

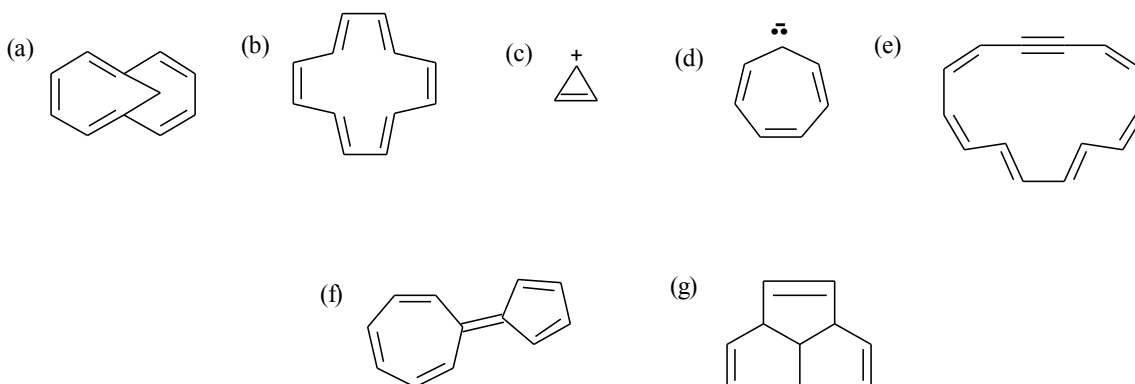
UNIVERSIDAD TECNOLÓGICA DE LA MIXTECA
Maestría en Ciencias: Productos Naturales y Alimentos
QUÍMICA ORGÁNICA
Propedéutico



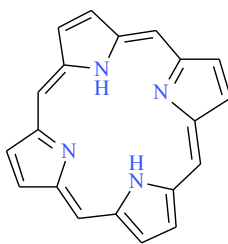
Ejercicios.

AROMATICIDAD, BENCENO Y COMPUESTOS RELACIONADOS

1. Escriba la definición de *energía de resonancia*.
2. ¿Cuáles de los compuestos o iones siguientes podrían ser aromáticos?



3. ¿Qué establece la regla de Hückel?
4. Escriba todas las estructuras de resonancia para la piridina.
5. Determine si la porfirina es o no un compuesto aromático y fundamente su respuesta.



porfirina

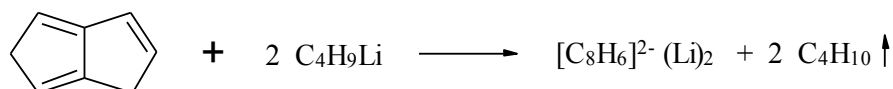
6. La polarización fuerte de un grupo carbonilo se puede representar por un par de estructuras en resonancia:



La ciclopropenona y la cicloheptatrienona son más estables de lo que se puede esperar. La ciclopentadienona, sin embargo, es relativamente más inestable.

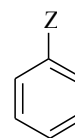


7. El hidrocarburo siguiente reacciona con dos equivalentes de butilitio para formar un dianión con fórmula $[C_8H_6]^{2-}$. Proponga la estructura para este dianión, y sugiera porqué se forma así de fácil.



8. Para cada uno de los enunciados de la Columna I, escoja un sustituyente de la Columna II que corresponda a la descripción del compuesto de la derecha e indique la letra correspondiente:

Columna I	Columna II
a. Z es un donador de electrones por efecto inductivo, pero no es un donador de electrones por resonancia	OH
b. Z es un electroattractor por efecto inductivo y electroattractor por resonancia	Br
c. Z desactiva el anillo y dirige <i>orto-para</i>	$^+\text{NH}_3$
d. Z es un electroattractor por efecto inductivo, dona electrones por resonancia, y activa el anillo	CH_2CH_3
e. Z es un electroattractor por efecto inductivo, pero no dona o atrae electrones por resonancia	NO_2



1. The average C - C bond distance in benzene is?

- ☐ the same as C-C single bonds.
- ☐ the same as C-C double bonds.
- ☐ the same as C-C triple bonds.
- ☐ intermediate between C-C single and double bonds.
- ☐ intermediate between C-C double and triple bonds.

