Andrea Landella
MSc in Chemical Engineering – POLITECNICO DI MILANO

Solution to exercises from 2019 IChO Preparatory Problems

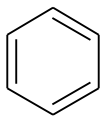
Problem 2. Localization and delocalization in benzene

Historically, benzene was first isolated from benjoin (essence of the "Papier d'Arménie"). It was then synthesized by the French chemist M. Berthelot in the middle of the 19th century using acetylene trimerization. In this problem, the objective is to study the electronic properties of this compound, which is a representative of aromatic molecules. Let us start with benzene by referring to the carbon atoms as C_i, $i = 1 - 6$ in a clock-wise manner.

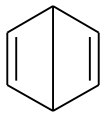
1. **Write** the reaction from acetylene C_2H_2 generating benzene.

$$3C_2H_2 \rightarrow C_6H_6$$

2. **Draw** a structure of benzene using three single bonds and three double bonds between carbon atoms. It is referred to as Kekulé's benzene.



3. **Draw** a structure of benzene holding five single and two double bonds. This structure is called Dewar's benzene.



Let us start with a Kekulé structure K1, holding a double bond between C_1 and C_2 atoms. A simple model to describe the π bond between C_1 and C_2 consists of characterizing the delocalization of a single electron by an energy $t < 0$.

4. **Give** the energy E_π of the π-system of this bond as a function of t.

The energy of the π-system of the C_1C_2 bond has the 2-electron contribution, so $E_\pi = 2t$.

5. In K1, double bonds are supposed to be fixed. For this structure K1, **calculate** the energy of the π-system E_{K1} as a function of t.

In the proposed structure K1, there are three fixed π-systems, therefore $E_{K1} = 3E_\pi = 6t$.

6. **Write** an analog to K1. It will be called K2.

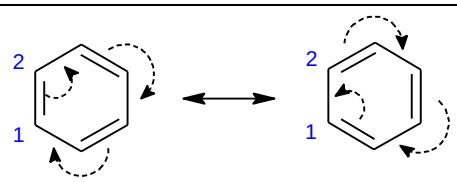
An analog of K1 is a Kekulé structure holding a single bond between C_1 and C_2 atoms, thus a double bond between C_3 and C_4 and so on. In other words, K2 has double bonds where K1 had single bonds, and K2 has single bonds where K1 had double bonds.

7. **Express** the energy E_{K2} of this structure K2.

In the proposed structure K2, there are three fixed π-systems, therefore $E_{K2} = 3E_\pi = 6t$.

Mathematically, the benzene molecule is expressed as a mix between K1 and K2, $K = c_1\,K1 + c_2\,K2$, where c_1 and c_2 are real numbers with $c_1^2 + c_2^2 = 1$ and $c_1 > 0$ and $c_2 > 0$. This expression stresses that a proper description of benzene cannot be restricted to K1 or K2.

8. On a scheme, **show** the displacement of the double bond localized between C_1 and C_2 and the movement of the other double bonds. These formulae are the resonance structures of benzene.



K1 K2

Starting from a localized view K1 or K2, the electronic delocalization over all the carbon atoms can be accounted for by the introduction of a supplementary energetic term. The energy E_K of K is thus defined as:

$$E_K = c_1^2\,E_{K1} + c_2^2\,E_{K2} + 2\,c_1\,c_2\,H_{12}$$

where H_{12} varies between t and 0, with $t < 0$. Therefore, E_K is a function of c_1 and c_2.

9. **Express** E_K as a function of c_1 only.

Since $c_2^2 = 1 - c_1^2$ and $c_2 = \sqrt{1 - c_1^2}$, then $E_K = c_1^2 E_{K1} + (1 - c_1^2)E_{K2} + 2c_1\sqrt{1 - c_1^2}H_{12}$

It can be shown that E_K is minimal for $c_1 = 1 / \sqrt{2}$. From now on, we assume that $c_1 = 1 / \sqrt{2}$.

10. If $H_{12} = 0$, what is the expression of E_K? The resonance energy is defined as the difference $\Delta E_1 = E_K(H_{12} = t) - E_K(H_{12} = 0)$. **Evaluate** ΔE_1 as a function of t.

When $H_{12} = 0$, then $E_K = c_1^2 E_{K1} + (1 - c_1^2)E_{K2}$. Since $c_1 = 1/\sqrt{2}$ then $c_1^2 = 1/2$. The resonance energy is then evaluated as $\Delta E_1 = 2c_1\sqrt{1 - c_1^2}t = t$, once substituting c_1.

11. **Specify** the sign of ΔE_1. **Choose** the correct statement between:
    - ☐ electronic delocalization contributes to stabilize the benzene molecule.
    - ☐ electronic delocalization contributes to destabilize the benzene molecule.

