

Benzyn structure

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Introduction: Benzyne is an important reactive intermediate in organic chemistry. Its structure differs from benzene by the presence of a triple bond between two adjacent carbon atoms in the aromatic ring, which significantly affects its chemical and physical properties.

In this study, the geometry of benzyne will first be examined using quantum chemical methods at the Hartree-Fock (HF), MP2, and B3LYP levels and compared with the structure of benzene, which serves as a reference molecule with a fully aromatic character. Furthermore, the hydrogenation enthalpy and Gibbs free energy of benzyne will be calculated to clarify its thermodynamic properties. In the next part, an analysis of the infrared (IR) spectra of both benzyne and benzene will be conducted to identify characteristic vibrations that differ due to the presence of the triple bond. The calculations were performed using the ORCA program, and the molecular structures were modeled in Molden.

1 Results:

1.1 Molecules structure optimization

The geometry of benzene and benzyne is compared based on the optimization results obtained using the **HF**, **MP2**, and **B3LYP** methods with the **6-31G*** basis set.

1.1.1 Hartree-Fock (HF) method:

Bond Lengths:

In **benzyne** (see Table 1), the length of the triple bond shortens to 1.223 Å (B(C 1, C 0)), while the adjacent single bonds (e.g., B(C 2, C 1) and B(C 5, C 0)) elongate to 1.383–1.410 Å. This change corresponds to the disruption of electron delocalization due to the presence of the triple bond.

In **benzene** (see Table 2), all C–C bond lengths are approximately equal (1.387 Å), confirming the regular arrangement of the aromatic ring with delocalized electrons.

Angles:

In **benzyne** (see Table 1), symmetry is disrupted, particularly around the triple bond, where bond angles increase to approximately 127° (e.g., A(C 1, C 0, C 5) = 127.44°).

Definition	FinalVal
B(C 1,C 0)	1.2233
B(C 2,C 1)	1.3833
B(C 3,C 2)	1.3921
B(C 4,C 3)	1.4103
B(C 5,C 4)	1.392
B(C 5,C 0)	1.3834
B(H 6,C 2)	1.0728
B(H 7,C 3)	1.0763
B(H 8,C 4)	1.0763
B(H 9,C 5)	1.0728
A(C 1,C 0,C 5)	127.44
A(C 0,C 1,C 2)	127.49
A(C 1,C 2,H 6)	127.13
A(C 1,C 2,C 3)	110.03
A(C 3,C 2,H 6)	122.84
A(C 2,C 3,C 4)	122.49
A(C 4,C 3,H 7)	118.48
A(C 2,C 3,H 7)	119.02
A(C 5,C 4,H 8)	119.02
A(C 3,C 4,H 8)	118.48
A(C 3,C 4,C 5)	122.5
A(C 4,C 5,H 9)	122.85
A(C 0,C 5,H 9)	127.11
A(C 0,C 5,C 4)	110.05

Table 1: Results of bond lengths (B) and bond angles (A) after geometry optimization of benzyne using the HF method.

In **benzene** (see Table 2), all bond angles in the aromatic ring are approximately 120° , confirming the high symmetry and planar structure of the molecule.

Energy:

The total SCF energy of **benzyne** is **-6241.92 eV**, indicating a higher energy (lower stability) due to the presence of the reactive triple bond.

The total SCF energy of **benzene** is **-6277.73 eV**, which corresponds to a stable aromatic molecule.

1.1.2 MP2 (Møller–Plesset) method:

Bond Lengths:

In **benzene** (see Table 4), all C–C bond lengths are nearly identical (1.3965 Å). This confirms the regular arrangement of the aromatic ring and the electron delocalization characteristic of benzene.

In **benzyne** (see Table 3), the length of the triple bond (B(C 1, C 0)) is shortened to 1.2691 Å, which corresponds to a typical triple bond length. The adjacent single bonds (e.g., B(C 2, C 1) and B(C 5, C 0)) are elongated to 1.390–1.411 Å, indicating the disruption of electron delocalization due to the presence of the triple bond.

Angles:

In **benzene** (see Table 4), all bond angles are approximately 120°, corresponding to the high symmetry and planar structure of the molecule.

