CHAPTER

20

Aromaticity

☑ SPECIAL TOPIC

THE SWEET BOUQUET OF AROMATIC COMPOUNDS

The word aromatic usually gets people's minds moving. Some people may associate the word with the beautiful scent of roses, while others may think instead of a freshly cut lawn on a warm spring morning. People with a somewhat darker mindset may think of things with a less pleasant smell such as garbage or sweaty socks.

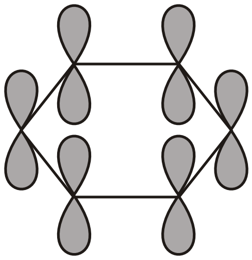
AROMATICITY

The compound we know as benzene was first isolated in 1825 by Michael Faraday, who extracted the compound from a liquid residue obtained after heating whale oil under pressure to produce a gas used to illuminate buildings in London. Because of its origin, chemists suggested that it should be called ''pheno'' from the Greek word phaine in (''to shine'').

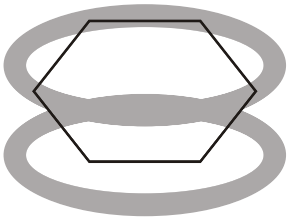
In 1834, Eihardt Mitscherlich correctly determined benzene's molecular formula (C_6H_6) and decided to call it benzin because of its relationship to benzoic acid, a known substituted form of the compound. Later its name was changed to benzene.

Compounds like benzene, which have relatively few hydrogens in relation to the number of carbons, are typically found in oils produced by trees and other plants. Early chemists called such compounds aromatic compounds because of their pleasing fragrances. In this way, they were distinguished from aliphatic compounds, with higher hydrogen-to-carbon ratios, that were obtained from the chemical degradation of fats. The chemical meaning of the word ''aromatic'' now signifies certain kinds of chemical structures. We will now examine the criteria that a compound must satisfy to be classified as aromatic.

At this point, we can define an aromatic compound to be a cyclic compound containing some number of conjugated double bonds and having an unusually large resonance energy. Using benzene as the example, we will consider how aromatic compounds differ from aliphatic compounds. Then we will discuss why an aromatic structure confers extra stability and how we can predict aromaticity in some interesting and unusual compounds.



(a)
Each carbon of Benzene
has a *p* orbital.



(b)
The overlap of the *p* orbitals
forms a cloud of π electrons
above and below the plane
of the Benzene ring.

☑ SPECIAL TOPIC

CHEMISTRIVIA

2,4,6-trinitrotoluene is better known as the explosive TNT. Before this explosive property was discovered, TNT was used as a yellow dye. Because TNT dyed their hair green and skin yellow, the women who filled explosive artillery shells during World War I were nicknamed “canary girls.”

Benzene is a planar, cyclic compound with a cyclic cloud of delocalized electrons above and below the plane of the ring. Because its   electrons are delocalized, all the C — C bonds have the same length-pathway between the length of a typical single and a typical double bond. We also saw that Benzene is a particularly stable compound because it has an unusually large resonance energy (36kcal/mol). Most compounds with delocalized electrons have much smaller resonance energies. Compounds such as benzene with unusually large resonance energies are called aromatic compounds.

HOW TO DETERMINE AROMATIC, ANTIAROMATIC AND NONAROMATIC COMPOUNDS

How can we tell whether a compound is aromatic by looking at its structure?

In other words, what structural features do aromatic compounds have in common?

To be classfied as aromatic, a compound must follow the criteria :

AROMATIC

1. The structure must be cyclic, containing some number of conjugated pi bonds.
2. Each atom in the ring must have an unhybridized *p* orbital. (The ring atoms are usually sp^2 hybridized or occasionally *sp* hybridized.)
3. The unhybridized *p* orbitals must overlap to form a continuous ring of parallel orbitals. In most cases, the structure must be planar (or nearly planar) for effective overlap to occur.
4. Delocalization of the pi electrons over the ring must *lower* the electronic energy.
5. Huckel rule :

   It must have $(4n \quad 2)$ -electrons where $n \quad 0, 1, 2, 3$ .... *n* represent the whole number.

$n \quad 0$	2 -electron
$n \quad 1$	6 -electron
$n \quad 2$	10 -electron
$n \quad 3$	14 -electron

ANTI-AROMATIC

1. The structure must be cyclic, containing some number of conjugated pi bonds.
2. Each atom in the ring must have an unhybridized *p* orbital. (The ring atoms are usually sp^2 hybridized or occasionally *sp* hybridized.)
3. The unhybridized *p* orbitals must overlap to form a continuous ring of parallel orbitals. In most cases, the structure must be planar (or nearly planar) for effective overlap to occur.
4. Delocalization of the electrons over the ring must *increase* the electronic energy.
5. It must have $(4n)$ -electrons where n 1, 2, 3 .... n always represent the natural number.

n 1 4 -electron
n 2 8 -electron
n 3 12 -electron

Non-aromatic

The compound which is neither aromatic nor anti-aromatic

RELATIVE STABILITIES

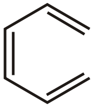
Aromatic compound > cyclic compound with localized electrons > antiaromatic compound

← increasing stability

Solved Example

▸

more stable (aromatic)

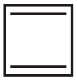


less stable

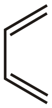
Sol. Aromatic structures are more stable than their open-chain counterparts. Hence, Benzene is more stable than hexa-1,3,5-triene.

Solved Example

▸



less stable (antiaromatic)



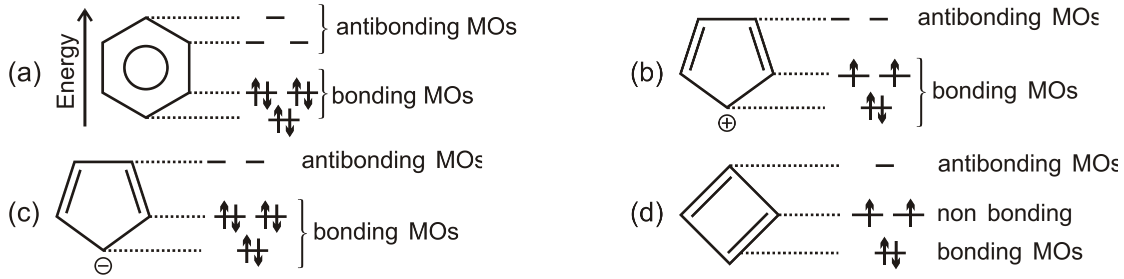
more stable

Sol. An anti aromatic compound is one that meets the first three criteria, but delocalization of the pi electrons over the ring increases the electronic energy. Cyclobutadiene meets the first three criteria for a continuous ring of overlapping p orbitals, but delocalization of the pi electrons increases the electronic energy. Cyclobutadiene is less stable than its open-chain counterpart (buta-1,3-diene), and it is antiaromatic.

MOLECULAR ORBITAL THEORY (M.O.T.) DESCRIPTION OF AROMATICITY AND ANTIAROMATICITY

Why are planar molecules with uninterrupted cyclic electron clouds very stable (aromatic) if they have an odd number of pairs of electrons and very unstable (anti-aromatic) if they have an even number of pairs of electrons? To answer this question, we must turn to molecular orbital theory.

The relative energies of the molecular orbitals of planar molecules with uninterrupted cyclic electron clouds can be determined, without having to use any math, by first drawing the cyclic compound with one of its vertices pointed down. The relative energies of the molecular orbitals correspond to the relative levels of the vertices (Figure). Molecular orbitals below the midpoint of the cyclic structure are bonding molecular orbitals, those above the midpoint are antibonding molecular orbitals, and any at the midpoint are nonbonding molecular orbitals. Notice that the number of molecular orbitals is equal to the number of atoms in the ring since each ring atom contributes a orbital.



The distribution of electrons in the molecular orbitals of

(a) Benzene (b) Cyclopentadienyl cation

(c) Cyclopentadienyl anion, and (d) Cyclobutadiene.

The relative energies of the molecular orbitals in a cyclic compound correspond to the relative levels of the vertices. Molecular orbitals below the midpoint of the cyclic structure are bonding, those above the midpoint are antibonding, and those at the midpoint are non-bonding.

THE POLYGON RULE

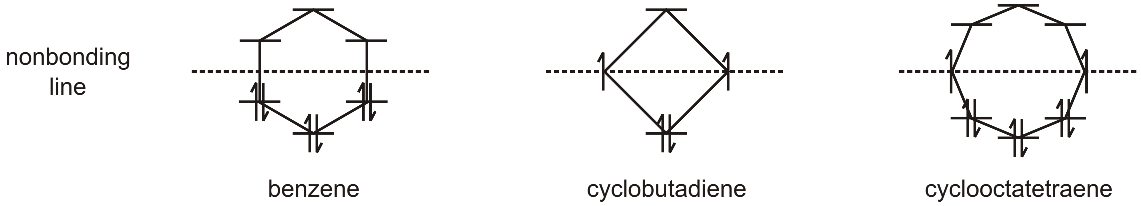
The patterns of molecular orbitals in benzene and in cyclobutadiene are similar to the patterns in other annulenes : The lowestlying MO is the unique one with no nodes; thereafter, the molecular orbitals occur in degenerate (equal-energy) pairs until only one highest-lying MO remains. In benzene, the energy diagram looks like the hexagon of a benzene ring. In cyclobutadiene, the pattern looks like the diamond of the cyclobutadiene ring.

The **polygon rule** states that the molecular orbital energy diagram of a regular, completely conjugated cyclic system has the same polygonal shape as the compound, with one vertex (the all-bonding MO) at the bottom. The nonbonding line cuts horizontally through the center of the polygon. Following solved example shows how the polygon rule predicts the MO energy diagrams for benzene, cyclobutadiene, and cyclooctatetraene. The pi electrons are filled into the orbitals in accordance with the aufbau principle (lowest energy orbitals are filled first) and Hund's rule.

Solved Example

- Does the MO energy diagram of cyclooctatetraene (see figure) appear to be a particularly stable or unstable configuration? Explain.

Ans.



benzene cyclobutadiene cyclooctatetraene

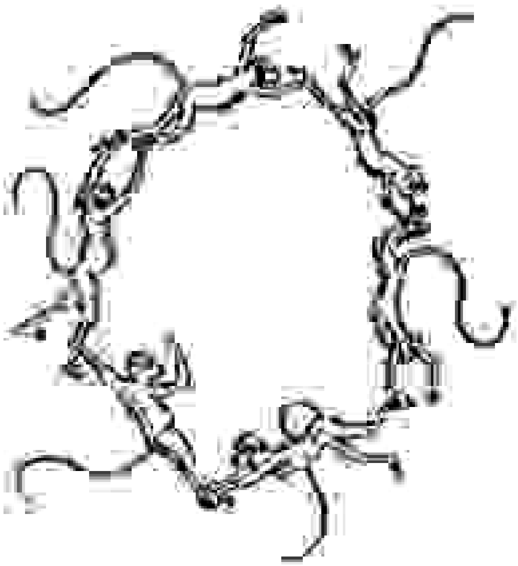
The polygon rule predicts that the MO energy diagrams for these annulenes will resemble the polygonal shapes of the annulenes.

☑ SPECIAL TOPIC

SPECIAL TOPIC : KEKULE'S DREAM

Friedrich August Kekulé von Stradonitz (1829–1896) was born in Germany. He entered the University of Giessen to study architecture but switched to chemistry after taking a course in the subject. He was a professor of chemistry at the University of Heidelberg, at the University of Ghent in Belgium, and then at the University of Bonn. In 1890, he gave an extemporaneous speech at the twenty-fifth-anniversary celebration of his first paper on the cyclic structure of benzene. In this speech, he claimed that he had arrived at the structures as a result of dozing off in front of a fire while working on a textbook. He dreamed of chains of carbon atoms twisting and turning in a snakelike motion, when suddenly the head of one snake seized hold of its own tail and formed a spinning ring.

Recently, the veracity of Kekulé's snake story has been questioned by those who point out that there is no written record of the dream from the time he experienced it in 1861 until the time he related it in 1890. Others counter that dreams are not the kind of evidence one publishes in scientific papers, and it is not uncommon for scientists to experience creative ideas emerging from their subconscious at moments when they were not thinking about science.



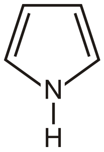
Kekule's snake dream inspired this figure that appeared in a spoof edition of the German chemical Journal, Berichte der Deutschen Chemischen Geselischaft in 1886.

HETEROCYCLIC AROMATIC COMPOUNDS

Solved Problem

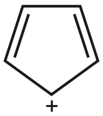
- Designate whether each of the following compounds is aromatic, non-aromatic or anti-aromatic.

(a)

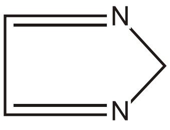


(b)

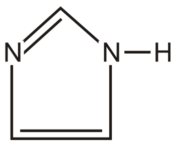
(c)



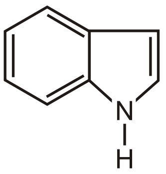
(d)



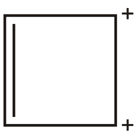
(e)



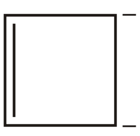
(f)



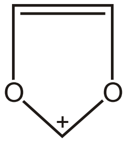
(g)



(h)



(i)



Ans. (a) 6 e. All carbons are sp^2 hybridized. The compound is aromatic.

(b) 6 e. All carbons are sp^2 hybridized. The compound is aromatic.

(c) 4 e. All carbons are sp^2 hybridized. The compound is anti-aromatic.

(d) The compound is non-aromatic.

(e) 6 e. The compound is aromatic.

(f) 10 e. The compound is aromatic.

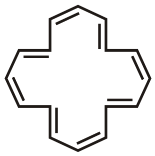
(g) 2 e. The compound is aromatic.

(h) 6 e. The compound is aromatic.

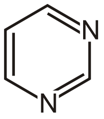
(i) 6 e. The compound is aromatic.

Solved Example

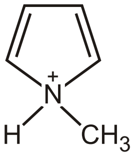
- Describe the following as aromatic, anti-aromatic or non-aromatic (neither aromatic nor anti-aromatic). Assume each is planar.



