Organic Chemistry – Exercise 3

Distribution: October 9, 2025

Help: October 16, 2025

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1. This exercise is about the planar tropylium ion (cycloheptatrienyl cation). This structure is frequently detected when organic molecules containing benzyl fragments are analyzed with mass spectrometry. Upon ionization, the benzyl fragment forms a cation that quickly rearranges into the highly stable tropylium ion. Its structure is given below.

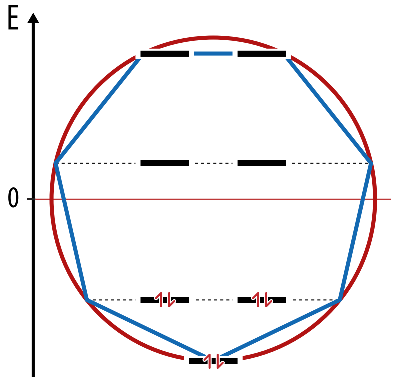
   a. How many π molecular orbitals are there in the tropylium ion? How many π electrons are there in total?

   There are 7 π molecular orbitals that come from the p atomic orbitals of the 7 participating carbon atoms. There are 6 π electrons in total.

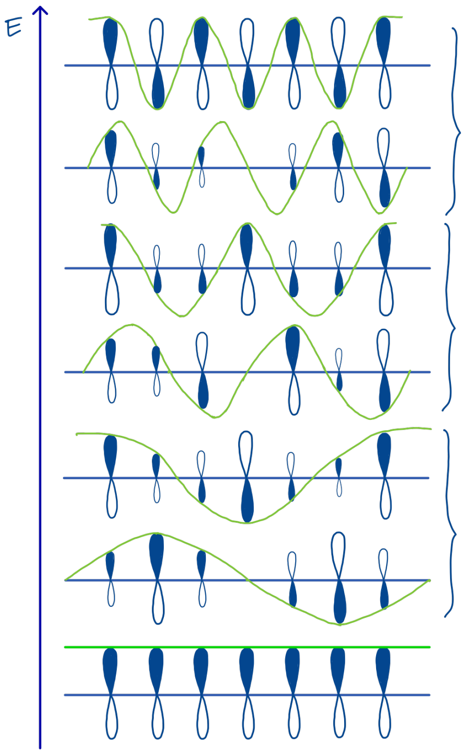
   b. Explain whether or not the tropylium ion is aromatic!

   As there are 6 π electrons in total, and the molecule is planar and monocyclice, it satisfies the Hückel rule and is therefore considered aromatic.

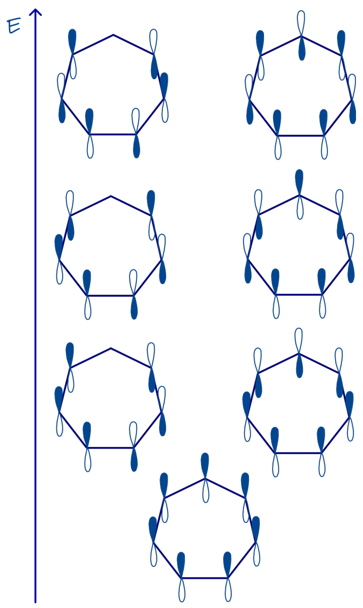
   c. Draw a simplified MO diagram of tropylium ion. Consider only π orbitals and schematically justify the energy levels you have assigned to the different MO.



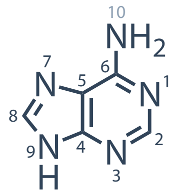
d. Using the "electron in a box with steady boundary conditions" model show in a simplified way how the participating p atomic orbitals contribute (qualitatively!) to the π MO.



e. According to the previous answer draw simplified LCAO representations of the different molecular orbitals in the cyclic monomer.



2. Adenine (9*H*-purin-6-amine) is a purine nucleotide base found in DNA, RNA and ATP. The shape of adenine is complementary with either thymine in DNA or uracil in RNA. In this exercise, the nature of its electron system is going to be discussed. The structure of adenine is shown below.



   a. What are the hybridization states of the C and N atoms in adenine? Is the cyclic system of the molecule planar or not?

   All C and N atoms in the molecule have sp^2 hybridization (sp^3 hybridization acceptable for the N atom of the amine side group). The cyclic system is hence planar.

   b. In what type of atomic or hybrid orbital are the electron lone pairs on each of the nitrogen atoms?

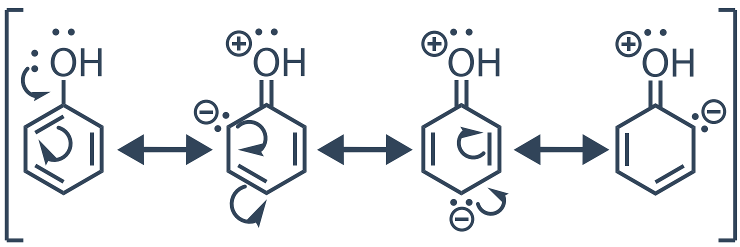
   The lone pairs of nitrogen atoms 1, 3 and 7 are located in sp^2 orbitals, as their p orbitals are participating in the π MO system. The lone pair of nitrogen atom 9 is located in the p orbital, as three sp^2 orbitals are used for bonding to two neighboring C atoms and one H atom. The lone pair of nitrogen atom 10 is located in a sp^2 orbital (sp^3 also acceptable).

   c. How many π electrons are there in adenine molecule? According to the Hückel rule, discuss the aromaticity of adenine.

