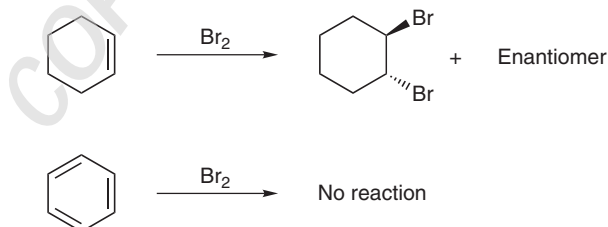
Consider the structure of benzene:



Benzene is resonance-stabilized, as shown above, and is sometimes drawn in the following way:



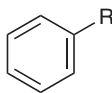
This type of drawing (a hexagon with a circle in the center) is not suitable when drawing mechanisms of reactions, because mechanisms require that we keep track of electrons meticulously. But, it is helpful to see this type of drawing, even though we won't use it again in this book, because it represents all six π electrons of the ring as a single entity, rather than as three separate π bonds. Indeed, a benzene ring should be viewed as one functional group, rather than as three separate functional groups. This is perhaps most evident when we consider the special stability associated with a benzene ring. To illustrate this stability, we can compare the reactivity of cyclohexene and benzene:



Cyclohexene is an alkene, and it will react with molecular bromine (Br_2) via an addition process, as expected for alkenes. In contrast, no reaction occurs when benzene is treated with Br_2 , because the stability associated with the ring (of six π electrons) would be destroyed by an addition process. That is, the six π electrons of the ring represent a single functional group that does not react with Br_2 , as alkenes do.

Understanding the source of the stability of benzene requires MO (molecular orbital) theory. You may or may not be responsible for MO theory in your course, so you should consult your textbook and/or lecture notes to see whether MO theory was covered.

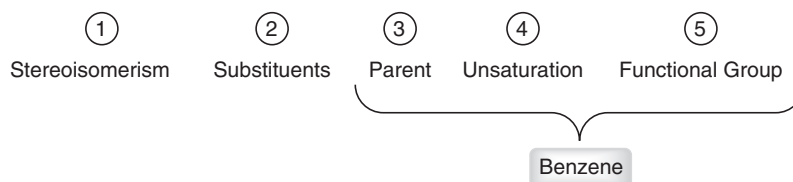
Derivatives of benzene, called substituted benzenes, also exhibit the stability associated with a ring of six π electrons:



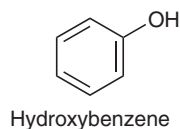
The ring can be monosubstituted, as shown above, or it can be disubstituted, or even polysubstituted (the ring can accommodate up to six different groups). Many derivatives of benzene were originally isolated from the fragrant extracts of trees and plants, so these compounds were described as being *aromatic*, in reference to their pleasant odors. Over time, it became apparent that many derivatives of benzene are, in fact, odorless. Nevertheless, the term *aromatic* is still currently used to describe derivatives of benzene, whether those compounds have odors or not.

1.2 NOMENCLATURE OF AROMATIC COMPOUNDS

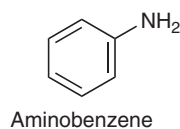
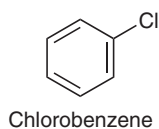
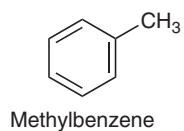
As we have mentioned, an aromatic ring should be viewed as a single functional group. Compounds containing this functional group are generally referred to as *arenes*. In order to name arenes, recall that there are five parts of a systematic name, shown here (these five parts were discussed in Chapter 5 of the first volume of *Organic Chemistry as a Second Language: First Semester Topics*):



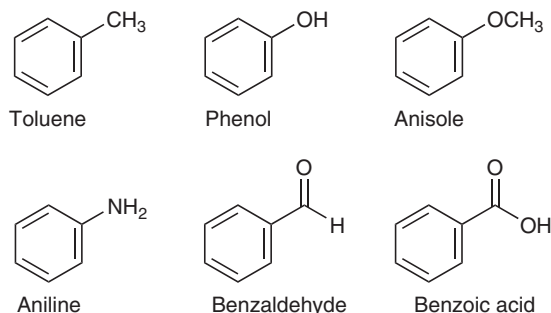
For benzene and its derivatives, the term *benzene* represents the parent, the unsaturation AND the suffix. Any other groups (connected to the ring) must be listed as substituents. For example, if a hydroxy (OH) group is connected to the ring, we do not refer to the compound as benzenol. We cannot add another suffix (-ol) to the term benzene, because that term is already a suffix itself. Therefore, the OH group is listed as a substituent, and the compound is called hydroxybenzene:



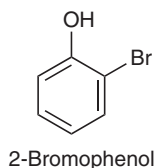
Similarly, other groups (connected to the ring) are also listed as substituents, as seen in the following examples:



Many monosubstituted derivatives of benzene (and even some disubstituted and polysubstituted derivatives) have common names. Several common names are shown here:

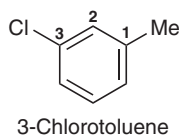


So, for example, the first compound above can either be called methylbenzene (systematic name) or toluene (common name). Similarly, the second compound above can either be called hydroxybenzene (systematic name) or phenol (common name). When more than one substituent is present, common names are often used as parents. For example, the following compound exhibits a benzene ring with two substituents. But if we use the term *phenol* as the parent (rather than benzene), then we only have to list one substituent (bromo):

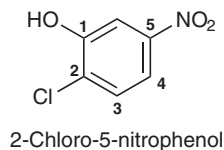


The number (2) indicates the position of Br relative to the OH group. Notice that this compound can also be called 1-bromo-2-hydroxybenzene. Both names are acceptable, although it is generally more efficient to use the common name (2-bromophenol, rather than 1-bromo-2-hydroxybenzene).

When more than one group is present, numbers must be assigned, as seen in the previous example. When assigning numbers, the #1 position is determined by the parent. For example, the following compound will be named as a substituted toluene, so the methyl group is (by definition) at the #1 position:



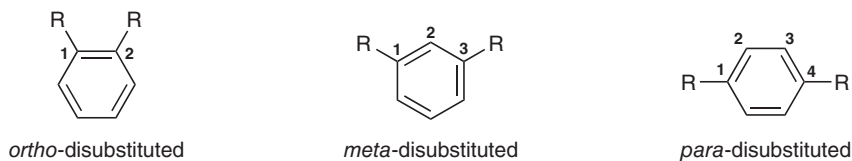
The numbers are assigned in a manner that gives the lower possible number to the next substituent (Cl). So, in this case, we assign the numbers in a counterclockwise fashion, because that gives a lower number (3-chloro, rather than 5-chloro). The same method is applied for polysubstituted rings: first we choose the parent, and then we assign numbers in the direction that gives the lower possible number to the second substituent. Consider the following example:



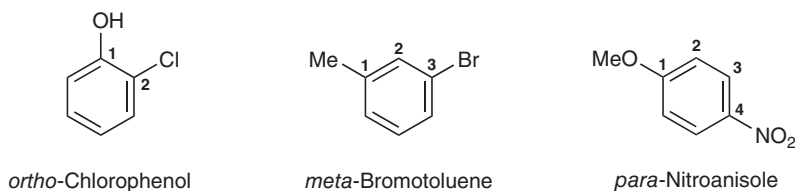
This compound can be named as a disubstituted phenol, rather than a trisubstituted benzene. So, the OH group is assigned the #1 position. Then, we continue assigning numbers in the direction that gives the lower possible number to the second substituent (2-chloro, rather than 3-nitro).

4 CHAPTER 1 AROMATICITY

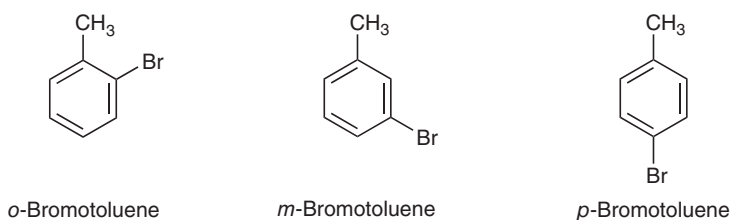
For disubstituted benzenes, there is special terminology that describes the proximity of the two groups:



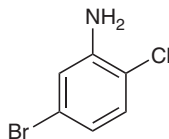
The term *ortho* is used to describe 1,2-disubstitution, the term *meta* is used to describe 1,3-disubstitution, and the term *para* is used to describe 1,4-disubstitution. These terms may be used instead of numbers, as seen in the following examples:



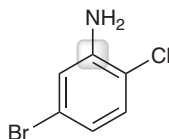
These terms (*ortho*, *meta*, and *para*) will be used frequently, so it is certainly worthwhile to commit them to memory right now. Sometimes, you might see the prefixes abbreviated to just one letter (*o*, *m*, and *p*), as seen in the following examples:



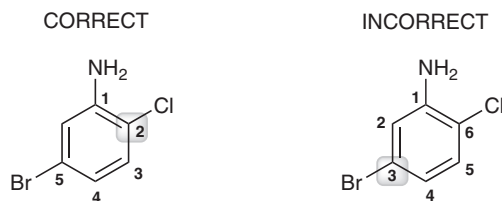
WORKED PROBLEM 1.1 Provide a systematic name for the following compound:



Answer This compound is a trisubstituted benzene, and it can be named as such, although it will be more efficient to name the compound as a disubstituted derivative of aniline. Since we are using a common name (aniline) as our parent, the position bearing the amino group is, by definition, position #1:



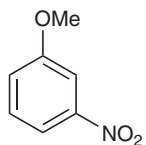
Then, we assign numbers in a clockwise fashion, rather than counterclockwise, so that the next substituent is at C2 rather than C3:



Therefore, the name is 5-bromo-2-chloroaniline. Notice that the substituents appear in the name in alphabetical order, in accordance with the general rules for IUPAC nomenclature.

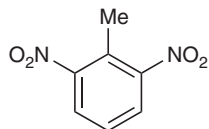
PROBLEMS Provide a systematic name for each of the following compounds:

1.2



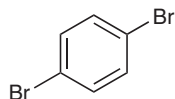
Name: _____

1.3



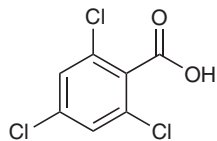
Name: _____

1.4



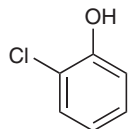
Name: _____

1.5



Name: _____

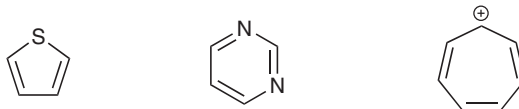
1.6



Name: _____

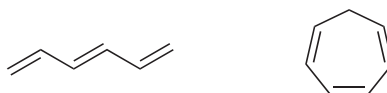
1.3 CRITERIA FOR AROMATICITY

In the previous section, we saw that benzene and its derivatives exhibit a special stability that is associated with the ring of six π electrons. We will now see that aromatic stabilization is not limited to benzene and its derivatives. Indeed, there are a large number of compounds and ions that exhibit aromatic stabilization. A few examples are shown here:



These structures are also said to be aromatic, illustrating that aromaticity is not strictly limited to six-membered rings, but indeed, even five-membered rings and seven-membered rings can be aromatic (if they meet certain criteria). In this section, we will explore the two criteria for aromaticity. Let's begin with the first criterion:

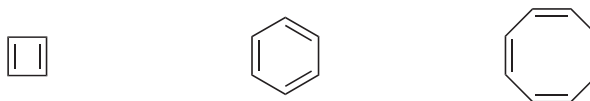
- 1) *There must be a ring comprised of continuously overlapping p orbitals.* The structures below do NOT satisfy this first criterion:



The first structure is not aromatic because it is not a ring, and the second structure is not aromatic because it lacks a continuous system of overlapping p orbitals. Six of the seven carbon atoms are sp^2 hybridized (and each of these carbon atoms does have a p orbital), but the seventh carbon atom (at the top of the ring) is sp^3 hybridized, thereby interrupting the overlap. The overlap of p orbitals must continue all the way around the ring, and it doesn't in this case because of the intervening sp^3 hybridized carbon atom.