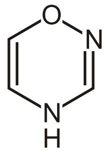
Anti-Aromatic



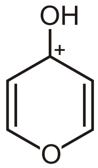
Aromatic



Anti-Aromatic



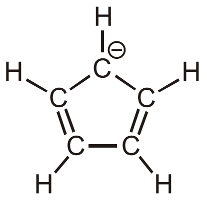
Anti-Aromatic



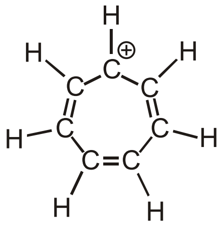
Aromatic

AROMATIC IONS

According to the Huckel criteria for aromaticity, a molecule must be cyclic, conjugated (nearly planar with a *p* orbital on each atom), and have $4n\ \ 2$ electrons. Nothing in this definition says that the number of *p* electrons must be the same as the number of atoms in the ring or that the substance must be neutral. In fact, the numbers can be different and the substance can be an ion. Thus, both the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic even though both are ions and neither contains a six-membered ring.



Cyclopentadienyl anion



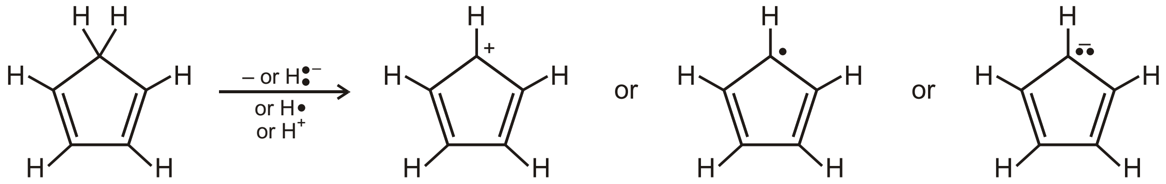
Cycloheptatrienyl cation

Six π electrons; aromatic ions

To see why the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic, imagine starting from the related neutral hydrocarbons, 1,3-cyclopentadiene and 1,3,5-cycloheptatriene, and removing one hydrogen from the saturated CH_2 carbon in each. If that carbon then rehybridizes from sp^3 to sp^2, the resultant products would be fully conjugated, with a *p* orbital on every carbon. There are three ways in which the hydrogen might be removed.

- The hydrogen can be removed with both electrons ($H{:}^-$) from the C — H bond, leaving a carbocation as product.
- The hydrogen can be removed with one electron ($H\bullet$ from the C — H bond, leaving a carbon radical as product.
- The hydrogen can be removed with no electrons (H+) from the C — H bond, leaving a carbanion as product.

Solved Example



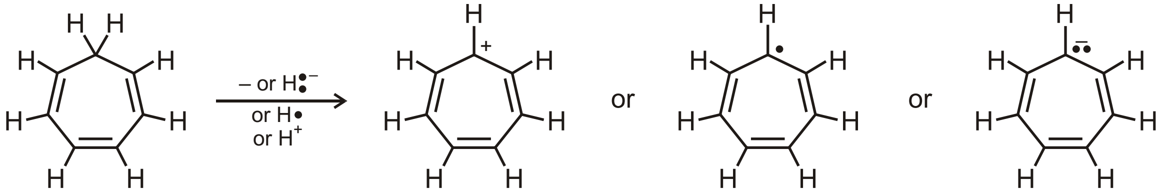
1,3-Cycloentadiene

Cyclopentadienyl cation
(four π electrons)

Cyclopentadienyl radical
(five π electrons)

Cyclopentadienyl anion
(six electrons)
(Aromatic)

Solved Example

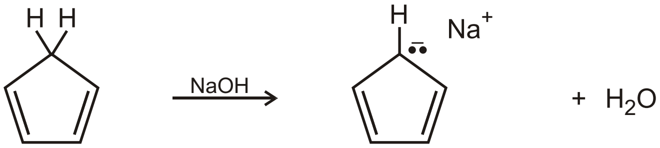


1,3,5-Cycloheptatriene

Cycloheptatrienyl cation
(six π electrons)

Cycloheptatrienyl radical
(seven π electrons)

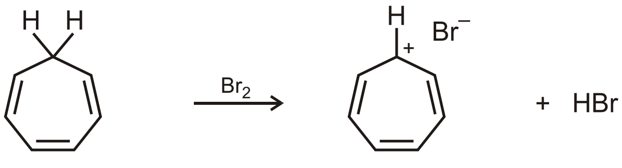
Cycloheptatrienyl anion
(eight π electrons)
(not Aromatic)



1,3,-Cyclopentadiene

Cyclopentadienyl anion (Aromatic)

Solved Example

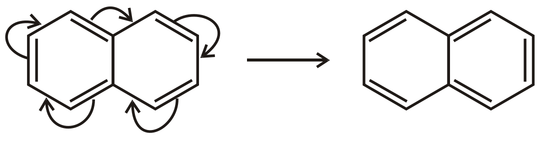


1,3,5-Cycloheptatriene

Cycloheptatrienyl cation

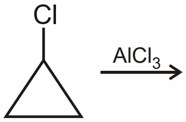
PERIPHERAL OR PERIMETER RESONANCE

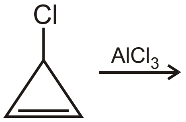
Although Huckel's rule strictly applies only to monocyclic compounds, it does appear to have application to certain bicyclic compounds, provided the important resonance structures involve only the perimeter double bonds, as in naphthalene below.

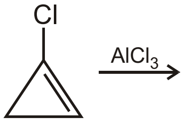


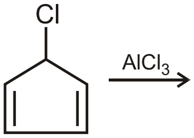
Solved Example

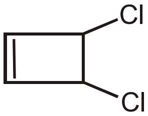
- X Number of reactions in which aromatic compound are formed.

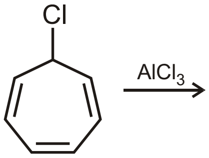
(a) 

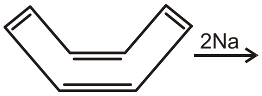
(b) 

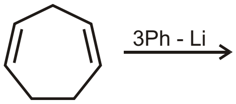
(c) 

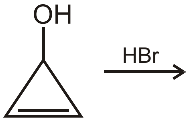
(d) 

(e) 

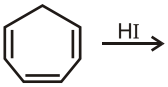
(f) 

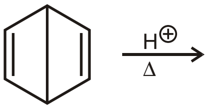
(g) 

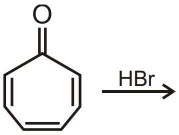
(h) 

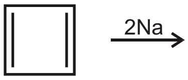
(i) 

(j) 

(k) 

(ℓ) 

(m) 

(n) 

Find the value of (x 4) ?

Ans. 7

Sol. Reactions in which aromatic compound are formed are : (b), (e), (f), (g), (h), (i), (j), (k), (ℓ), (m), (n)

X 11; (X 4) 7

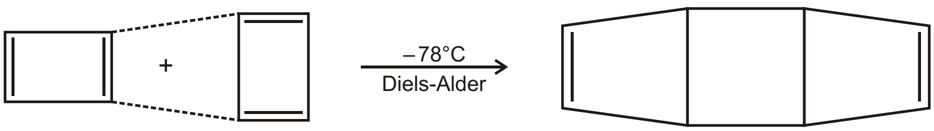
CYCLOBUTADIENE

Cyclobutadiene has four *p* electrons and is antiaromatic. The electrons are localized in two double bonds rather than delocalized around the ring, as indicated by an electrostatic potential map.

Cyclobutadiene

Two double bonds; four electrons

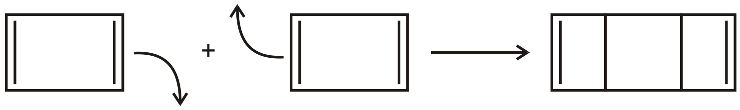
Cyclobutadiene is highly reactive and shows none of the properties associated with aromaticity. In fact, it was not even prepared until 1965, when Rowland Pettit of the University of Texas was able to make it at low temperature. Even at 78 C, however, cyclobutadiene is so reactive that it dimerizes by a Diels-Alder reaction. One molecule behaves as a diene and the other as a dienophile.



Solved Problem

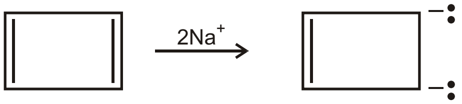
- Explain why the given compound undergoes dimerization at room temperature and readily reacts with active metals

Ans. The given compound dimerizes as follows :



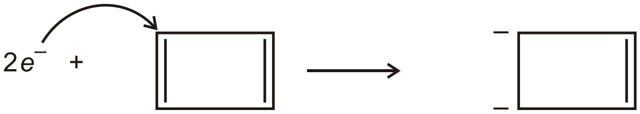
Here, the substrate is anti-aromatic and therefore unstable. It readily undergoes dimerization to give a product which is non-aromatic.

It reacts with an active metal as follows :



The mechanism of the above reaction is believed to proceed as follows :

2Na 2Na 2*e*

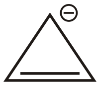
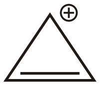
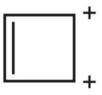
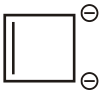
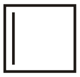


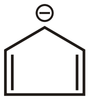
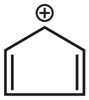
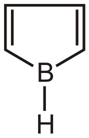
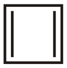
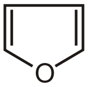
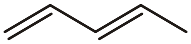
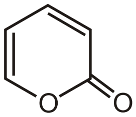
6πe, cyclic and planar systme,
(aromatic)

Obviously, the reaction with an a active metal converts the unstable anti-aromatic substrate into a stable aromatic system and proceeds readily.

Solved Example

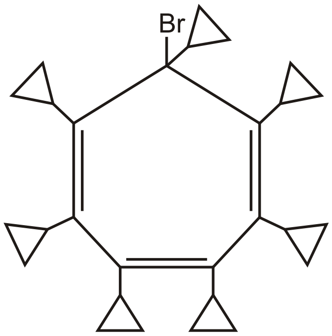
- Use the Huckel rule to indicate whether the following species are aromatic or antiaromatic or non aromatic ?

S.No.	Compound	Number of electron	Nature of compound
1.		2	Non aromatic
2.		4	Anti aromatic
3.		2	Aromatic
4.		2	Aromatic
5.		6	Aromatic
6.		2	Non aromatic
7.		4	Non aromatic

8.		6	Aromatic
9.		4	Anti aromatic
10.		4	Anti aromatic
11.		4	Anti aromatic
12.		6	Aromatic
13.		4	Non aromatic
14.		6	Aromatic

Solved Problem

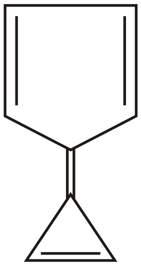
- In the given compound, will Br ionize in the form of (a) Br or (b) Br .



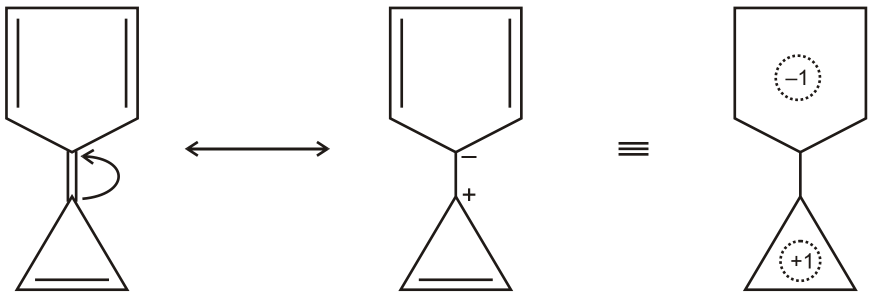
Ans. In this compound, Br will ionize in the form of Br so as to attain aromatic character for the molecule.

Solved Problem

- The given compound has high dipole moment. Explain.



Ans.

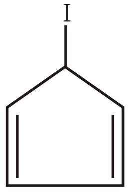


It is apparent that the given compound tends to acquire a resonance stabilized dipolar structure to gain aromaticity in each and so would have high dipole moment.

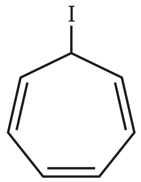
Solved Problem

- Compare the rate of reaction of the following compounds with $AgNO_3$.

(a)

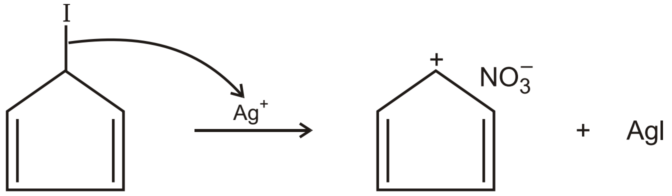


(b)



Ans. More the stability of the resultant carbocation, greater will be the rate of reaction.

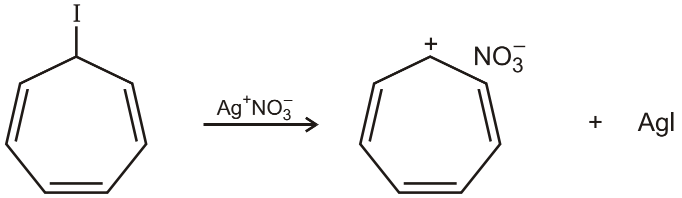
(a)



Anti-aromatic system

The carbocation is an antiaromatic system, so the rate of reaction is slow.

(b)

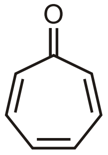


Aromatic system

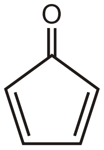
The carbocation in this case is stable aromatic system and so the reaction proceeds faster.

Solved Example

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

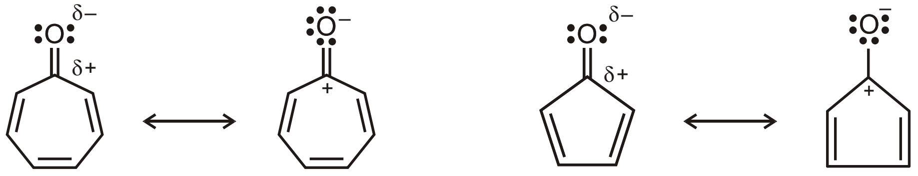


Cyclopropanone



Cyclopentadienone

Sol.



A B C D

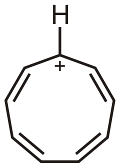
Cycloheptatrienone Cyclopentadienone

As in the previous problem, we can draw resonance forms in which both carbonyl n electrons are located on oxygen. The cycloheptatrienone ring in **B** contains six *n* electrons and is aromatic according to Huckel's rule. The cyclopentadienone ring in **D** contains four electrons and is antiaromatic.

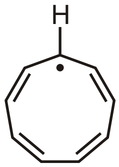
Solved Example

- Which would you expect to be most stable, cyclononatetraenyl radical, cation, or anion?