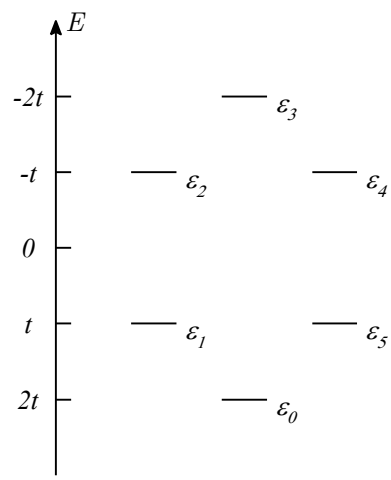
Since $\Delta E_1 = t$, then $\Delta E_1 < 0$. This is consistent because the electronic delocalization contributes to stabilize (lower the energy) of the benzene molecule. This is Option 1.

Alternatively, the π energy of a n carbon atom-system can be evaluated from the occupations of the molecular orbitals (MOs). C. A. Coulson (C. A. Coulson, Proc. Roy Soc., 1939) showed that the MOs energies ε_k of a cyclic n carbon atom-system, not necessarily in energy order, read:

$$\varepsilon_k = 2t\cos\frac{2k\pi}{n}\,;k \in \mathbb{N}, k \in [0\,;\,n-1]$$

12. **Draw** the MOs diagram of the π-system of benzene ($n = 6$) and calculate the corresponding energies for each MO.

The MO diagram for benzene is drawn as follows:

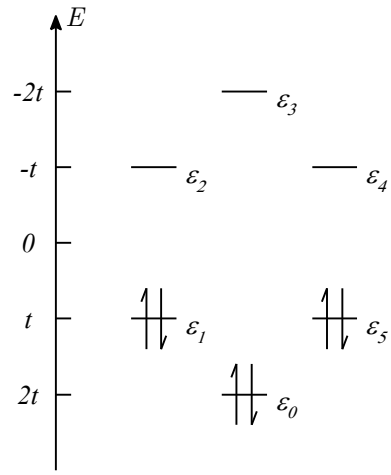


While the MO energies are calculated from the Coulson formula as:

$$\varepsilon_0 = 2t\cos 0 = 2t$$
$$\varepsilon_1 = 2t\cos \pi/3 = t$$
$$\varepsilon_2 = 2t\cos 2\pi/3 = -t$$
$$\varepsilon_3 = 2t\cos \pi = -2t$$
$$\varepsilon_4 = 2t\cos 4\pi/3 = -t$$
$$\varepsilon_5 = 2t\cos 5\pi/3 = t$$

13. **Fill** the MOs diagram.

Since benzene has 6 π-electrons, the MO orbitals are filled with the Hund Rule as follows:



14. **Evaluate** the π-system energy of benzene, E_{MO}, from the filling of the MOs in ascending order. Then, **calculate** the resonance energy $\Delta E_2 = E_{MO} - E_K(H_{12} = 0)$.

The π-system energy of benzene is $E_{MO} = 2\varepsilon_5 + 2\varepsilon_1 + 2\varepsilon_0 = 4t + 4t = 8t$. The energy $E_K(H_{12} = 0) = c_1^2 E_{K1} + (1 - c_1^2)E_{K2}$, with $c_1^2 = 1/2$ and $E_{K1} = E_{K2} = 6t$, equals $6t$. Therefore the resonance energy is $\Delta E_2 = 8t - 6t = 2t$.

15. **Compare** ΔE_2 and ΔE_1.

We have:

$\Delta E_2 = E_{MO} - E_K(H_{12} = 0) = 2t$

$\Delta E_1 = E_K(H_{12} = t) - E_K(H_{12} = 0) = t$

Thus, $\Delta E_2 = 2\,\Delta E_1$. As extra, it could be possible to calculate H_{12} from the equation:

$$E_{MO} - E_K(H_{12} = 0) = 2t = E_K(H_{12} = x) - E_K(H_{12} = 0) = 2c_1\sqrt{1 - c_1^2}x$$

Leading to, with $c_1^2 = 1/2$, $x = H_{12} = 2t$.

16. From the previous results, **choose** one expression for the relation between the standard hydrogenation enthalpy of cyclohexene ($\Delta_r H_c°$) and that of benzene ($\Delta_r H_b°$).

- ☐ $|\Delta_r H_b°| < 3\,|\Delta_r H_c°|$
- ☐ $|\Delta_r H_b°| > 3\,|\Delta_r H_c°|$
- ☐ $|\Delta_r H_b°| = 3\,|\Delta_r H_c°|$

It is "harder" to hydrogenate benzene than 3 molecules of cyclohexane, due to the additional resonance energy of benzene, therefore $|\Delta_r H_b°| > 3|\Delta_r H_c°|$ or Option 2.