In **benzyne** (see Table 3), symmetry is disrupted. For example, the angle A(C 1, C 0, C 5) increases to 126.62°, and A(C 0, C 1, C 2) to 126.57°, reflecting the presence of the reactive triple bond. Conversely, some angles around the single bonds (e.g., A(C 1, C 2, C 3)) decrease to 110.82°.

Energy:

The total SCF energy of benzene is **-6277.70 eV**, demonstrating its high stability due to its aromatic character.

The total SCF energy of benzyne is **-6241.80 eV**, reflecting its higher energy and lower stability compared to benzene.

1.1.3 B3LYP method:

Bond Lengths:

In **benzyne**, the expected shortening of the C1–C0 triple bond length (1.2641 Å) was observed, which is shorter than a double or single bond. Other adjacent bonds, such as C2–C1 (1.3938 Å) and C5–C0 (1.3938 Å), were longer, which is consistent with the effects of conjugation and the molecular structure (see Table 5).

For **benzene**, all C–C bond lengths were nearly identical (around 1.407 Å), confirming its symmetric and fully aromatic nature (see Table 6).

Angles:

In **benzene**, all bond angles were close to 120° (e.g., C0–C1–C2 = 120.00° and C3–C4–C5 = 120.00°), which corresponds to a planar aromatic molecule (see Table 6).

In **benzyne**, molecular symmetry was disrupted, leading to changes in bond angles around the triple bond. For instance, the C1–C0–C5 angle increased to 127.03°, which is larger than a typical angle in aromatic structures, while the C1–C2–C3 angle decreased to 110.57° (see Table 5).

Energy:

Benzene: The total molecular energy was calculated as **-6316.47 eV**.

Benzyne: The total molecular energy was calculated as **-6280.67 eV**. The energy difference between benzyne and benzene is approximately 35.80 eV, reflecting the **higher stability of benzene** due to its aromatic nature.

1.2 Calculation of Hydrogenation Enthalpy and Hydrogenation Gibbs Free Energy for Benzyne

The aim of this section is to determine the hydrogenation enthalpy and Gibbs free energy of benzyne.

The hydrogenation enthalpy (ΔH) and Gibbs free energy (ΔG) were then calculated using the following equations:

$$\Delta H = H_{\text{benzen}} - H_{\text{benzyn}} - H_{\text{vodík}} \quad (1)$$

$$\Delta G = G_{\text{benzen}} - G_{\text{benzyn}} - G_{\text{vodík}} \quad (2)$$

where:

- H_{benzene} , H_{benzyne} , and H_{hydrogen} represent the total enthalpies obtained from calculations.
- G_{benzene} , G_{benzyne} , and G_{hydrogen} correspond to the Gibbs free energies of the respective molecules.

Using the total enthalpy and Gibbs free energy of individual molecules (see Table 7), the hydrogenation enthalpy and Gibbs free energy values were calculated and are presented in Table 8.

A comparison of different methods (HF, MP2, and B3LYP) reveals differences in energy values. The results show that MP2 and B3LYP yield lower total energy values than HF, which is expected since they account for electron correlation corrections. It is also observed that the hydrogenation Gibbs free energies are negative, confirming that the reaction is spontaneous under standard conditions.

1.3 IR Spectra of Benzyne and Benzene

The third part of this study focuses on the analysis of the IR spectra of benzene and benzyne. The spectral calculations were performed using the ORCA program. The individual vibrations were visualized and analyzed using Python, and IR spectra graphs were generated for benzene (see Figure 2) and benzyne (see Figure 1).

These graphs allowed for the identification of characteristic vibrations and a comparison of differences between the two molecules, particularly regarding the presence of the triple bond in benzyne.

The analysis of individual molecular vibrations was conducted only using the B3LYP method, and the results were recorded in Tables 9 and 10. In the case of benzyne, the $\text{C}\equiv\text{C}$ triple bond vibration was identified at a frequency of 3214.32 cm^{-1} . In contrast, no triple bond vibration was observed in this region for benzene; instead, C–H stretching was identified.