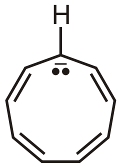
Sol. Check the number of electrons in the system of each compound. The species with a Huckel (4n 2) number of electrons is the most stable.



Cation
8π electrons



Radical
9π electrons



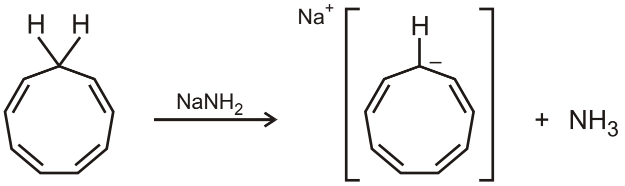
anion
10π electrons

The 10 electron anion is the most stable.

Solved Example

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

Sol. Treat 1,3,5,7-cyclononatetraene with a strong base to remove a proton.

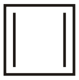


FAILURES OF THE RESONANCE

Large-Ring Annulenes

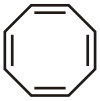
Like cyclooctatetraene, larger annulenes with (4N) systems do not show antiaromaticity because they have the flexibility to adopt nonplanar conformations. Even though [12] annulene, [16] annulene and [20] annulene are (4N) systems (with N 3, 4 and 5 respectively), they all react as partially conjugated polyenes.

For many years, chemists assumed that benzene's large resonance energy resulted from having two identical, stable resonance structures. They thought that other hydrocarbons with analogous conjugated systems of alternating single and double bonds would show similar stability. These cyclic hydrocarbons with alternating single and double bonds are called annulenes. For example, benzene is the six-membered annulene, so it can be named [6] annulene. Cyclobutadiene is [4] annulene, cyclooctatetraene is [8] annulene, and larger annulenes are named similarly.

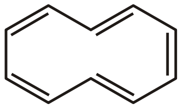


cyclobutadiene
[4] annulene

benzene
[6] annulene



cyclooctatetraene
[8] annulene

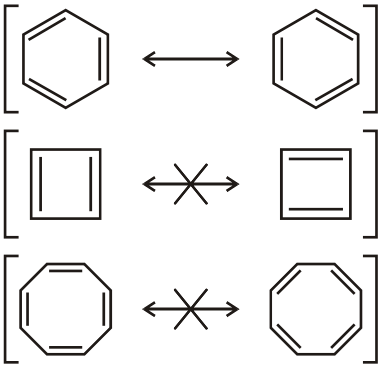


cyclodecapentaene
[10] annulene

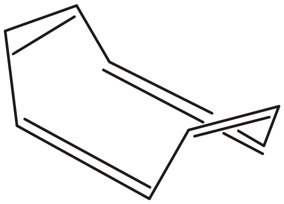
For the double bonds to be completely conjugated, the annulene must be planar so the *p* orbitals of the pi bonds can overlap. As long as an annulene is assumed to be planar, we can draw two Kekulé-like structures that seem to show a benzene-like resonance. The given figure shows proposed benzene-like resonance forms for cyclobutadiene and cyclooctatetraene. Although these resonance structures suggest that the [4] and [8] annulenes should be unusually stable (like benzene), experiments have shown that cyclobutadiene and cyclooctatetraene are not unusually stable. These results imply that the simple resonance picture is incorrect.

Cyclobutadiene has never been isolated and purified. It undergoes an extremely fast Diels–Alder dimerization. To avoid the Diels–Alder reaction, cyclobutadiene has been prepared at low concentrations in the gas phase and as individual molecules trapped in frozen argon at low temperatures. This is not the behavior we expect from a molecule with exceptional stability!

In 1911, Richard Willstäer synthesized cyclooctatetraene and found that it reacts like a normal polyene. Bromine adds readily to cyclooctatetraene, and permanganate oxidizes its double bonds. This evidence shows that cyclooctatetraene is much less stable than benzene. In fact, structural studies have shown that cyclooctatetraene is not planar. It is most stable in a ‘‘tub’’ conformation, with poor overlap between adjacent pi bonds.



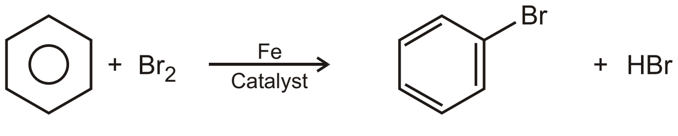
Cyclobutadiene and cyclooctatetraene have alternating single and double bonds similar to those of benzene. These compounds were mistakenly expected to be aromatic.



“tub” conformation of cyclooctatetraene

RESONANCE ENERGY

Benzene (C_6H_6) has six fewer hydrogens than the corresponding six-carbon cycloalkane (C_6H_{12}) and is clearly unsaturated, usually being represented as a six-membered ring with alternating double and single bonds. Yet it has been known since the mid-1800s that benzene is much less reactive than typical alkenes and fails to undergo typical alkene addition reactions. Cyclohexene, for instance, reacts rapidly with Br_2 and gives the addition product 1,2-dibromocyclohexane, but benzene reacts only slowly with Br_2 and gives the substitution product C_6H_5Br.



Bromobenzene
(substitution product)

We can get a quantitative idea of benzene’s stability by measuring heats of hydrogenation. Cyclohexene, an isolated alkene, has H_{hydrog} 118 kJ/mol (–28.2 kcal/mol), and 1,3-cyclohexadiene, a conjugated diene, has H_{hydrog} 230 kJ/mol (–55.0 kcal/mol). As noted before, this value for 1,3-cyclohexadiene is a bit less than twice that for cyclohexene because conjugated dienes are more stable than isolated dienes.

Carrying the process one step further, we might expect H hydrog for ‘‘cyclo-hexatriene’’ (benzene) to be a bit less than – 356 kJ/mol, or three times the cyclohexene value. The actual value, however, is – 206 kJ/mol, some 150 kJ/mol (36 kcal/mol) less than expected. Since 150 kJ/mol less heat than expected is released during hydrogenation of benzene, benzene must have 150 kJ/mol less energy to begin with. In other words, benzene is more stable than expected by 150 kJ/mol (Figure).

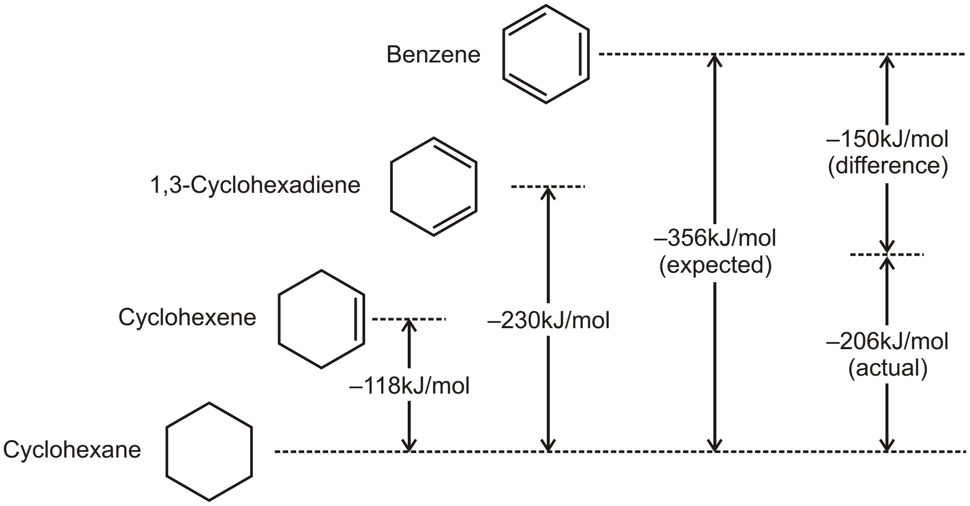


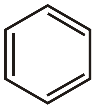
Figure : A comparison of the heats of hydrogenation for cyclohexene, 1,3-cyclohexadiene and benzene. Benzene is 150 kJ/mol (36 kcal/mol) more stable than might be expected for "cyclohexatriene."

Further evidence for the unusual nature of benzene is that all its carbon-carbon bonds have the same length—139 pm—intermediate between typical single (154 pm) and double (134 pm) bonds. In addition. Thus, benzene is a planar molecule with the shape of a regular hexagon. All C — C — C bond angles are 120°, all six carbon atoms are sp^2-hybridized, and each carbon has a *p* orbital perpendicular to the plane of the six-membered ring.

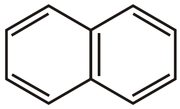
Because all six carbon atoms and all six *p* orbitals in benzene are equivalent, it's impossible to define three localized bonds in which a given *p* orbital overlaps only one neighboring *p* orbital. Rather, each *p* orbital overlaps equally well with both neighboring *p* orbitals, leading to a picture of benzene in which all six electrons are free to move about the entire ring. In resonance terms, benzene is a hybrid of two equivalent forms. Neither form is correct by itself; the true structure of benzene is somewhere in between the two resonance forms but is impossible to draw with our usual conventions. Because of this resonance, benzene is more stable and less reactive than a typical alkene.

Solved Example

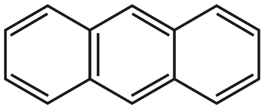
- Shown below are the structures of the first four benzene-based aromatic hydrocarbons and their associated resonance energies.



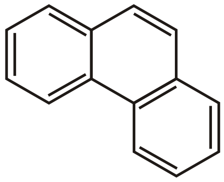
Benzene
36 kcal/mol



Naphthalene
61 kcal/mol



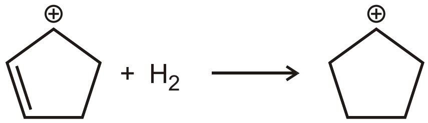
Anthracene
84 kcal/mol



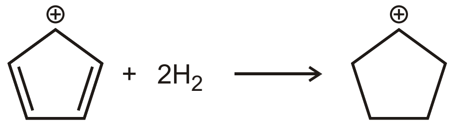
Phenanthrene
92 kcal/mol

Solved Example

- From the following, calculate the resonance energy of the cyclopentadienyl cation.



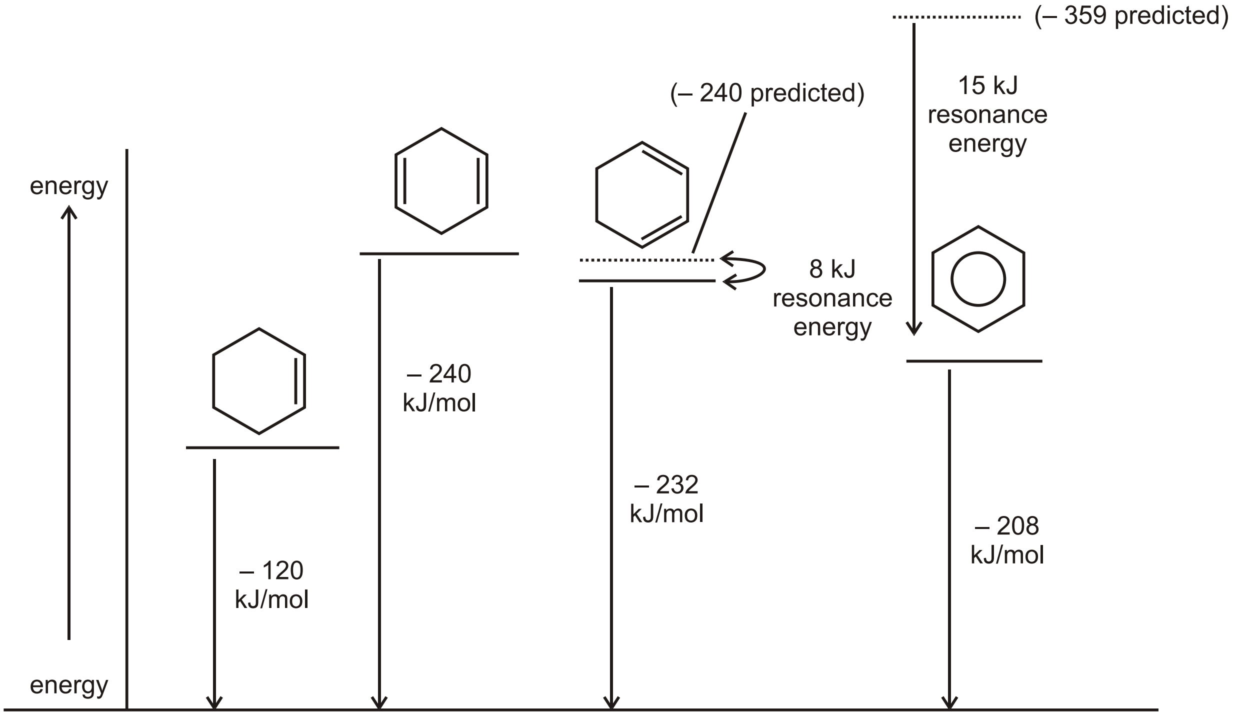
$\Delta H = -14.58$ kcal/mol



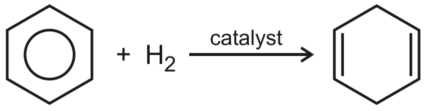
$\Delta H = -72.91$ kcal/mol

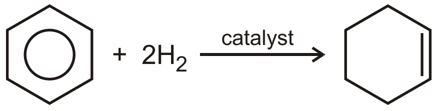
Sol. One hydrogeneration of the allyl cation liberates – 14.58 kcal/mol, so two should liberate – 29.16 kcal/mol. Hydrogenation actually gains – 72.91 kcal/mol making the cation HIGHER in energy by 43.75 kcal/mol. The resonance energy is NEGATIVE : – 43.75 kcal/mol.