Now let's explore the second criterion for aromaticity:

- 2) *The ring must contain an odd number of pairs of π electrons* (one pair of electrons, three pairs of electrons, five pairs of electrons, etc.). If we compare the following compounds, we find that only the middle compound (benzene) has an odd number of pairs of π electrons (three pairs of π electrons = 6 π electrons):

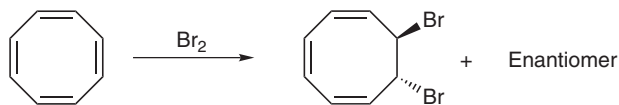


The first compound (cyclobutadiene) has two pairs of π electrons, and the last compound (cyclooctatetraene) has four pairs of π electrons. In order to understand the requirement for an odd number of pairs of π electrons, MO theory is required. Once again, consult your textbook and/or lecture notes for any coverage of MO theory. Another way of saying "an odd number of pairs of π electrons" is to say that the number of π electrons must be among the following series of numbers: 2, 6, 10, 14, 18, etc. These numbers are called Hückel numbers, and they can be summarized with the following formula: $4n + 2$, where n represents a series of integers (1, 2, 3, etc.). If we look closely at benzene (middle structure above), we find that there are six π electrons, which is a Hückel number. Therefore, benzene is aromatic. In contrast, each of the other two compounds above (cyclobutadiene and cyclooctatetraene) has an even number of pairs of π electrons. Cyclobutadiene has 4 π electrons, and cyclooctatetraene has 8 π electrons. These numbers (4 and 8) are NOT Hückel numbers. These numbers can be represented by the formula $4n$, where n represents a series of integers (1, 2, 3, etc.). These compounds are remarkably unstable (an observation that can be justified by MO theory). They are said to be *antiaromatic*. In order for a compound to be antiaromatic, it must satisfy the first criterion (it must possess a ring with a continuous system of overlapping p orbitals), but it must fail the second criterion (it must have $4n$, rather than $4n + 2$, π electrons).

Cyclooctatetraene can relieve much of the instability by puckering out of planarity, as shown:



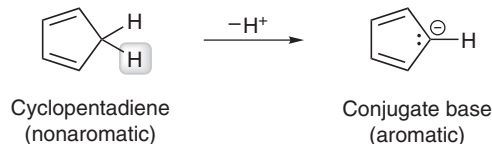
In this way, the extent of continuous overlap (of p orbitals) is significantly reduced, so the first criterion (a ring of continuous overlapping p orbitals) is not fully satisfied. The compound therefore behaves as if it were nonaromatic, rather than antiaromatic. That is, it can be isolated, unlike antiaromatic compounds, which are generally too unstable to isolate. Moreover, it is observed to undergo addition reactions, unlike aromatic compounds which do not undergo addition reactions:



Now let's explore ions (structures that have a net charge). We will identify ions that are classified as aromatic, as well as examples of antiaromatic ions. Consider the structure of the following anion, which is resonance-stabilized. Draw all of the resonance structures in the space provided:



The remarkable stability of this anion cannot be explained with resonance alone. This anion is also aromatic, because it satisfies both criteria for aromaticity. To see how this is the case, we must recognize that the lone pair occupies a p orbital (because any lone pair that participates in resonance must occupy a p orbital), so this structure does indeed exhibit a ring with a continuous system of overlapping p orbitals, with a Hückel number of π electrons. The delocalized lone pair represents two π electrons, and the rest of the ring has another four π electrons, for a total of six π electrons. Indeed, the aromatic nature of this anion explains why cyclopentadiene is so acidic:



Cyclopentadiene is nonaromatic, but when it is deprotonated, the resulting conjugate base IS aromatic. Since the conjugate base is so stable, this renders cyclopentadiene fairly acidic (for a hydrocarbon). If we compare the $\text{p}K_a$ values of cyclopentadiene and water, we find that they are similar in acidity:



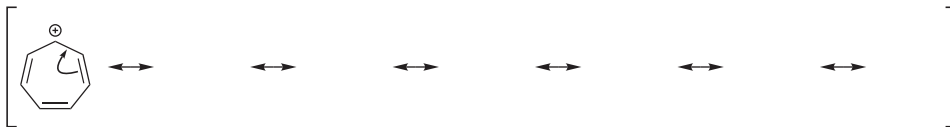
This is truly remarkable, because it means that the following conjugate bases are similar in stability:



You often think of hydroxide as a strong base, but remember that basicity and acidity are relative concepts. Sure, hydroxide is a strong base when compared with certain weak bases, such as the acetate ion. But hydroxide is actually a relatively weak base when compared with other very strong bases, such as the amide ion (H_2N^-) or carbanions (C^-). Above, we see an example of a carbanion that is similar in stability to a hydroxide ion. You will not find many other examples of carbanions with such remarkable stability. And as we have seen, this stability is due to its aromatic nature.