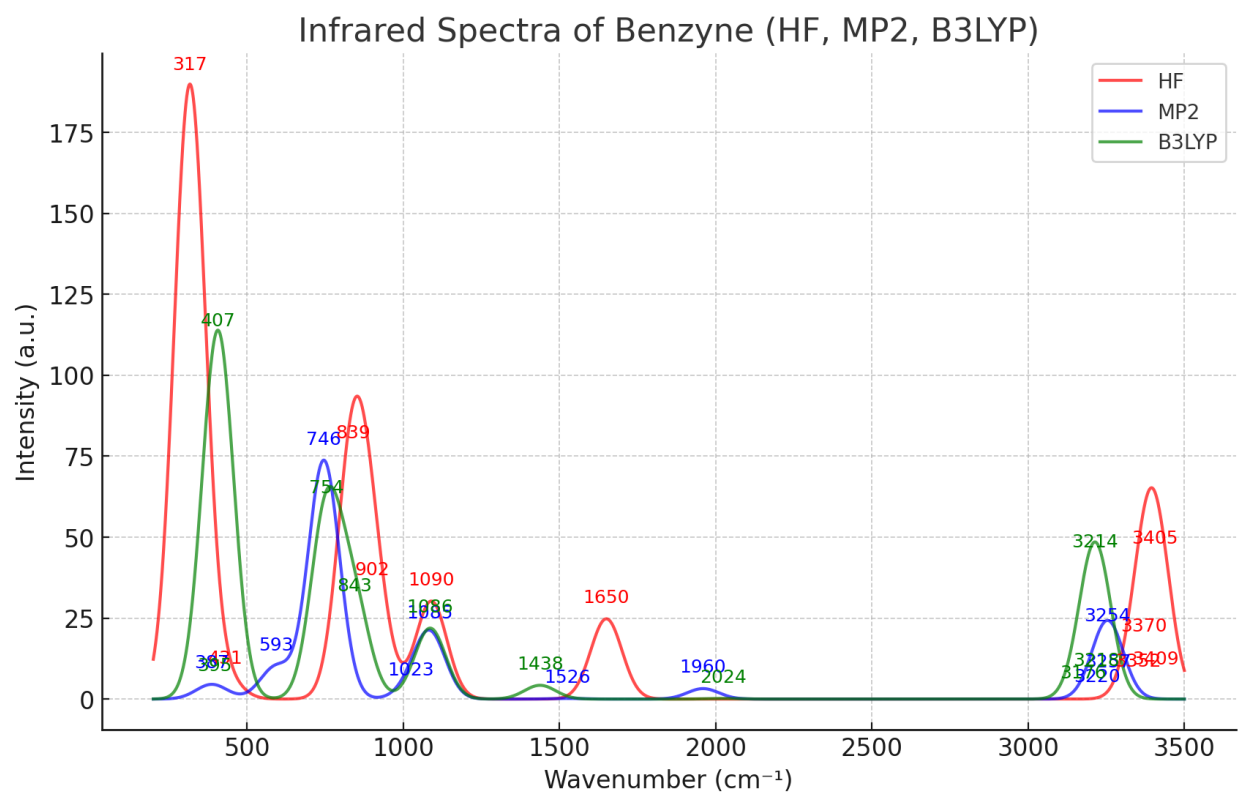


Figure 1: IR spectra benzyne (HF, MP2, B3LYP)