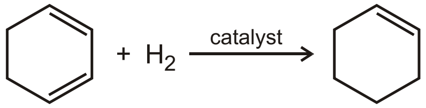
Solved Example



Using the information in figure, calculate the values of H for the following reactions :

(a) 

(b) 

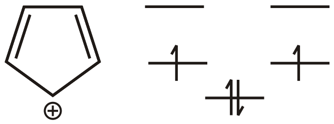
(c) 

Ans. (a) + 32 kJ/mol (b) – 88 kJ/mol (c) – 112 kJ/mol

Solved Example

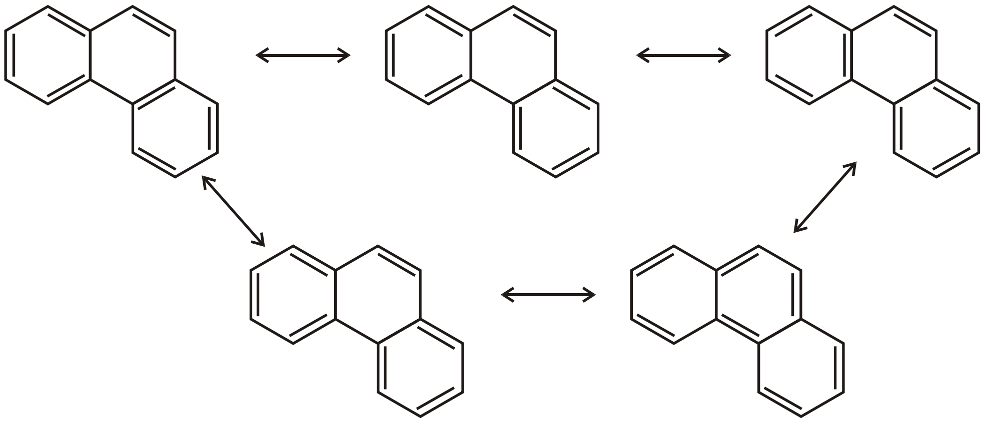
- Sketch the MO diagram for this species and use it to determine whether this is an aromatic or antiaromatic molecule. Is this consistent with the resonance energy?

Sol.

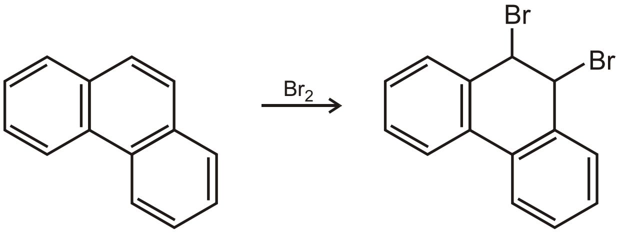


Solved Example

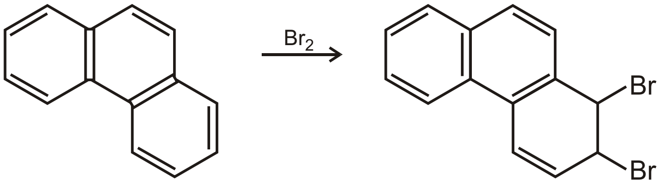
- Phenanthrene has five Kekule resonance structures. One of the bonds of phenanthrene reacts with bromine to give an **addition reaction** just like an alkene. Which bonds? Explain.



Reaction at this bond costs 92-72 (two benzenes) = 20 kcal/mol in resonance.



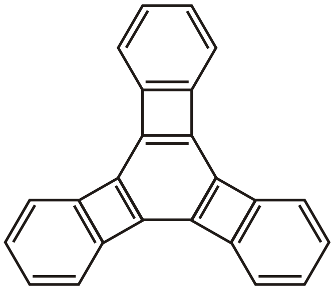
Sol.



Reaction in the other ring costs 92-61 or 31 Kcal/mol

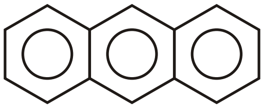
Solved Examples

- (i)



$\xrightarrow{3H_2/Pd}$ (x) number of product including stereo isomers

(ii)

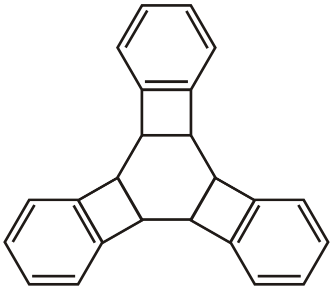


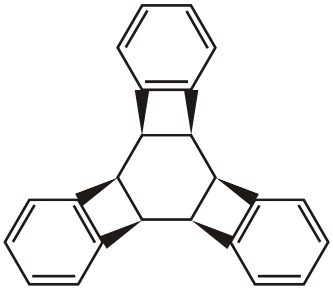
When two hydrogen of anthracene is replaced by bromine then number of meso isomer (y) obtained is so,

x y ?

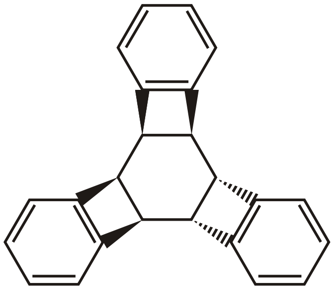
Ans. 2 0 2

Sol. (i) After hydrogenation we get here we get 3 aromatic 4 non aromatic rings in all other cases we get at least 1 anti aromatic ring which is very unstable. Possible isomers.





All three on the same side



Any two on same side

Hence x 2.

(ii) For a meso product, we need at least 2 chiral centres.

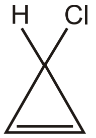
After dibromination we don't get any such products.

Hence y 0

x y 2

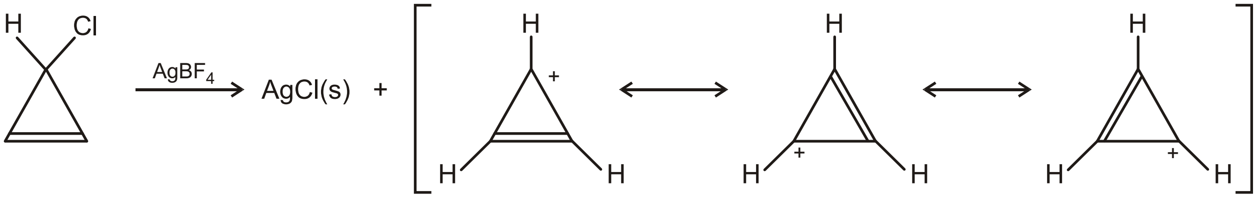
Solved Example

- 3-Chlorocyclopropene, on treatment with $AgBF_4$, gives a precipitate of AgCl and a stable solution of a product. What is a likely structure for the product, and what is its relation to Huckel's rule?



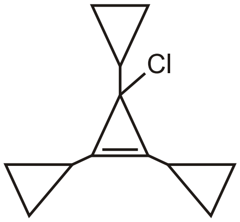
3-Chlorocyclopropene

Sol.

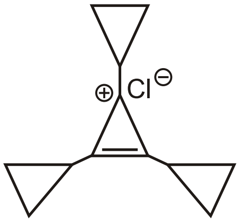


Solved Example

- When this compound ionizes, is Cl or Cl formed?

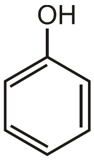


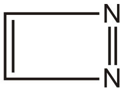
Sol. Chlorine atom will ionised in the form of chloride ion



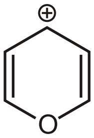
Solved Example

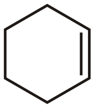
- Number of aromatic compounds in the following

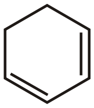
(a) 

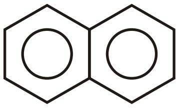
(b) 

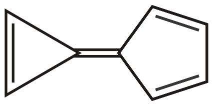
(c) 

(d) 

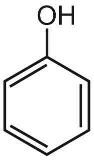
(e) 

(f) 

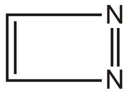
(g) 

(h) 

Ans. 4

Sol. (a) 

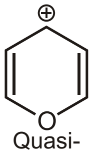
Aromatic

(b) 

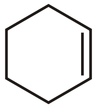
Anti-aromatic

(c) 

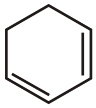
Non-aromatic

(d) 

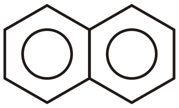
Quasi-
Aromatic

(e) 

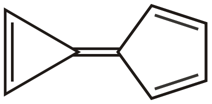
Non-aromatic

(f) 

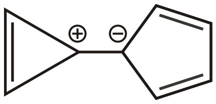
Non-aromatic

(g) 

Aromatic

(h) 

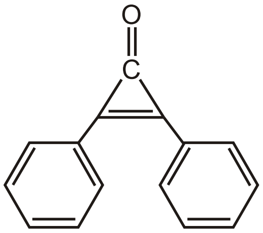
Aromatic

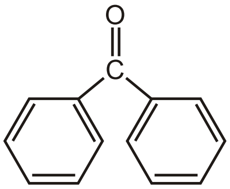


Quasi-aromatic

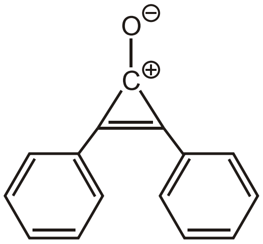
Solved Example

- Which of the following compounds has the greater dipole moment?





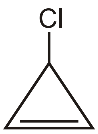
Sol. Ist compound has the greater dipole moment



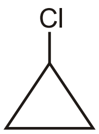
quasi aromatic compound
(highly stable)

Solved Example

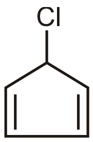
- Order of rate of reaction with $AgNO_3$



(I)



(II)



(III)

(A) I > III > II

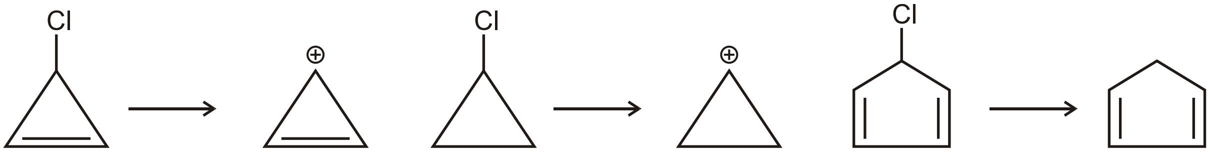
(B) II > III > I

(C) I > II > III

(D) III > I > II

Ans. (C)

Sol.

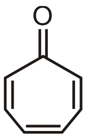


(I) Quasi-aromatic (II) Non-aromatic (III) Anti-aromatic

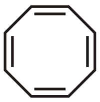
Solved Example

- Comment on the nature of given compounds

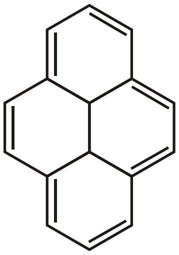
1.



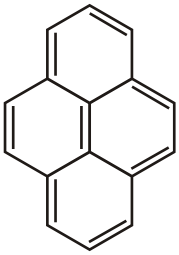
2.



3.

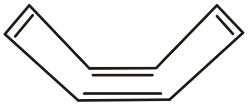


4.



Sol. (1) 6- -electron are present in the compound (-bond outside the ring will not counted in number of -electrons so compound is **aromatic** in nature.

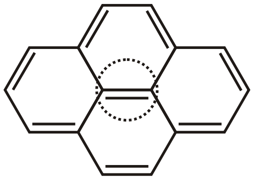
(2) This compound is not planar, actually it is **tub** shaped so it's **non-aromatic** in nature.



Tub shaped due to ring strain

(3) 14- -electron's are present in the compound (so the value of n is 3) so it is aromatic in nature.

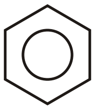
(4) The circled -bond will not be counted in number of -electron. 14- -electron's are present in the compound (so the value of n is 3) so it is aromatic in nature.

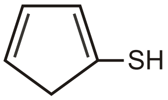
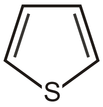


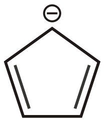
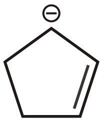
EXERCISE

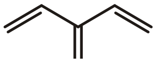
SINGLE CHOICE QUESTIONS

1. In which of the following pair Ist compound has more resonance energy than IInd?

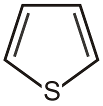
(A)  (I)  (II)

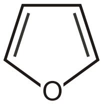
(B)  (I)  (II)

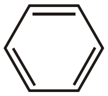
(C)  (I)  (II)

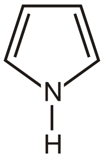
(D)  (I)  (II)

2. Which of the following aromatic compounds is the most stable?

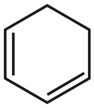
(A) 

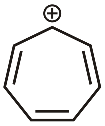
(B) 

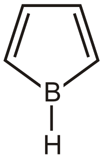
(C) 

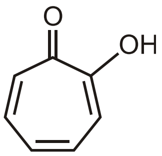
(D) 

3. Which of the following is unstable at room temperature?

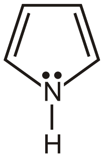
(A) 

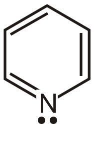
(B) 

(C) 

(D) 

4. Which of these would you expect to have significant resonance energy?

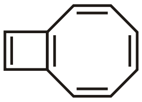
 (I)

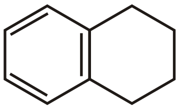
 (II)

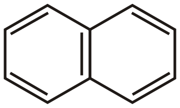
 (III)

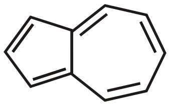
(A) I
(B) II
(C) III
(D) All of the above
(E) None of the above

5. Which of these is the single best representation for naphthalene?

 (I)

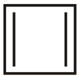
 (II)

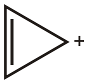
 (III)

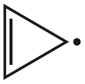
 (IV)

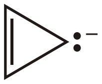
(A) I
(B) II
(C) III
(D) IV

6. Which cyclization(s) should occur with a decrease in pi-electron energy?

(I) $CH_2 \quad CH—CH \quad CH_2$  H_2

(II) $CH_2 \quad CH—CH_2$  H_2

(III) $CH_2 \quad CH—CH_2$  H_2

(IV) $CH_2 \quad CH—CH_2$  H_2

(A) I (B) II (C) III (D) IV

(E) All of the above

7. Which of the following statements about cyclooctatetraene is NOT true?

(A) The compound rapidly decolorizes Br_2/CCl_4 solutions. (test for unsaturated hydrocarbon)

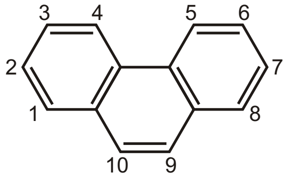
(B) The compound rapidly decolorizes aqueous solutions of $KMnO_4$. (test for unsaturated hydrocarbon)

(C) The compound readily adds hydrogen.

(D) The compound is nonplanar.

(E) The compound is comparable to benzene in stability.

8. Recalling that benzene has a resonance energy of 152 kJ mol^{1} and naphthalene has a resonance energy of 255 kJ mol^{1}, predict the positions which would be occupied by bromine when phenanthrene (below) undergoes addition of Br_2.



(A) 1, 2 (B) 1, 4 (C) 3, 4 (D) 7, 8

(E) 9, 10

9. Which of the following are not aromatic :

(A) Benzene (B) Cyclo-octatetrarenyl dianion

(C) Tropyllium cation (D) Cyclopentadienyl cation

10. Which of the following statements is correct for the given molecule?

(A) Shape of the given molecule is square

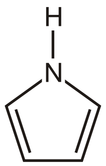
(B) Shape of the given molecule is rectangular

(C) Given molecule is Non-aromatic

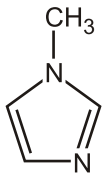
(D) Given molecule is more stable than Non-aromatic molecules

Cyclobutadiene

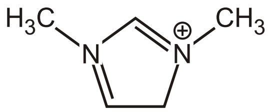
11. Choose the aromatic nitrogen heterocycles.