8 CHAPTER 1 AROMATICITY

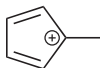
The previous example was an anion. Let's now explore an example of a cation. The cation below, called a tropylium cation, is resonance-stabilized. Draw all of the resonance structures in the space provided.



The remarkable stability of this cation is not fully explained by resonance. If we consider both criteria for aromaticity, we will find that this cation does indeed satisfy both criteria. Recall that a carbocation represents an empty p orbital, so we do have a ring with a continuous system of overlapping p orbitals, AND we have six π electrons (a Hückel number). Therefore, both criteria are satisfied, and this cation is aromatic.

Let's get some practice determining whether ions are aromatic, nonaromatic, or antiaromatic.

WORKED PROBLEM 1.7 Characterize the following ion as aromatic, nonaromatic, or antiaromatic:

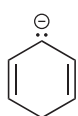


Answer In order to be nonaromatic, it must fail the first criterion for aromaticity. In this case, it satisfies the first criterion, because the carbocation represents an empty p orbital, so we do have a ring with a continuous system of overlapping p orbitals. Since the first criterion is satisfied, we conclude that the structure will either be aromatic or antiaromatic, depending on whether the second criterion is met (a compound can only be nonaromatic if it fails the first criterion).

When we count the number of π electrons, we do NOT have a Hückel number in this case. With 4 π electrons, we expect this structure to be antiaromatic. That is, we expect this ion to be very unstable.

PROBLEMS Characterize each of the following structures as aromatic, nonaromatic, or antiaromatic:

1.8



Answer: _____

1.9



Answer: _____

1.10



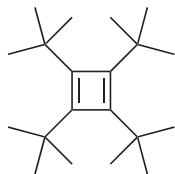
Answer: _____

1.11



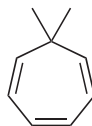
Answer: _____

1.12



Answer: _____

1.13



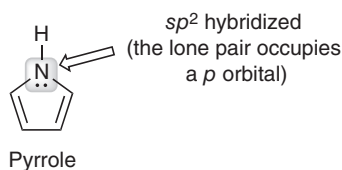
Answer: _____

1.4 LONE PAIRS

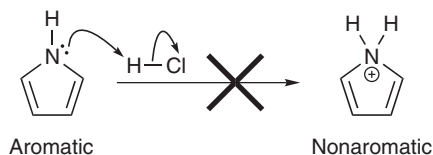
Compare the following two structures:



We saw in the previous section that the first structure is aromatic. The second structure, called pyrrole, is also aromatic, for the same reason. The nitrogen atom adopts an sp^2 hybridized state, which places the lone pair in a p orbital, thereby establishing a continuous system of overlapping p orbitals,

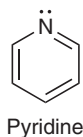


and there are six π electrons (two from the lone pair + another two from each of the π bonds = 6). Both criteria for aromaticity have been satisfied, so the compound is aromatic. Notice that the lone pair is part of the aromatic system. As such, the lone pair is less available to function as a base:

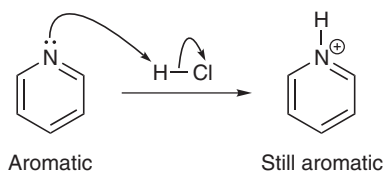


This doesn't occur, because the ring would lose aromaticity. If the nitrogen atom were to be protonated, the resulting nitrogen atom (with a positive charge) would be sp^3 hybridized. It would no longer have a p orbital, so the first criterion for aromaticity would not be satisfied (thus, nonaromatic). Protonation of the nitrogen atom would be extremely uphill in energy and is not observed.