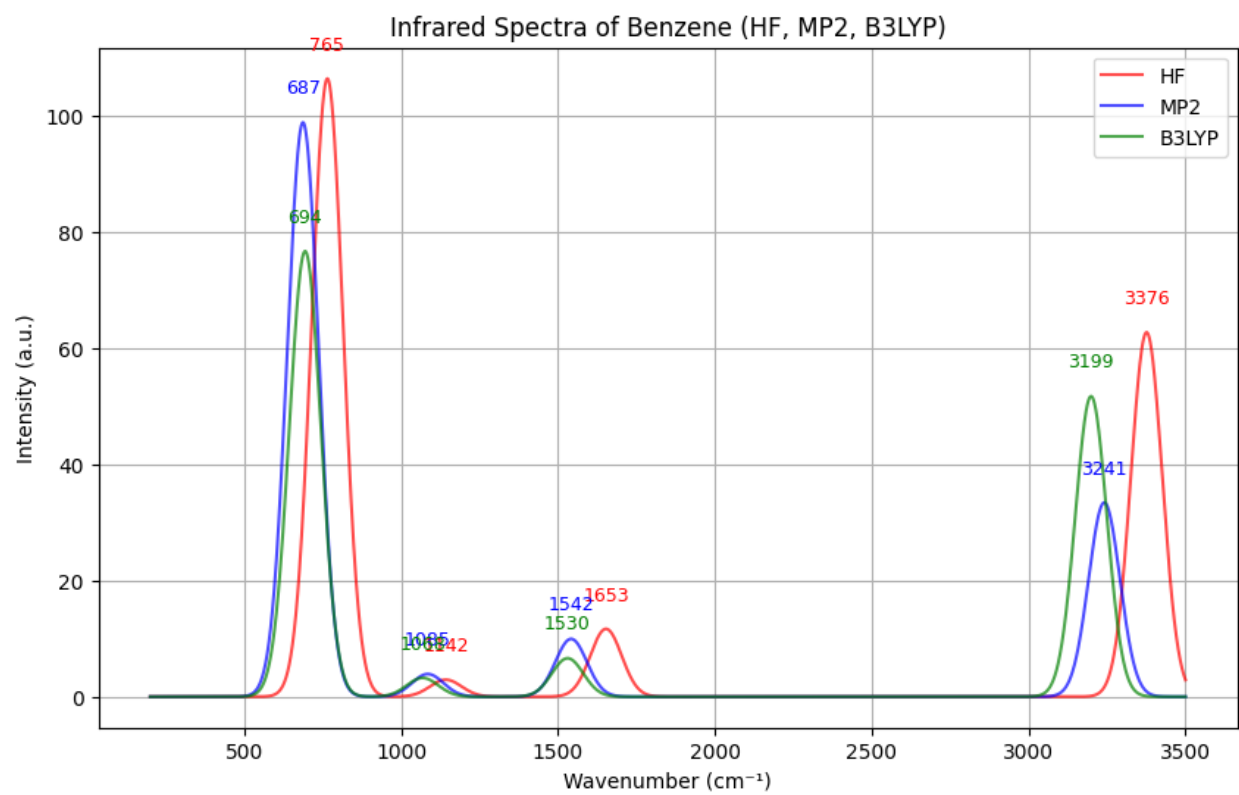


Figure 2: IR spectra benzenu (HF, MP2, B3LYP)

2 Conclusion

In this study, a quantum-chemical analysis of the structure of benzyne and benzene was performed using the Hartree-Fock (HF), MP2, and B3LYP methods with the 6-31G* basis set. The geometries of both molecules were optimized, and their bond lengths, bond angles, total energy, and thermodynamic properties were analyzed.

The results showed that the presence of the triple bond in benzyne significantly disrupts the molecular symmetry. The $\text{C}\equiv\text{C}$ triple bond shortened to approximately 1.22–1.27 Å, depending on the method used, while adjacent single bonds elongated up to 1.39–1.45 Å. In contrast, benzene exhibited a regular aromatic structure with uniform C–C bond lengths of approximately 1.39–1.41 Å and bond angles close to 120°.

The molecular energy values indicated that benzene is more stable than benzyne, as evidenced by the difference in total SCF energy (35 eV). This energy gap reflects the destabilization caused by the presence of the reactive triple bond in benzyne, which is further supported by the hydrogenation enthalpy and Gibbs free energy calculations.

Additionally, an infrared spectral analysis was performed. For benzyne, a characteristic $\text{C}\equiv\text{C}$ triple bond vibration was identified at 3214.32 cm^{-1} , whereas for benzene, C–H stretching was observed in this region. These spectral differences correspond to changes in the electronic structure and carbon atom hybridization.

Overall, the results confirm that quantum-chemical methods are a suitable tool for studying the structural and spectral properties of aromatic and polyaromatic compounds.