(i)



(ii)

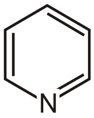


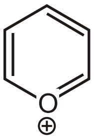
(iii)

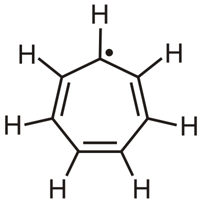
(A) i (B) ii (C) iii (D) i and ii

(E) i, ii and iii

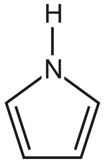
12. Which of the following compounds is not aromatic?

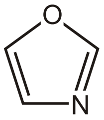
(A) 

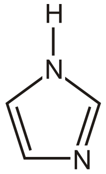
(B) 

(C) 

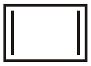
Cycloheptatrienyl radical

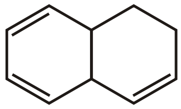
(D) 

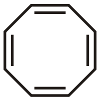
(E) 

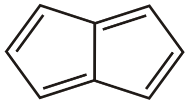
(F) 

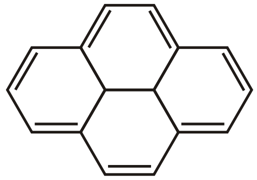
13. Which one of the following compounds is aromatic?

(A) 

(B) 

(C) 

(D) 

(E) 

14. Aromatic properties of benzene are proved by :

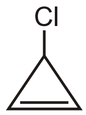
(A) Aromatic sextet theory (B) Resonance theory

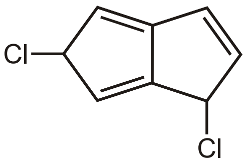
(C) Molecular orbital theory (D) All of these

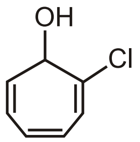
15. An aromatic compouns among other things should have a p-electron cloud containing (4n 2) electrons where n can't be (huckel rule) :

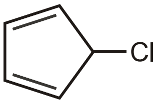
(A) 1/2 (B) 3 (C) 2 (D) 1

16. Which of the following reactions will NOT proceed?

(A)  $SbCl_5$

(B)  + 2 BuLi

(C)  $\xrightarrow{-HCl}$

(D)  $\xrightarrow{SN_1}$

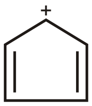
17. Which of the following statements regarding the cyclopentadienyl radical is correct?

(A) It is aromatic. (B) It is not aromatic.

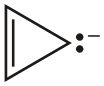
(C) It obeys Huckel's rule. (D) It undergoes reactions characteristic of benzene.

(E) It has a closed shell of 6 pi-electrons.

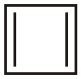
18. Which of the following would you expect to be aromatic?



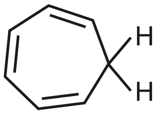
(I)



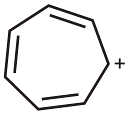
(II)



(III)



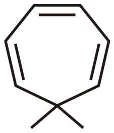
(IV)



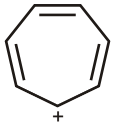
(V)

(A) I
(B) II
(C) III
(D) IV
(E) V

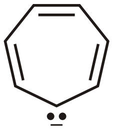
19. Which of the following would you expect to be aromatic?



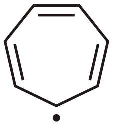
(I)



(II)



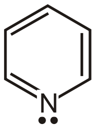
(III)



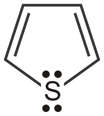
(IV)

(A) I
(B) II
(C) III
(D) IV
(E) None of these

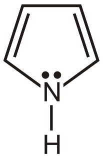
20. Which compound would you NOT expect to be aromatic?



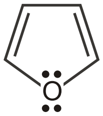
(I)



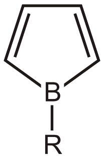
(II)



(III)



(IV)



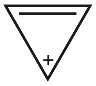
(V)

(A) I
(B) II
(C) III
(D) IV
(E) V

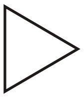
21. Which annulene would you NOT expect to be aromatic?

(A) [6]-Annulene
(B) [14]-Annulene
(C) [16]-Annulene
(D) [18]-Annulene
(E) [22]-Annulene

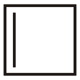
22. Which of the following would you expect to be aromatic?



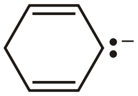
(I)



(II)



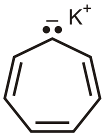
(III)



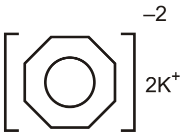
(IV)

(A) I
(B) II
(C) III
(D) IV
(E) None of these

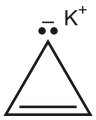
23. Which of the following structures would be aromatic?



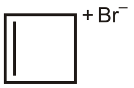
(I)



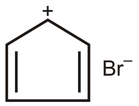
(II)



(III)



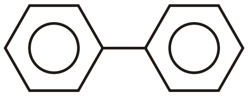
(IV)



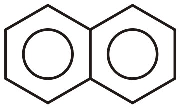
(V)

(A) I
(B) II
(C) III
(D) IV
(E) V

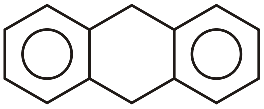
24. Compare resonance Energy of following



(a)



(b)



(c)

(A) c > a > b (B) b > a > c (C) a > b > c (D) a > c > b

25. In the molecular orbital model of benzene, how many pi-electrons are delocalized about the ring?

(A) 2 (B) 3 (C) 4 (D) 5

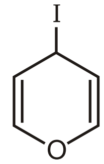
(E) 6

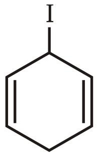
26. In the molecular orbital model of benzene, how many pi-electrons are in bonding molecular orbitals?

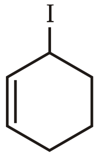
(A) 6 (B) 5 (C) 4 (D) 3

(E) 2

27. Compare the stability of carbocation which are formed when react with $AgNO_3$.

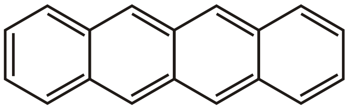


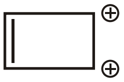


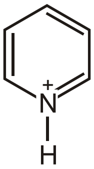


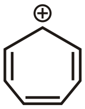
(A) a > b > c (B) a > c > b (C) b > c > a (D) b > a > c

28. How many compounds are aromatic :

(A) 

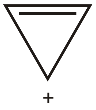
(B) 

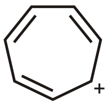
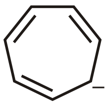
(C) 

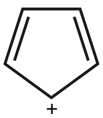
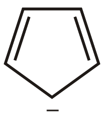
(D) 

(E) All of above

29. Which of the following pairs indicates correct order of stability?

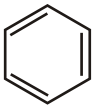
(A)  > 

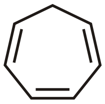
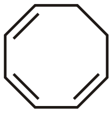
(B)  < 

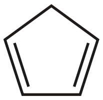
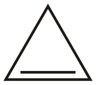
(C)  > 

(D) All are correct

30. Which member of each of the following pairs of compounds is more readily deprotonated?

(A)  > 

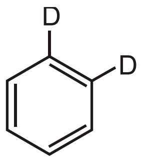
(B)  < 

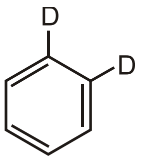
(C)  > 

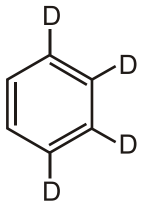
(D) All are correct

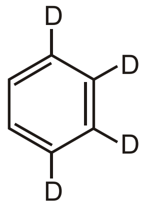
MULTIPLE CHOICE QUESTIONS

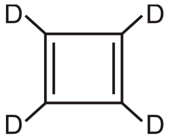
1. Which of the following represents same molecules.

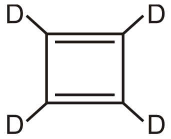
(A) 

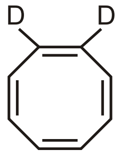
and 

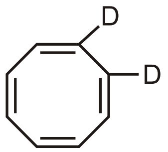
(B) 

and 

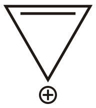
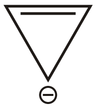
(C) 

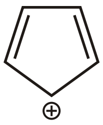
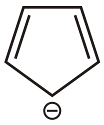
and 

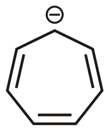
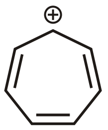
(D) 

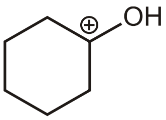
and 

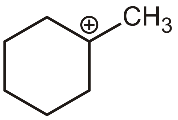
2. In which pair second ion is more stable than first ?

(A) 


(B) 


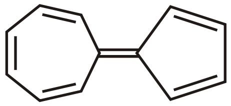
(C) 


(D) 

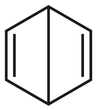


UNSOLVED EXAMPLE

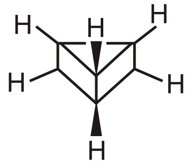
1. The following hydro carbon has an unusually high large dipole moment, explain why



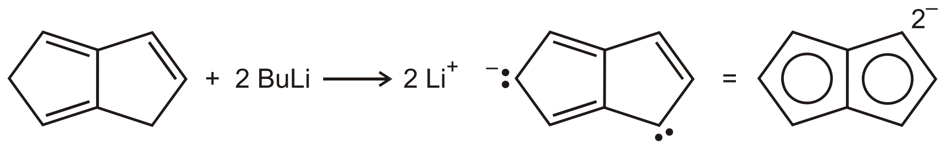
2. Between 1865 and 1890, other possible structures were proposed for benzene such as those shown here. Considering what nineteenth-century chemists knew about benzene, which is a better proposal for benzene's structure, Dewar benzene or Ladenburg benzene? Why?



Dewar benzene

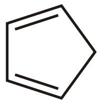


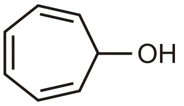
Ladenburg benzene

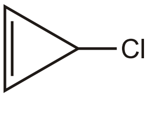
3. 

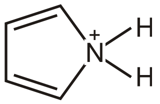
pentalene dianion

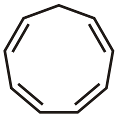
4. How would you convert the following compounds to aromatic compounds?

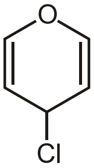
(a) 

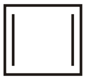
(b) 

(c) 

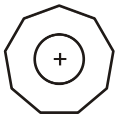
(d) 

(e) 

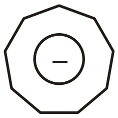
(f) 

(g) 

5. Is either of the following ions aromatic?

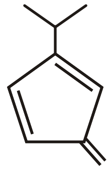
(a) 

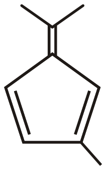
Cyclononatetraenyl
cation

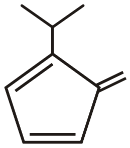
(b) 

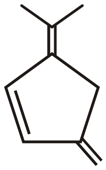
Cyclononatetraenide
anion

6. One of the following hydrocarbon is much more acidic than the others. Explain why?

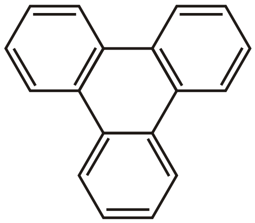




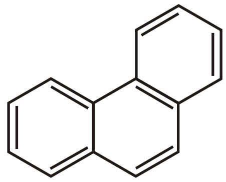




7. Explain why compound **A** is much more stable than compound **B**.



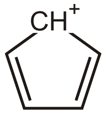
triphenylene
(A)

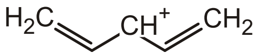


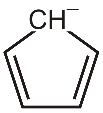
phenanthrene
(B)

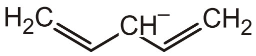
WORK SHEET - 1

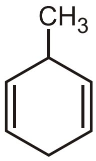
1. Compare Resonance energy between the given compounds:

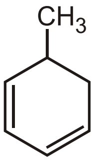
(a) 

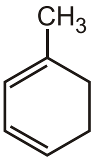


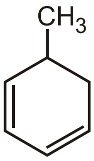
(b) 

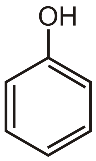


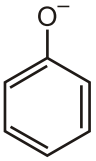
(c) 

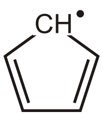


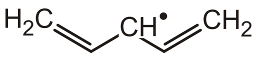
(d) 

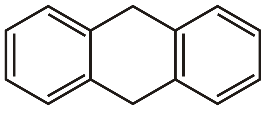


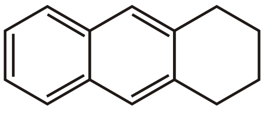
(e) 

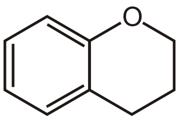


(f) 

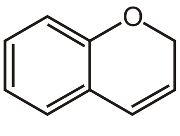


(g) 



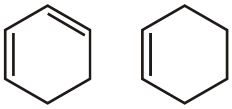
(h) 

Chroman

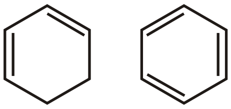


2H-Chromene

(i)



(j)



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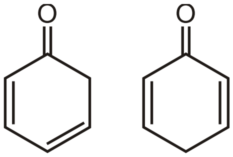
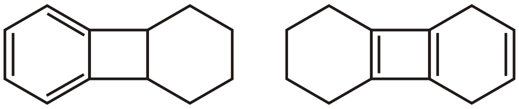


(l)



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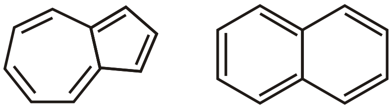

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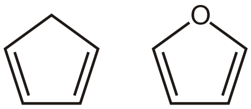
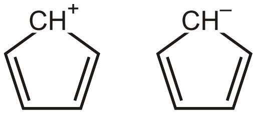


(o)



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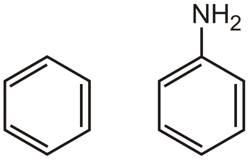
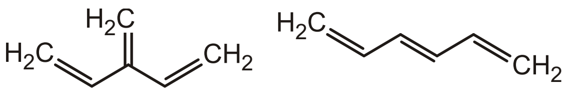
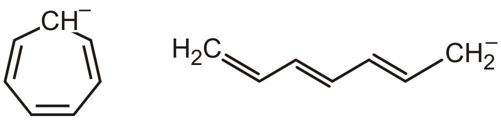


