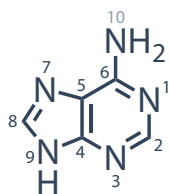




d. Using the “electron in a box with steady boundary conditions” model show in a simplified way how the participating p atomic orbitals contribute (qualitatively!) to the  $\pi$  MO.

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?
- b. In what type of atomic or hybrid orbital are the electron lone pairs on each of the nitrogen atoms?
- c. How many  $\pi$  electrons are there in adenine molecule? According to the Hückel rule, discuss the aromaticity of adenine.





- 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-methoxyphenol according to their acidity and explain your choice of order.

- 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.

**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**.