Definition	FinalVal
B(C 1,C 0)	1.3867
B(C 2,C 1)	1.386
B(C 3,C 2)	1.3868
B(C 4,C 3)	1.386
B(C 5,C 4)	1.3868
B(C 5,C 0)	1.3861
B(H 6,C 1)	1.0756
B(H 7,C 2)	1.0755
B(H 8,C 3)	1.0755
B(H 9,C 4)	1.0755
B(H 10,C 5)	1.0755
B(H 11,C 0)	1.0755
A(C 2,C 1,H 11)	120.02
A(C 5,C 0,H 11)	119.99
A(C 1,C 0,C 5)	119.99
A(C 0,C 1,C 2)	120.02
A(C 2,C 1,H 6)	120.04
A(C 0,C 1,H 6)	119.94
A(C 3,C 2,H 7)	119.99
A(C 1,C 2,H 7)	120.02
A(C 1,C 2,C 3)	119.99
A(C 2,C 3,C 4)	120
A(C 4,C 3,H 8)	119.99
A(C 2,C 3,H 8)	120.02
A(C 5,C 4,H 9)	119.97
A(C 3,C 4,H 9)	120.02
A(C 4,C 5,C 0)	120.01
A(C 0,C 5,H 10)	120.07
A(C 0,C 5,C 4)	119.99
A(C 4,C 5,H 10)	119.94

Table 2: Results of bond lengths (B) and bond angles (A) after geometry optimization of benzene using the HF method.

Definition	FinalVal
B(C 1,C 0)	1.2691
B(C 2,C 1)	1.3908
B(C 3,C 2)	1.4067
B(C 4,C 3)	1.4115
B(C 5,C 4)	1.4068
B(C 5,C 0)	1.3906
B(H 6,C 2)	1.0861
B(H 7,C 3)	1.0883
B(H 8,C 4)	1.0883
B(H 9,C 5)	1.0861
A(C 1,C 0,C 5)	126.62
A(C 0,C 1,C 2)	126.57
A(C 1,C 2,H 6)	126.75
A(C 1,C 2,C 3)	110.82
A(C 3,C 2,H 6)	122.44
A(C 2,C 3,C 4)	122.6
A(C 4,C 3,H 7)	118.77
A(C 2,C 3,H 7)	118.63
A(C 5,C 4,H 8)	118.64
A(C 3,C 4,H 8)	118.77
A(C 3,C 4,C 5)	122.59
A(C 4,C 5,H 9)	122.44
A(C 0,C 5,H 9)	126.76
A(C 0,C 5,C 4)	110.8

Table 3: Results of bond lengths (B) and bond angles (A) after geometry optimization of benzyne using the MP2 method.

Definition	FinalVal
B(C 1,C 0)	1.3965
B(C 2,C 1)	1.3965
B(C 3,C 2)	1.3967
B(C 4,C 3)	1.3965
B(C 5,C 4)	1.3968
B(C 5,C 0)	1.3967
B(H 6,C 1)	1.0874
B(H 7,C 2)	1.0874
B(H 8,C 3)	1.0874
B(H 9,C 4)	1.0874
B(H 10,C 5)	1.0874
B(H 11,C 0)	1.0874
A(C 1,C 0,H 11)	120.02
A(C 5,C 0,H 11)	119.99
A(C 1,C 0,C 5)	119.99
A(C 0,C 1,C 2)	120.02
A(C 2,C 1,H 6)	120.03
A(C 0,C 1,H 6)	119.95
A(C 3,C 2,H 7)	119.99
A(C 1,C 2,H 7)	120.01
A(C 1,C 2,C 3)	119.99
A(C 2,C 3,C 4)	119.99
A(C 4,C 3,H 8)	119.98
A(C 2,C 3,H 8)	120.03
A(C 5,C 4,H 9)	119.97
A(C 3,C 4,H 9)	120.02
A(C 3,C 4,C 5)	120.01
A(C 0,C 5,H 10)	120.06
A(C 0,C 5,C 4)	119.99
A(C 4,C 5,H 10)	119.95

Table 4: Results of bond lengths (B) and bond angles (A) after geometry optimization of benzene using the MP2 method.