In contrast, consider the nitrogen atom of pyridine:

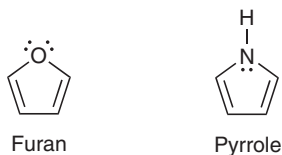


In this case, the lone pair is NOT part of the aromatic system. This localized lone pair is not participating in resonance, and it does not occupy a p orbital. The nitrogen atom is sp^2 hybridized, and it does have a p orbital, but the p orbital is occupied by a π electron (as illustrated by the double bond that is drawn on the nitrogen atom). The lone pair actually occupies an sp^2 hybridized orbital, and it is therefore not contributing to the aromatic system. As such, it is available to function as a base, because protonation does not destroy aromaticity:



Indeed, pyridine is often used as a mild base, especially in reactions where HCl is a byproduct. The presence of pyridine effectively neutralizes the acid as it is produced, and for this reason, pyridine is often referred to as “an acid sponge.”

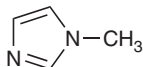
Let’s explore one last example of an aromatic compound. This compound, called furan, is similar in structure to pyrrole:



The oxygen atom of furan is sp^2 hybridized (much like the nitrogen atom of pyrrole), which places one of the lone pairs in a p orbital, thereby establishing a continuous system of overlapping p orbitals, with a Hückel number of electrons (6π electrons). Therefore, furan is aromatic, for the same reason that pyrrole is aromatic. Notice that the oxygen atom in furan has two lone pairs, but only one of them occupies a p orbital. The other lone pair occupies an sp^2 hybridized orbital. As such, we only count one of the lone pairs of the oxygen atom (not both lone pairs) when we are counting to see if we have a Hückel number.

PROBLEMS

1.14 In the following compound, identify whether each lone pair is available to function as a base, and explain your choice:



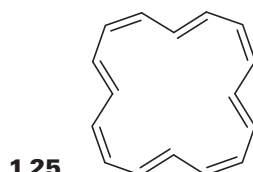
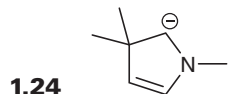
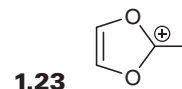
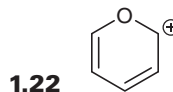
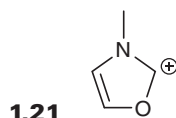
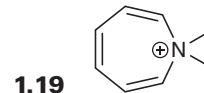
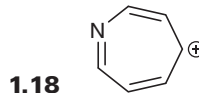
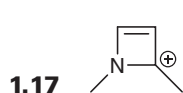
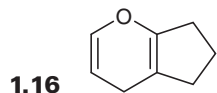
1.15 Only one of the following compounds is aromatic. Identify the aromatic compound, and justify your choice:



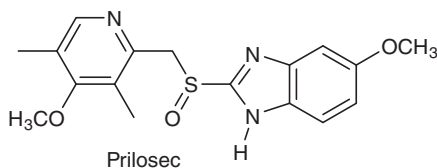
END-OF-CHAPTER PROBLEMS

PRACTICE PROBLEMS (*Problems that involve only one skill*)

Identify whether each of the following structures is aromatic, antiaromatic, or nonaromatic.



1.26 Below is the structure of Prilosec, a drug used for the treatment of ulcers and acid reflux. This structure has three rings. Determine whether each ring is aromatic or not.

**INTEGRATED PROBLEMS** (*Problems that involve more than one skill*)

1.27 Cyclopentadiene and cycloheptatriene are both conjugated, cyclic hydrocarbons. Despite their similarity in structure, cyclopentadiene is relatively acidic (with a pK_a near that of H_2O), while cycloheptatriene does not function as an acid. Explain this significant difference in acidity.

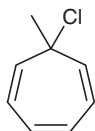
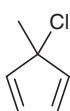


Cyclopentadiene

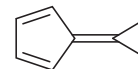


Cycloheptatriene

1.28 Which of the following compounds will undergo an S_N1 reaction more rapidly? Explain your choice.



1.29 Calicene, shown below, has a measurable molecular dipole moment. Draw a resonance structure that justifies the observed dipole moment, and explain why that resonance structure contributes so much character to the overall resonance hybrid. (Note: when drawing resonance structures, we generally don't break $C=C$ bonds to draw both C^+ and C^- , but this case represents an exception.)

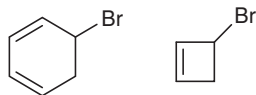


Calicene

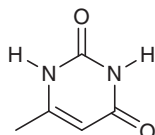
1.30 Which of the following compounds will undergo an S_N1 reaction more rapidly? Explain your choice.