(q)



(r)



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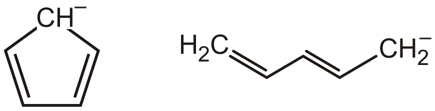

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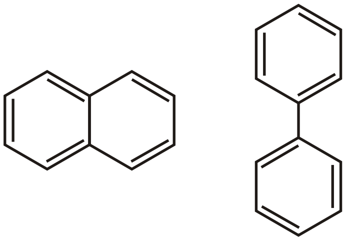
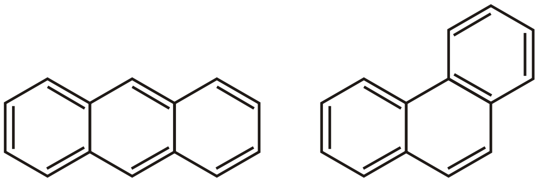
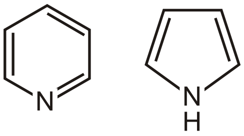


(u)

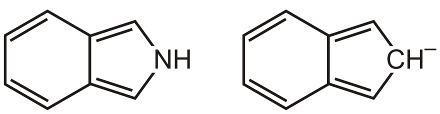


Anthracene Phenanthrene

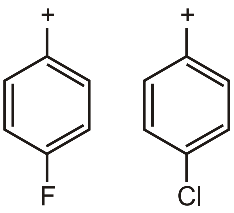
(v)



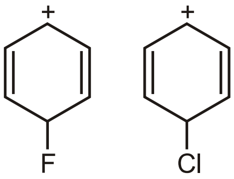
(w)



(x)

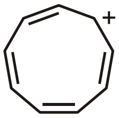


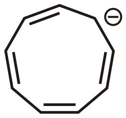
(y)



WORK SHEET - 2

1. Classify each as aromatic or antiaromatic or non-aromatic :

(1)

thecyclonona-
tetraenecation

(2)

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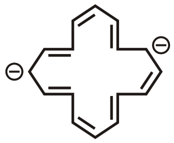
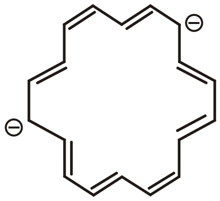
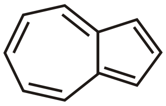
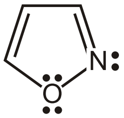
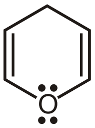
tetraeneanion

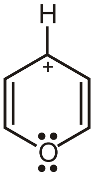
(3)

the[16]annulene
dianion

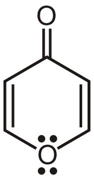
(4)

[18]annulenedianion

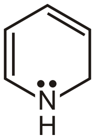
(5)

azulene

(6)

isoxazole

(7)

pyran

(8)

pyrylium ion

(9)

γ-pyrone

(10)

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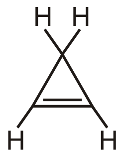

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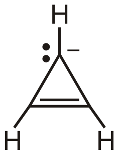

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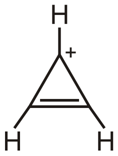

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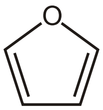

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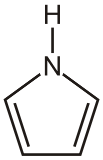

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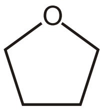

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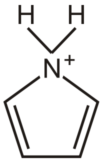

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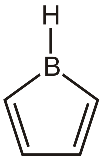

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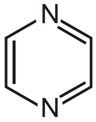

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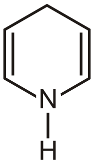

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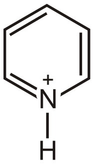

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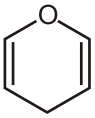

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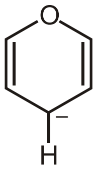

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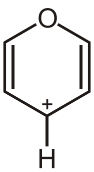

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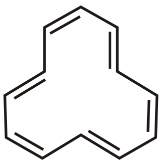

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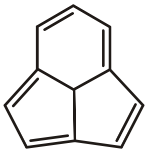

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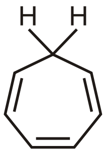

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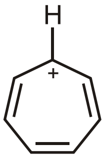

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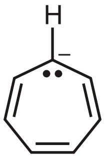

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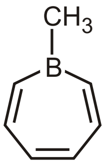

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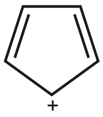

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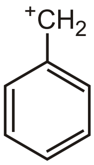

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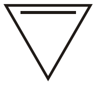

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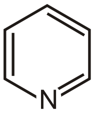

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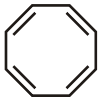

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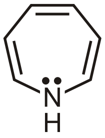

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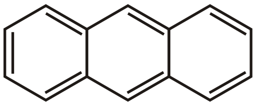

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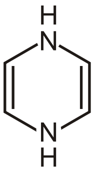

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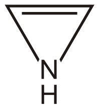

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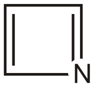

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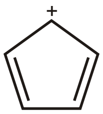

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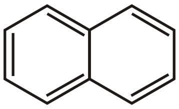

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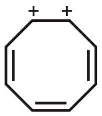

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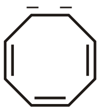

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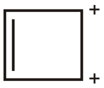

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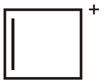

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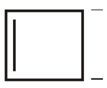

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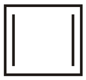

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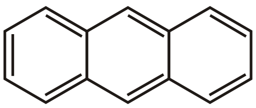

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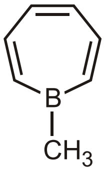

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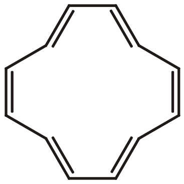

[12] annulene

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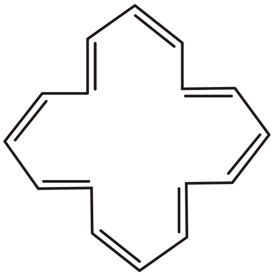

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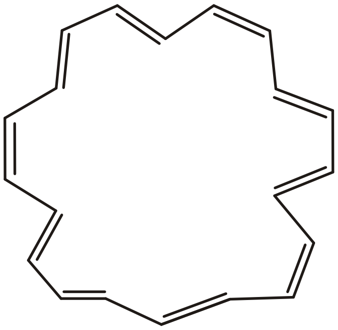

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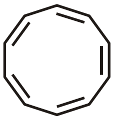
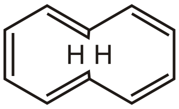


all-cis

(56)



naphthalene

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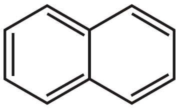

naphthalene

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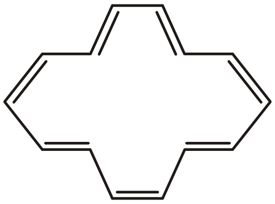

[14] annulene

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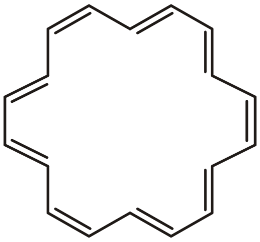
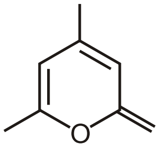
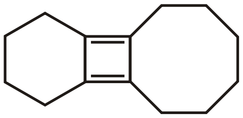


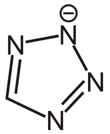
[18] annulene

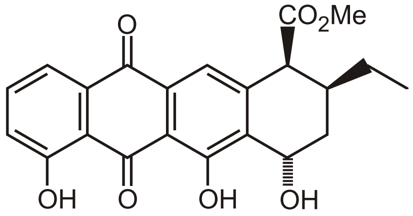
SUBJECTIVE TYPE QUESTIONS

1. Which of these compounds are aromatic? Justify your answer with some electron counting. You are welcome to treat each ring separately or two or more rings together, whichever you prefer,

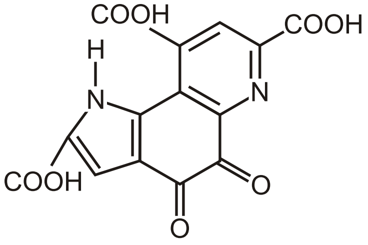




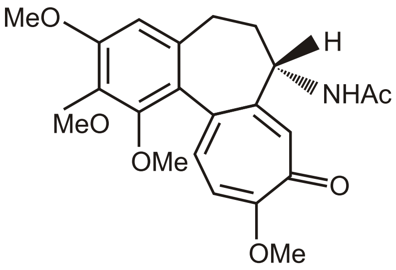




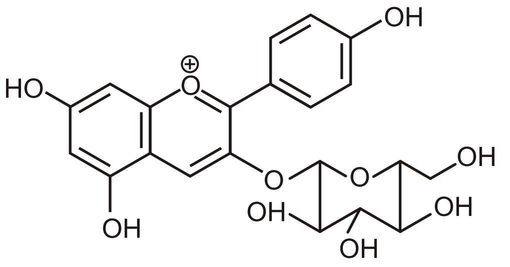
alkavinone : tetracycline antibotic



methoxatin coenzyme
from bacteria
living on methane



colchicine : compound from
Autumn crocus used to treat gout



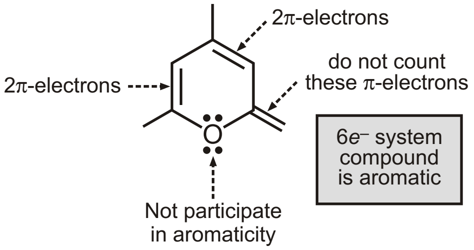
callistephin; natural red flower pigment

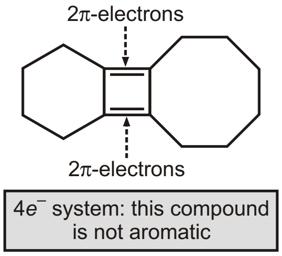
Purpose of the problem

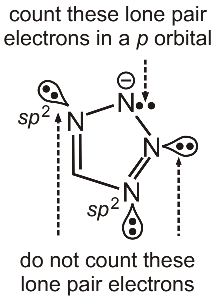
A simple exploration of the idea of aromaticity; can you count to six?

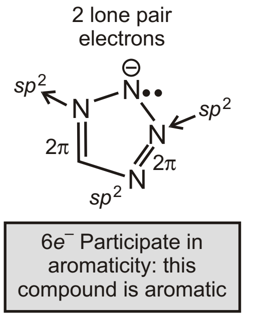
Suggested solution

The first three compound are straight forward providing you count lone pair electron on atomic in the ring and do not count electrons outside the ring such as those in the carbonyl bond in the first compound. Nor should you count the lone pair represented by the negative charge in the third compound. They are in an sp^2 orbital in the plane of the ring.

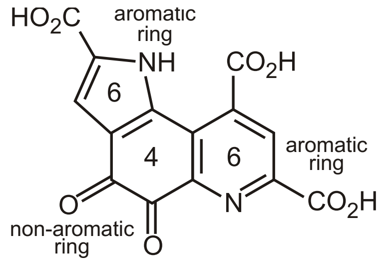




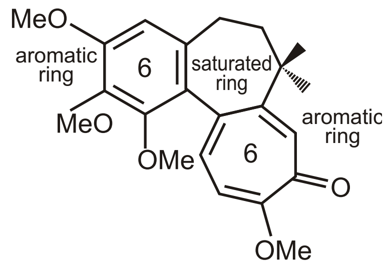


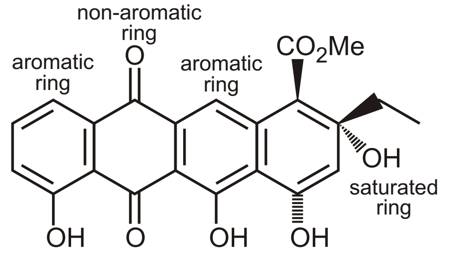


The rest offer variations on the benzene ring and each ring must be considered separately. Methoxatin has five-and six-membered ring with nitrogen in them. Count the lone pair in a *p*-orbital on the nitrogen atom in the five-membered ring but not those in an sp^2 orbital in the six-membered ring (pyridine). Both are aromatic. Colchicine has an aromatic seven-membered ring with six electrons (don't count the C O group) while callistephin has an interesting positively charged aromatic ring with three double bonds. We summarize these answer briefly by giving the number of electrons in each conjugated ring.

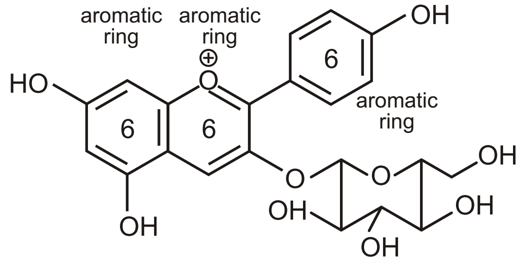


methoxatin: coenzyme from bacteria living on methane



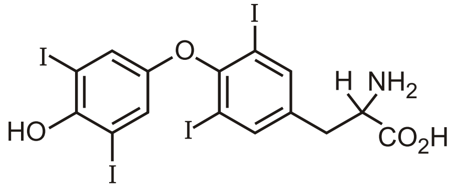


aklavinone: a tetracycline antibiotic



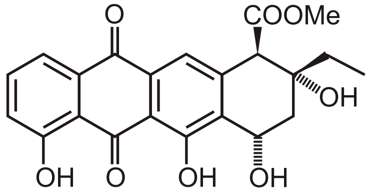
callistephin: natural red flower pigment

2. All you have to do is to spot the aromatic rings in these compounds. It may not be as easy as you think and you should state some reasons for your choice.