2. Benzene can exist in chair and boat conformations?

- ☐ True.
- ☐ False.

3. Aromatic compounds can only have a single six membered ring?

- ☐ True.
- ☐ False.

4. Arenes predominantly react by?

- ☐ nucleophilic substitution.
- ☐ nucleophilic addition.



- ☐ electrophilic substitution.
- ☐ electrophilic addition.
- ☐ all of the above.
5. *Arenes as substituents can affect the reaction of the functional group it is attached by?*
- ☐ acting as an electron withdrawing/donating group.
- ☐ stabilizing benzylic carbocations.
- ☐ stabilizing benzylic carbon radicals.
- ☐ stabilizing benzylic alkenes.
- ☐ all of the above.
6. *Oxidation of alkylbenzenes produces?*
- ☐ aromatic ethers.
- ☐ aromatic esters.
- ☐ benzoic acids.
- ☐ phenyl alkanoic acids.
- ☐ phenyl alkenoic acids.
7. *Benzylic halides are very reactive to?*
- ☐ nucleophilic substitution.
- ☐ nucleophilic addition.
- ☐ electrophilic substitution.
- ☐ electrophilic addition.
8. *Additions to alkenylbenzenes are controlled by?*
- ☐ the stability of the benzonium carbocation intermediate.
- ☐ the stability of the benzyl carbanion intermediate.
- ☐ the stability of the benzyl radical intermediate.
- ☐ the stability of the benzyl carbocation intermediate.
- ☐ the stability of the benzonium carbanion intermediate.
9. *Defining aromatic compounds as: planar, fully conjugated, cyclic polyenes having $(4n + 2)$ π electrons is known as?*
- ☐ Beer's Law.
- ☐ Huckel's Rule.
- ☐ Zaitsev's Law.



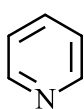
- ☐ Henry's law.
- ☐ Markovnikov's Rule.

10. Aromatic heterocyclic π systems larger or smaller than 6 membered ring can be aromatic?

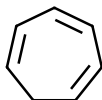
- ☐ True.
- ☐ False.

Arenes and Aromaticity

Qu 1 Use the following list of compounds to answer the questions below:



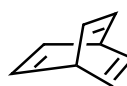
A



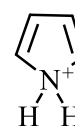
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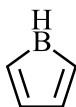
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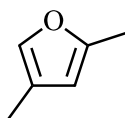
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E



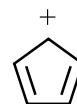
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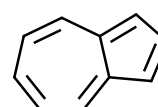
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H



I



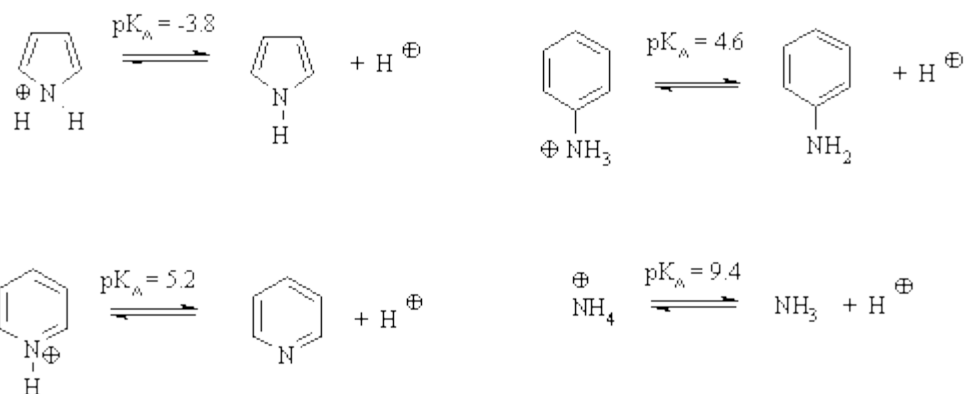
J

Select the compound that is best described as:

- (a) A neutral, 4 π -electron, anti-aromatic system.
- (b) A 6 π -electron, aromatic system.
- (c) An aromatic system because $n = 2$ in the Huckel $4n + 2$ rule.
- (d) A non-aromatic, conjugated 6 π -electron system
- (e) A non conjugated hydrocarbon.
- (f) Non-aromatic as drawn, but if H^- were removed would give an aromatic cation.
- (g) Non-aromatic as drawn, but has an important resonance structure that is aromatic.
- (h) Non-aromatic as drawn but has an aromatic conjugate base.



Qu 2: Consider the pK_a data for the following aromatic N containing systems:

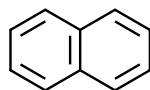


Henderson-Hasselbach equation: $pK_a = \text{pH} - \log ([A^-]/[HA])$

Based on the scheme provided,

- Which species is the strongest acid?
- At $\text{pH} = 4.2$, what is the relative ratio of pyridine to its conjugate acid?
- Which is the better base: pyridine or aniline, and why?
- Why is pyrrole is a weaker base than pyridine?

Qu 3: Rate the resonance energies (in comparison to one another) of each of the following:



(i)



(ii)



(iii)

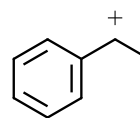
Qu 4: Rate the relative stability of the following carbocations (in comparison to one another):



(i)

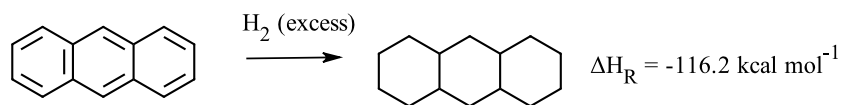
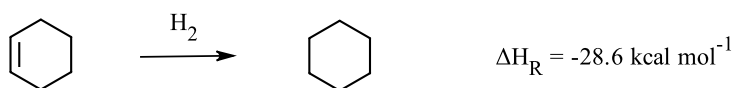


(ii)



(iii)

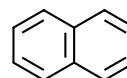
Qu 5: Use the following data to answer the questions below:



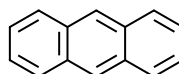
Resonance Energies (kcal mol^{-1})



36

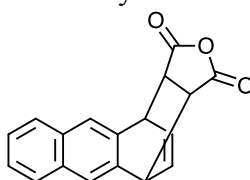


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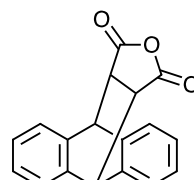


(a) Calculate the resonance energy of anthracene,

(b) Anthracene is known to react with maleic anhydride in a Diels-Alder reaction. Predict which of the products shown is obtained. Why?

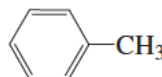
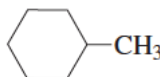


A

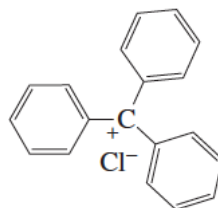


B

Which can lose a proton more readily, a methyl group bonded to cyclohexane or a methyl group bonded to benzene?



The triphenylmethyl cation is so stable that a salt such as triphenylmethyl chloride can be isolated and stored. Why is this carbocation so stable?

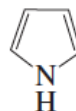


triphenylmethyl chloride

Why is the resonance energy of pyrrole (21 kcal/mol) greater than the resonance energy of furan (16 kcal/mol)?



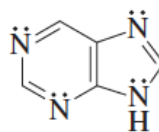
furan



pyrrole



- . Purine is a heterocyclic compound with four nitrogen atoms.
- Which nitrogen is most apt to be protonated?
 - Which nitrogen is least apt to be protonated?



purine

Investigation has shown that cyclobutadiene is actually a rectangular molecule rather than a square molecule. In addition, it has been established that there are two different 1,2-dideuterio-1,3-cyclobutadienes. Explain the reason for these unexpected observations.



cyclobutadiene