Definition	FinalVal
B(C 1,C 0)	1.2641
B(C 2,C 1)	1.3938
B(C 3,C 2)	1.4253
B(C 4,C 3)	1.415
B(C 5,C 4)	1.4252
B(C 5,C 0)	1.3938
B(H 6,C 2)	1.0926
B(H 7,C 3)	1.0953
B(H 8,C 4)	1.0953
B(H 9,C 5)	1.0926
A(C 1,C 0,C 5)	127.03
A(C 0,C 1,C 2)	127.01
A(C 1,C 2,H 6)	127.05
A(C 1,C 2,C 3)	110.57
A(C 3,C 2,H 6)	122.38
A(C 2,C 3,C 4)	122.4
A(C 4,C 3,H 7)	119.07
A(C 2,C 3,H 7)	118.53
A(C 5,C 4,H 8)	118.52
A(C 3,C 4,H 8)	119.07
A(C 3,C 4,C 5)	122.41
A(C 4,C 5,H 9)	122.39
A(C 0,C 5,H 9)	127.04
A(C 0,C 5,C 4)	110.57

Table 5: Results of bond lengths (B) and bond angles (A) after geometry optimization of benzyne using the B3LYP method.

Definition	FinalVal
B(C 1,C 0)	1.4069
B(C 2,C 1)	1.4069
B(C 3,C 2)	1.407
B(C 4,C 3)	1.4069
B(C 5,C 4)	1.4071
B(C 5,C 0)	1.407
B(H 6,C 2)	1.0943
B(H 7,C 3)	1.0943
B(H 8,C 4)	1.0943
B(H 9,C 5)	1.0943
A(C 1,C 0,C 5)	119.99
A(C 0,C 1,C 2)	120
A(C 1,C 2,H 6)	120.03
A(C 1,C 2,C 3)	120
A(C 3,C 2,H 6)	119.97
A(C 2,C 3,C 4)	120
A(C 4,C 3,H 7)	119.99
A(C 2,C 3,H 7)	120
A(C 5,C 4,H 8)	119.98
A(C 3,C 4,H 8)	120.02
A(C 3,C 4,C 5)	120
A(C 4,C 5,H 9)	119.98
A(C 0,C 5,H 9)	120
A(C 0,C 5,C 4)	119.96

Table 6: Results of bond lengths (B) and bond angles (A) after geometry optimization of benzene using the B3LYP method.

	HF		MP2		B3LYP	
	Benzyne	Hydrogen	Benzyne	Hydrogen	Benzyne	Hydrogen
Gibbs energy [eV]	-6240.46	-30.69	-6261.88	-31.16	-6277.94	-31.84
Benzene	-6275.55		-6296.48		-6313.49	
Total Enthalpy [eV]	-6239.59	-30.28	-6260.99	-30.76	-6277.04	-31.44
Benzene	-6274.67		-6295.58		-6312.60	

Table 7: Gibbs free energy and total enthalpy for individual molecules and applied methods.

[eV]	HF	MP2	B3LYP
Hydrogen. Gibbs energy	-4.40495096	-3.44	-3.72
Hydrogenation enthalpy	-4.79726941	-3.83	-4.12

Table 8: Comparison of Gibbs energy and hydrogenation enthalpy using different methods.

Frekvence [cm⁻¹]	Intenzita km/mol	Typ vibrace
406,98	110,26	Out-of-plane bending
754,5	58,61	C-C skeletal stretching
843,15	28,29	In-plane C-H bending
1086,02	21,91	Out of plane C-H bending
1485,96	13,1	C=C stretch (in-ring)
3214,32	41,95	C(triple bond)C stretching

Table 9: Type of vibrations and their characteristics for benzyne (B3LYP).

Frekvence (cm⁻¹)	Intenzita (km/mol)	Typ vibrace
693,67	76,62	Out-of-plane deformation C-H
1068,01	3,23	In-plane deformace C-H
1530,4	6,61	Valenční vibrace C=C v aromatickém kruhu
3198,99	51,67	Valenční vibrace C-H (stretch)

Table 10: Type of vibrations and their characteristics for benzene (B3LYP).