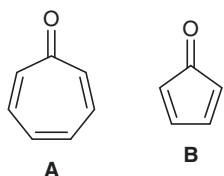
1.31 Which of the following compounds undergoes a rapid E2 reaction under weakly basic conditions? Explain your choice.



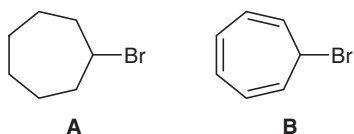
1.32 The following compound is aromatic. Draw resonance structures that justify this classification.



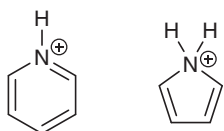
1.33 Explain why compound **A** is significantly more stable than compound **B**.



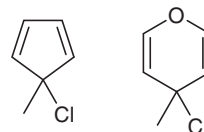
1.34 Compound **A** is insoluble in water, while compound **B** is highly water-soluble and functions much like a salt, by dissociating into a cation and an anion. Explain the observed behavior of compound **B**.



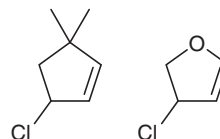
1.35 Which of the following is expected to be the stronger acid? Explain your choice.



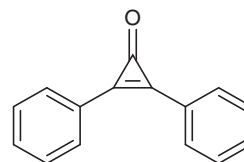
1.36 Which of the following compounds will undergo an S_N1 reaction more rapidly? Explain your choice.



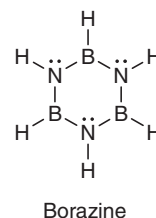
1.37 Which of the following compounds undergoes a rapid E2 reaction under weakly basic conditions? Explain your choice.



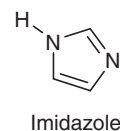
1.38 When treated with a strong acid, such as HBr, the following compound is protonated to give a highly stabilized cation. Draw the structure of this cation, and explain why it is so stable.



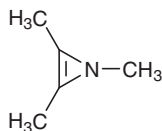
1.39 Borazine, shown below, is called “inorganic benzene” because of its remarkable stability. Identify the source of this stability.



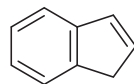
1.40 Identify which nitrogen atom in imidazole is more basic, and draw the conjugate acid that is formed when imidazole is protonated by a strong acid, such as HBr.



1.41 The following compound is too unstable to be made. Identify the source of its instability.

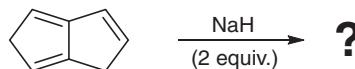


1.42 Draw the conjugate base that is formed when indene is deprotonated by a strong base, such as NaNH_2 .



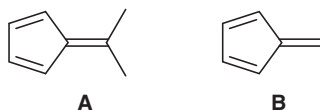
Indene ($\text{p}K_{\text{a}} = 20$)

1.43 When treated with two equivalents of a strong base, such as NaH , the following compound is deprotonated to give a dianion that is particularly stable. Draw the structure of the dianion, and explain the source of its stability.



CHALLENGE PROBLEMS

1.44 Compound **A** is significantly more acidic than compound **B**. Explain the difference in acidity.



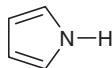
A

B

1.45 In general, a negative charge on a carbon atom is less stable than a negative charge on a nitrogen atom. As a result, alkanes are generally less acidic than amines. Nevertheless, cyclopentadiene is significantly more acidic than pyrrole. Explain.

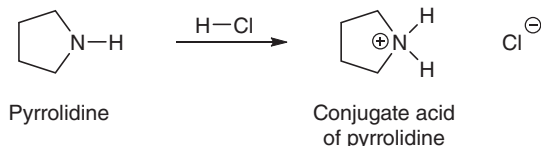


Cyclopentadiene



Pyrrole

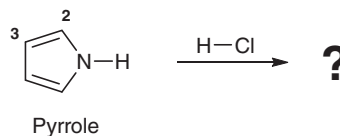
1.46 When treated with a strong acid, such as HCl , pyrrolidine is protonated to give a conjugate acid with a positive charge on the nitrogen atom.



Pyrrolidine

Conjugate acid of pyrrolidine

In contrast, when pyrrole is treated with a strong acid, the C2 position (indicated below with the number 2) is protonated, rather than the nitrogen atom. Draw the conjugate acid of pyrrole, and explain why protonation occurs at C2, rather than occurring at the nitrogen atom.



Pyrrole