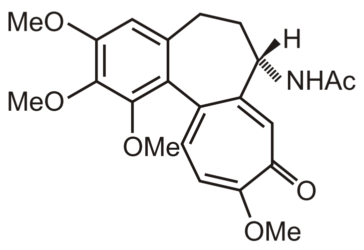


Thyroxine-T$_4$

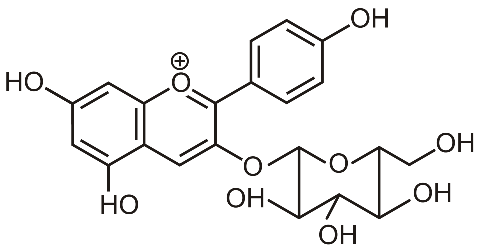
thyroxine
(human hormone)
Iodine carrier
in thyroid gland



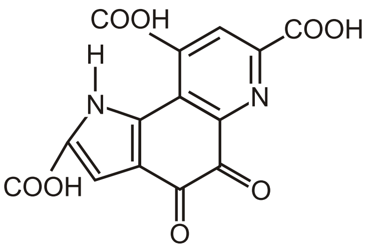
aklavinone
tetracycline
antibiotic
[why tetracycline ?]



colchiche compound
from autumn treat gout



calistephin
natural red flower pigment



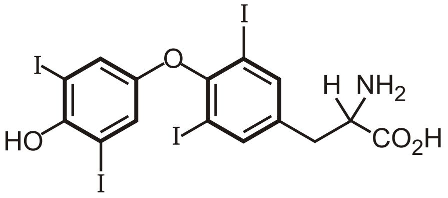
methoxatin coenzyme from
bacteria living on methane

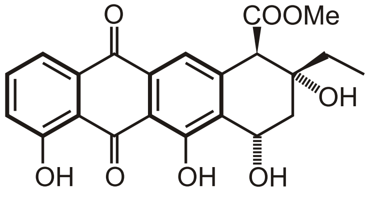
Purpose of the problem

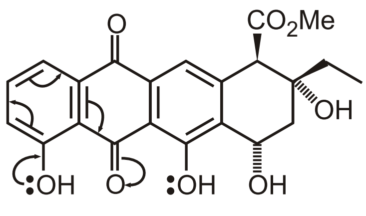
Simple exercise in counting electrons with a few hidden tricks.

Suggested solution

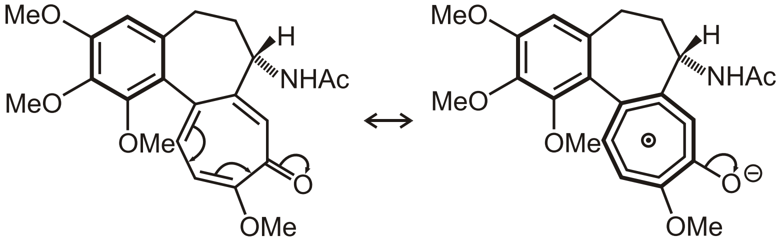
Truly aromatic rings are marked with thick lines. Thyroxine has two benzene rings, which are aromatic and c that is that. Aklavinone has again two aromatic rings, one definitely nonaromatic ring (D) and one (B) that we might argue about. However, try as you may you can't get six electrons into ring B (one extreme delocalized version is shown). 'Tetracycline' because of the four rings.

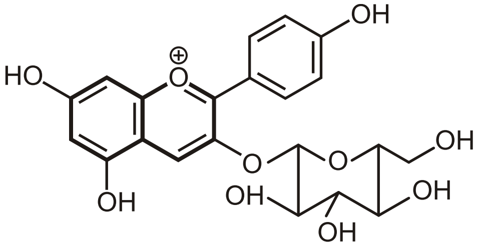






Colchicine has one benzene ring and one aromatic seven-membered ring with six electrons (don't count the electrons in the C O bond) as the delocalized structure makes clear. Callistephin has a benzene ring and a two-ring oxygen-based cation, which is like a naphthalene. You can count it as one ten electron system or as two fused six-electron systems sharing one C C bond, whichever you perfer.





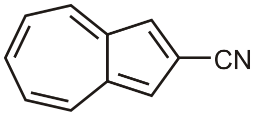
3. Azulene has an unexpectedly high dipole moment. Explain.

4. Compare the dipole moments of compounds in each of the following pairs.

(a) *p*-Toluidine and *p*-Anisidine
(b) Vinyl bromide and Ethyl bromide
(c) 2,3-Diphenylcyclopropenone and Acetophenone
(d) MeCl and MeF
(e) *p*-chlorophenol and *p*-Fluorophenol
(f) Tropolone and 2-Hydroxytropolone

5. Compare the dipole moments of the following compounds with reasons.

(a)



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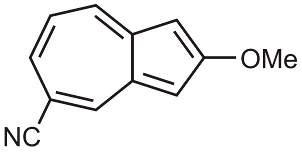
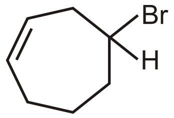


(i)

(ii)

(b)



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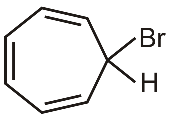
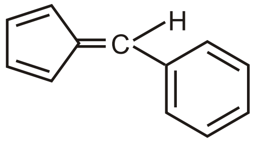


(iii)

(iv)

(c)



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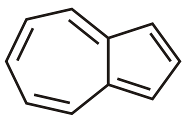


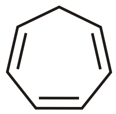
(v)

(vi)

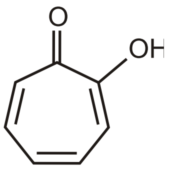
6. Predict which member of each of the following pairs of compounds has higher resonance energy and justify our choice :

(a) Anthracene or phenanthrene
(b) Ammonium acetate or acetamide
(c) Cyclooctatetraene or styrene
(d) Benzene or hexamethylbenzene
(e) *p*-benzoquinone or benzaldehyde
(f) furan or thiophene

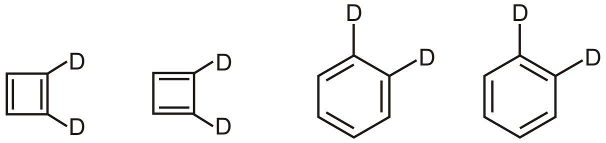
(g)



or

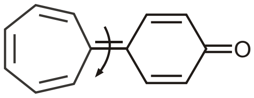


7. Using the theory of aromaticity, explain the fact that *A* and *B* are different compounds, but *C* and *D* are identical?

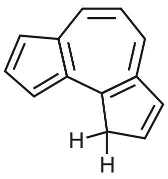


8. Account for the following observations.

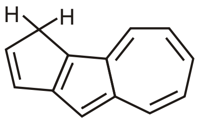
(a) The barrier for rotation about the marked bond in the following compound is only about 14 kcal/mol.



(b) Hydrocarbon *A* (pK – 14) is much more acidic than *B* (pK-22)



(A)

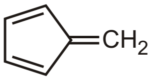


(B)

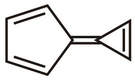
(c) Cyclopentadienone is a kinetically unstable molecule.

9. (a) In what direction is the dipole moment in fulvene? Explain.

(b) In what direction is the dipole moment in calicene? Explain.



fulvene



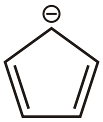
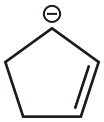
calicene

10. Why is [18] annulene more stable than [14] annulene ?

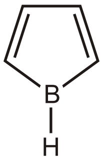
Answers

Single Choice Questions

1. (C) **2.** (C) **3.** (C) **4.** (D) **5.** (C) **6.** (B) **7.** (E) **8.** (E)
9. (B) **10.** (B) **11.** (D) **12.** (C) **13.** (E) **14.** (D) **15.** (A) **16.** (D)
17. (B) **18.** (E) **19.** (B) **20.** (E) **21.** (C) **22.** (A) **23.** (B) **24.** (D)
25. (E) **26.** (A) **27.** (A) **28.** (E) **29.** (A) **30.** (C)

1.  > 

2. Benzene has highest resonance energy.

3. 

Contain 4 electrons is the loop undergoing resonance and boron contains vacant p orbital to undergo complete resonance.

Multiple Choice Questions

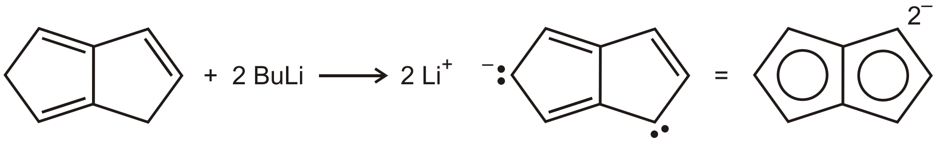
1. (A, B, C) **2.** (B, C)

Unsolved Example

1. It exist in zewterion form

2. Dewar

3.

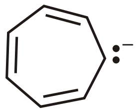


Pentalene dianion

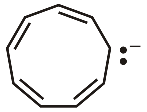
4. (a) NaH (b) HI (c) $AlCl_3$ (d) NaOH

(e) NaH (f) $AlCl_3$ (g) 2Na

5. (a) The cycloheptatrienyl anion has 8 electrons and does not obey Huckel's rule; the cyclononatetraenyl anion with 10 *p* electrons obeys Huckel's rule.



Cucloheptatrienyl anion
8π-electrons
Antiaromatic



Cyclononatetraenyl anion
10π-electrons
Aromatic

Work Sheet - 1

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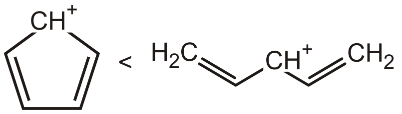

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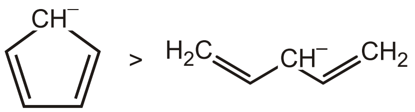

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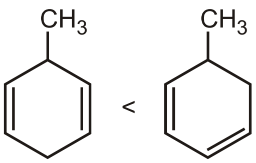

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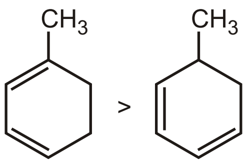

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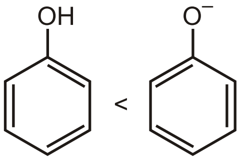

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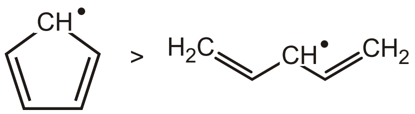

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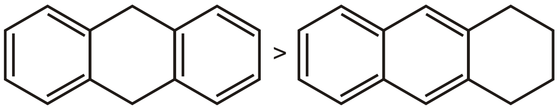

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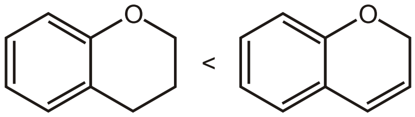
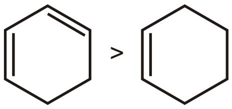
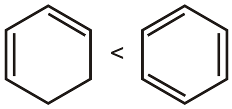


Chroman 2H-Chromene

(i)



(j)



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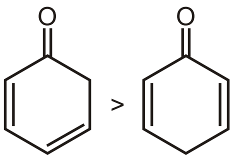

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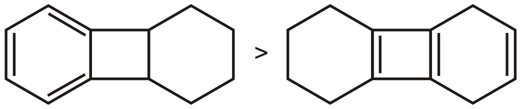
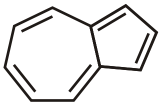
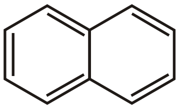
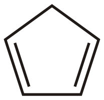
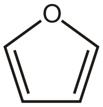
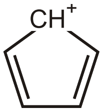
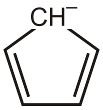
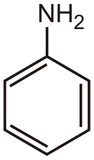


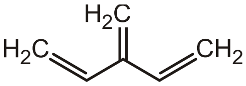
(m)  > 

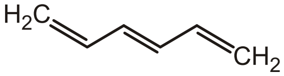
(n)  < 

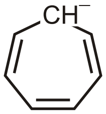
(o) 

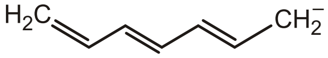
< 

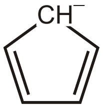
(p)  < 

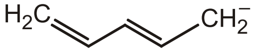
(q) 

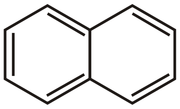
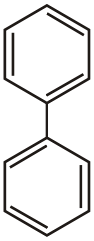
< 

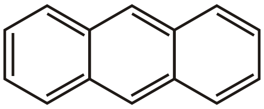
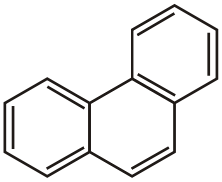
(r) 

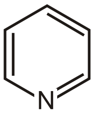
< 

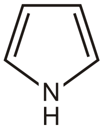
(s) 

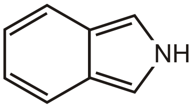
> 

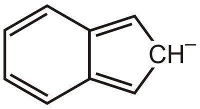
(t)  < 

(u) 
Anthracene
< 
Phenanthrene

(v) 

> 

(w) 

< 

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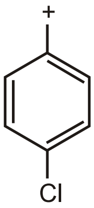
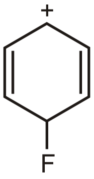
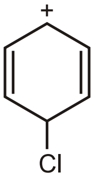
> 

(y) 

< 

Work Sheet - 2

1. (1) Anti Aromatic
(2) Aromatic
(3) Aromatic
(4) Anti Aromatic
(5) Aromatic
(6) Aromatic
(7) Non Aromatic
(8) Aromatic
(9) Aromatic
(10) Non Aromatic
(11) Aromatic
(12) Anti Aromatic
(13) Aromatic
(14) Aromatic
(15) Aromatic
(16) Non Aromatic
(17) Non Aromatic
(18) Non Aromatic
(19) Anti Aromatic
(20) Aromatic
(21) Non Aromatic
(22) Aromatic
(23) Non Aromatic
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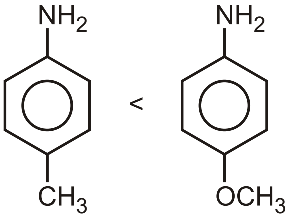
(43) Aromatic
(44) Aromatic

(45) Aromatic
(46) Aromatic
(47) Non Aromatic
(48) Aromatic
(49) Anti Aromatic
(50) Aromatic
(51) Aromatic
(52) Anti Aromatic
(53) Anti Aromatic
(54) Non Aromatic
(55) Non Aromatic
(56) Non Aromatic
(57) Aromatic
(58) Aromatic
(59) Aromatic

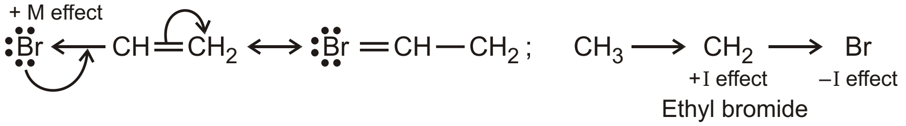
Subjective Type Questions

3. Azulene is a bycyclic compound with 10 -electrons. Distribution of these electrons between the two rings generates an aromatic system comprising a cycloheptatrienyl cation (tropylium ion) and a cyclopentadienyl ion. Since this aromatic system is quite stable, azulene remains mostly in bipolar form and shows high dipole moment value.