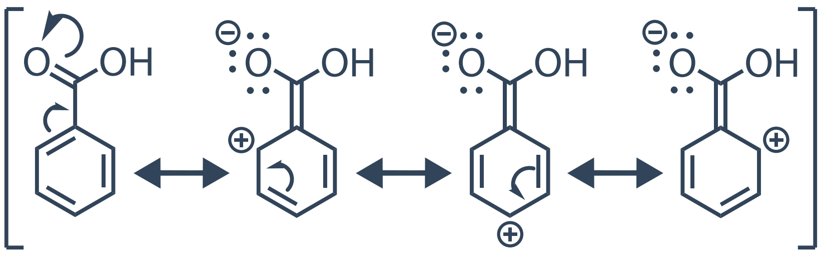
   Adenine has 10 π electrons (each carbon atom and nitrogen atoms 1, 3 and 7 contribute with 1 electron each, while nitrogen 9 contributes 2 electrons), so it is aromatic according to the Hückel rule.

3. This exercise is about understanding the electron-donating and electron-withdrawing effects in aromatic systems.

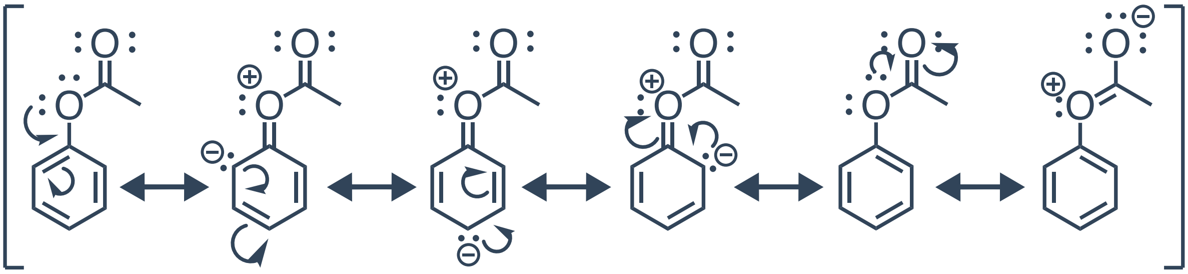
   a. Draw the resonance structures of phenol (C_6H_5-OH).



   b. Draw the resonance structures of benzoic acid (C_6H_5-COOH).



c. Draw the resonance structures of phenyl methanoate.



d. Discuss the mesomeric effect of different substituents on the benzene ring and discuss how they affect the electron density in the system.

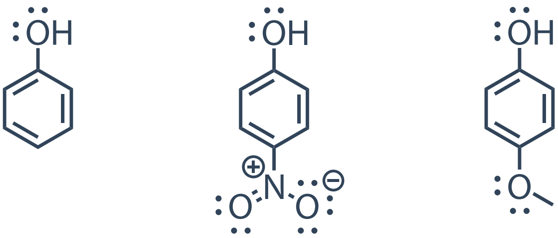
The hydroxyl group exerts a +M effect and increases the electron density in the benzene ring. It is an electron-donating group.

The carboxylic group (attached via the C atom) exerts a –M effect and decreases the electron density in the benzene ring. It is an electron-withdrawing group.

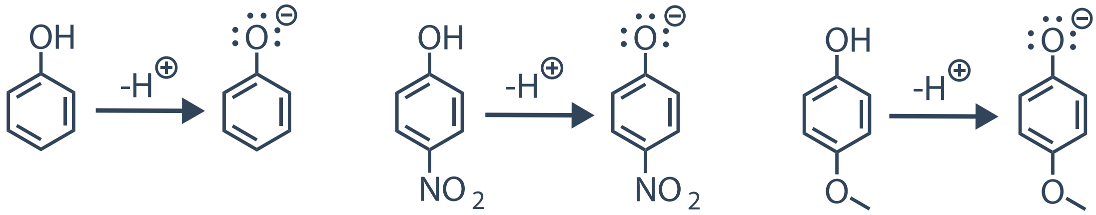
The ester group (attached via the O atom) exerts a +M effect and increases the electron density in the benzene ring. It is an electron-donating group. However, due to the additional delocalization of the lone pairs on the connecting oxygen atom to the neighboring C=O group, its mesomeric effect is weaker than the one of the hydroxyl group.

4. According to the Brønsted–Lowry theory, acids are substances that act as proton donors, and bases are substances that act as proton acceptors. The acidity/basicity depends on stability of the anions resulting from proton dissociation, and of the cations resulting from protonation, resecptively – the more stable the resulting ion, the stronger the acid or base. In this exercise, you shall compare the acidity of three aromatic compounds: phenol (C_6H_5-OH), 4-nitrophenol and 4-methoxyphenol.

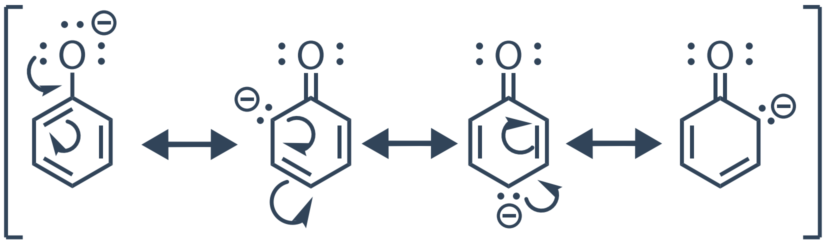
a. Draw Lewis structures of phenol, 4-nitrophenol and 4-methoxyphenol.

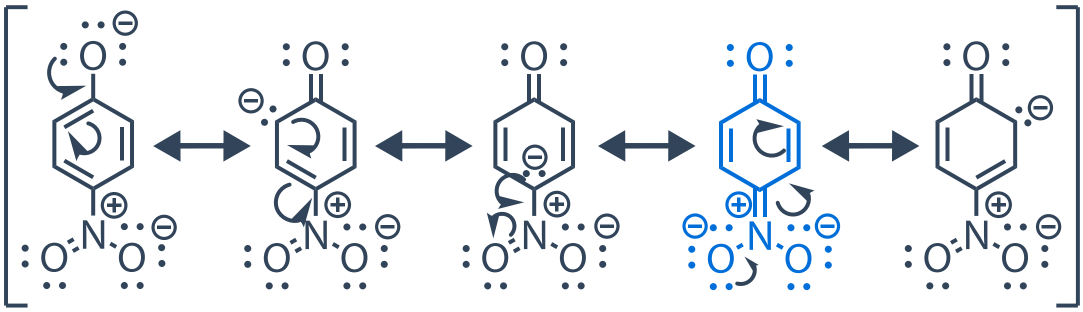


b. Write the chemical reactions that describe the deprotonation of these three compounds.

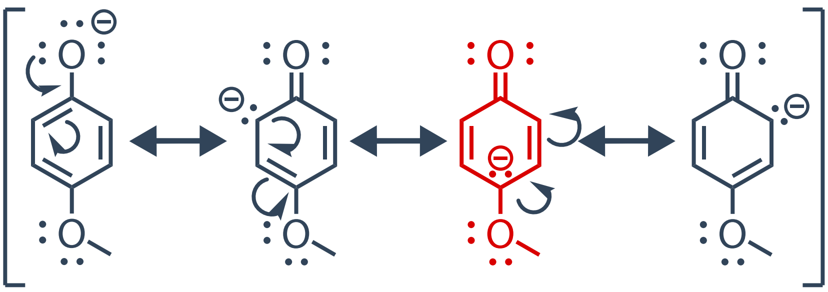


c. Draw the resonance structures of the phenoxide ion (conjugated base of phenol), 4-nitrophenoxide ion (conjugated base of 4-nitrophenol) and 4-methoxyphenoxide ion (conjugated base of 4-methoxyphenol). Based on these structures, order phenol, 4-nitrophenol and 4-methoxyophenol according to their acidity and explain your choice of order.





When compared to phenoxide ion, in 4-nitrophenoxide ion there is additional resonance structure (in blue) where the lone pair is delocalized into the nitro group, which additionally stabilizes this anion. Since 4-nitrophenoxide is a base that is more stabilized than the phenoxide ion, 4-nitrophenol is stronger acid than phenol.



When compared to phenoxide ion, in 4-methoxyphenoxide ion there is a resonance structure (in red) where the lone pair is next to the methoxy group and highly electronegative oxygen atom, which destabilizes this anion. Since 4-methoxyphenoxide is a base that is less stabilized than the phenoxide ion, 4-methoxyphenol is weaker acid than phenol.

According to their acidity, the given species are ordered as following:

4-nitrophenol > phenol > 4-methoxyphenol

d. **Bonus question**: Consider 3,5-dimethyl-4-nitrophenol. Even though it also has a nitro group in position 4, it is now **much less acidic** than 4-nitrophenol. Try to take an educated guess why this might be the case.

In 4-nitrophenol, the nitro group is coplanar with the benzene ring and electron delocalization occurs also into the nitro group. In the case of 3,5-dimethyl-4-nitrophenol, there are two methyl groups next to the nitro group and, due to sterical difficulties, the nitro group is not coplanar with the benzene ring, which disables electron delocalization into it (not right orbital orientation). Since the corresponding ion is much more stabilized in the case of 4-nitrophenol, it is a stronger acid.

Reading Suggestions:

Clayden, Greeves, Warren, *Oxford University Press*, **2012**.

Organic Chemistry, John McMurry, *Thomson Brooks/Cole*, **2008**.

Chimie Organique, Les Grands Principes, John McMurry, *Dunod Editeur*, **2009**.

Chimie Organique, Paul Arnaud, *Dunod Editeur*, **2009**.