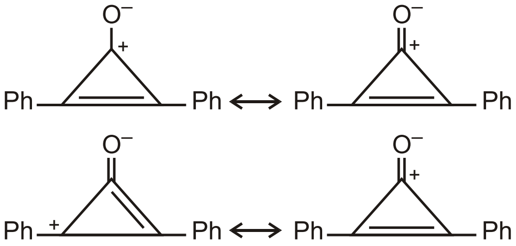
4. (a) *p*-Anisidine has greater dipole moment than *p*-Toluidine because in case of *p*-anisidine. Delocalization (*M*) effect is more pronounced due to the presence of an —NH_2 group having a lone pair of electrons on the nitrogen atom.



(b) Vinyl bromide has less dipole moment than ethyl bromide. In the case of vinyl bormide the *I* effect of bromine atom is opposed by the *M* effect due to pi-electrons delocalization. In case of ethyl bromide, *I* effect of the bromine atom is reinforced by the *I* effect of CH_3 group.

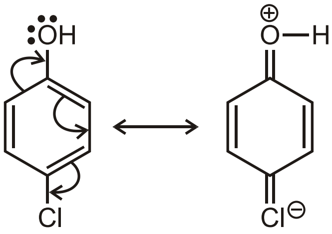


(c) 2,3-Diphenylcyclopropenone has higher dipole moment than acetophenone. Cyclopropenone system can assume aromatic stability due to delocalization. The generated cyclopropenium ion is further stabilized by the resonance involving benzene nucleus.

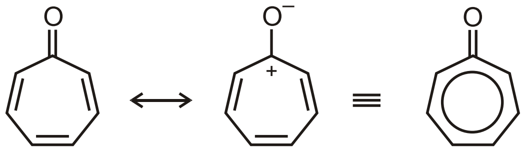


(d) CH_3Cl has higher dipole moment than CH_3F, because the C — Cl bond distance is much larger than the C — F bond distance in CH_3F, although CH_3F is more polar due to greater electronegativity of F atom. We know that dipole moment charge distance [q d].

(e) *p*-Chlorophenol has higher dipole moment than *p*-fluorophenol. The reason is that in case of *p*-chlorophenol, extended resonance is possible due to the available vacant *d*-orbital with the chlorine atom. In case of *p*-fluorophenol, extended delocalization is not possible due to the absence of the orbital with the fluorine atom.

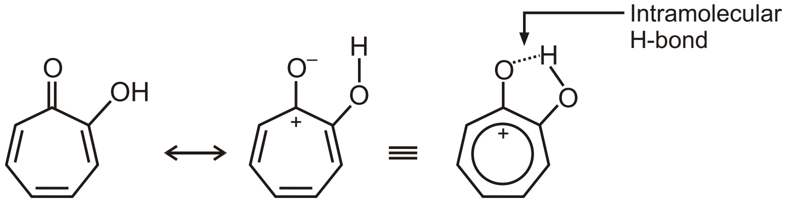


(f) Tropolone exhitibs aromatic character in its ionic form and hence has dipole moment. 2-Hydroxytropolone also exhibits greater dipole moment because of its aromatic ionic form but that ionic form further stabilized by intramolecular hydrogen bonding.



Tropolone

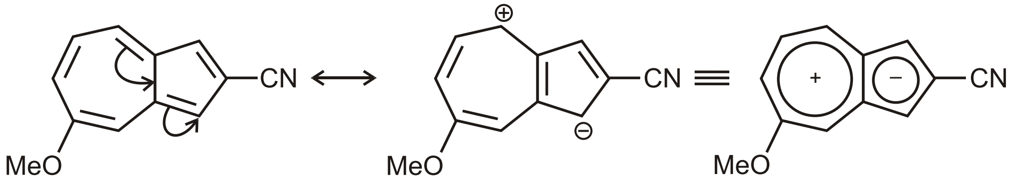
6π electron
atomatic system



2-Hydroxy tropolone

6π electron
atomatic system

5. (a) These two are substituted azulenes. Due to redistribution of pi-electrons, the seven-membered ring becomes electron deficient and the five-membered ring becomes electron rich. In this form, azulene exhibits aromatic stability. Therefore –OMe group can more stabilize the electron deficient ring. Therefore, compound (i) has higher dipole moment than compound.



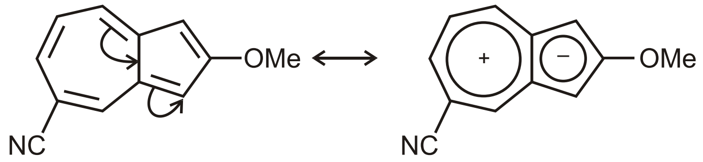
(i)

(i)

(i)

Stabilized molecule

(ii)

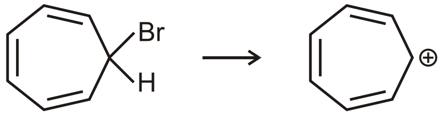


(ii)

(ii)

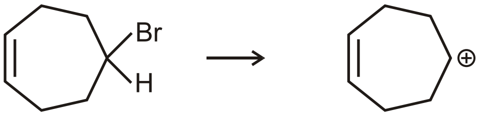
Less stable

(b) Between the compounds (iii) and (iv), (iv) is more polar and stable. Therefore, it has greater dipole moment.



(iv)

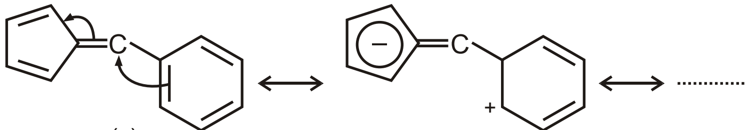
Stablize by
aromatic nature



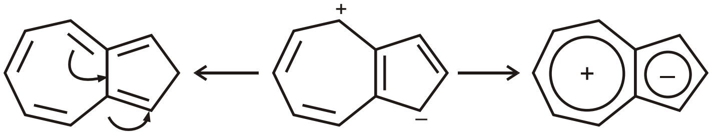
(iii)
Less ionic

Non aromatic unstable

(c) In this case, the compound (v) has higher dipole moment. In compound (v), extended resonance is possible along with the development of aromatic character to the five membered-ring. The compound (vi) is azulene and is also ionic due to delocalization of -electrons however charge separation is less.



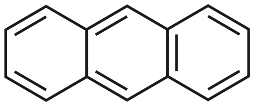
(v)



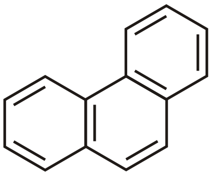
(vi)

6. It is known that the more stable a reasonating structure of the more would be its resonance energy and vice versa. Therefore, we will have to find out the more stable structure in each case of the compound in the above mentioned pairs of compounds.

(a) Between anthracene and phenanthrene, phenantherene has higher resonance energy. It has got the maximum number of benzenoid rings and can have greater number of resonating structures. Structures of anthracene and phenanthrene are given here.

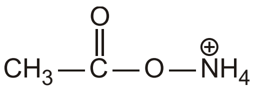


Anthracene



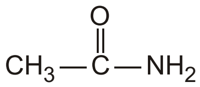
Phenanthrene

(b) Between ammonium acetate and acetamide, resonance is more effective in case of acetamide. In case of ammonium acetate, the negative charge on the oxygen atom of the acetate ion is not sufficiently free because of ammonium ion and therefore, resonance is inhibited. Therefore, acetamide has higher resonance energy.



$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\oplus}{N}H_4$

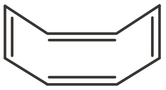
Ammonium acetate



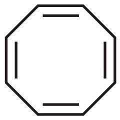
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

Acetamide

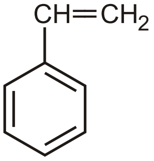
(c) Cyclooctatetraene almost always remains in non-planar tub-like structure with little scope for resonance. Planar structure of cyclooctatetraene is an unstable anti-aromatic system. Styrene is a planar molecule with an olefinic double conjugated to a phenyl ring and give a large number of resonating structures. Therefore, styrene has higher resonance energy,



Cyclooctatetraene
(Tub-like non-planar structure)



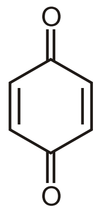
Cyclooctatetraene
(Planar, anti-aromatic structure)



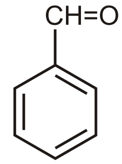
Styrene (Planar)

(d) Between beznene and hexamethylbenzene, hexamethylbenzene is more stable due to hyperconjugation. Therefore, it has higher resonance energy.

(e) *p*-benzoquinone is a crossed-conjugated system and has no aromatic stability. Benzaldehyde is an aromatic compound with an extended conjugation. Therefore, benzaldehyde is a very stable molecule having higher resonance energy.



p-Benzoquinone

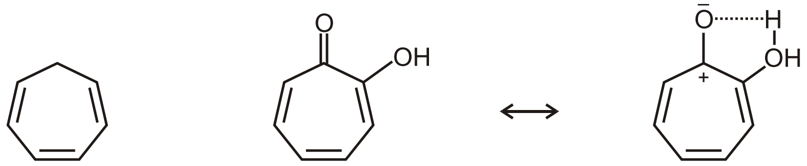


Benzaldehyde

(f) Between furan and thiophene, thiophene has higher aromatic character due to greater polarizability of the electron pair on the sulphur atom. Therefore, thiophene is more stable and has higher resonance energy.

Furan (Less effective resonance) Thiophene (More effective resonance)

(g) Between cyclohepta-1, 3, 5-triene and 2-hydroxycyclohepta-2, 4, 6-trienone, the latter is more stable, because it can form a stable aromatic system by the ionization of the ketonic group followed by intramolecular hydrogen bonding. Therefore, 2-hydroxycyclohepta-2, 4, 6-trienone has higher resonance energy.

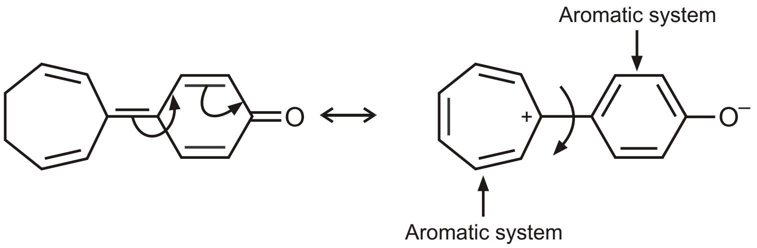


Cyclohepta-1, 3, 5-triene 2-Hydroxycyclohepta-2, 4,6-trienone Cycloheptatrienyl cation from (Very stable due to the formation of aromatic system)

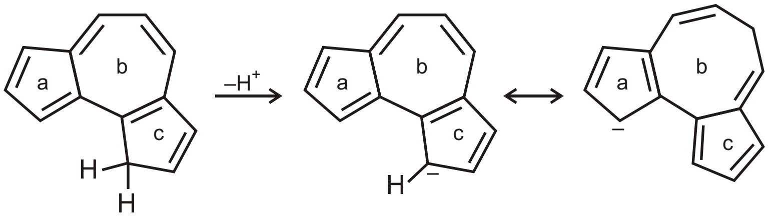
7. According to the condition of aromaticity, the contributing structures should differ in -framework. Now in case of compounds *A* and *B*. They differ in framework and antiaromatic system and one cannot be transformed into another by delocalization of -bonds. Two deuterium atoms are differently attached to the cyclobutadiene systems. Both *A* and *B* represent antiaromatic system but are not the same compounds.

The compounds *C* and *D* represent aromatic systems and are interconvertible by delocalization. Therefore they represent the same compound.

8. In the case of (a) delocalization of -electrons gives a stable aromatic system and concomitantly the double bond joining the two rings becomes a single bond appreciably. This is why rotational barrier between the two rings is only 14 kcal/mol.

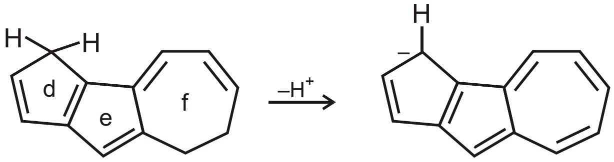


In problem (b), the acidity of compound depends on the stabilities of the conjugate base (carbanion after the loss of a proton.



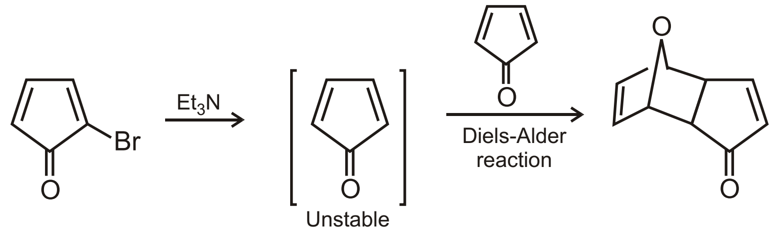
In compound (I), the terminal five-membered rings (a, c) can assume stable cyclopentadienyl anion (aromatic anion) by delocalization, after deprotonation from the *sp*^{3} carbon.

II compound (II), only one terminal ring (d) can have aromatic stability after deprotonation, being converted into cyclopentadienide ion. further delocalization makes the cyclohetptatrienyl ring antiaromatic.

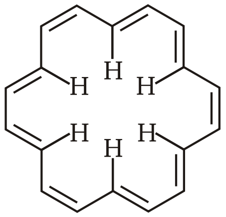


This is why, (I) is more acidic than (II).

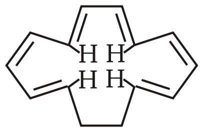
(c) Cyclopenta-2, 3-dienone is a very unstable compound because by electromerization of the C O group, the ring becomes an antiaromatic system and consequently its reactivity is enhanced requiring less activation energy (kinetic instability). In fact, attempt to prepare cyclopentadienone by treatment of 5-bromocyclopentadienone with Et_3N : gave virtually a quantitative yield of Diels-Alder adduct showing extreme instability of the cyclopentadienone compound.



10. The structure of [18] annulene and [14] annulene are given here.



[18] Annulene



[14] Annulene

Both [18] annulene and [14] annulene are aromatic in the sense that both of them satisfy the so called Huckel's rule for exhibiting aromatic character. however, because of a greater number of carbon atoms in the [18] annulene ring system, interannular space is more and as a result of which interannular steric greater aromatic character. In case of [14] annulene, interannular steric interactions of hydrogen atoms is large alnd the system assumes some non-planarity. This inhibits delocalization of the -electron system and reduce aromatic character.

❑❑❑