

INTRODUCTION

- The word aromatic can be used to describe fragrant substances such as benzaldehyde (from cherries, almonds), and toluene (from Tolu balsam).
- However, in the early nineteenth century such substances were discovered to behave in a different chemical manner from other organic compounds. Thus, in chemistry, the term aromatic is now used to refer to benzene and its structural relatives.
- The Cambridge Structural Database can be used to explore the structural requirements for aromaticity. By investigating the structure of such compounds we can explain their special stability.

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OBJECTIVES

- To investigate the concept of aromaticity by analysing experimental crystal structure data.
- To determine the structural requirements for aromaticity by examining a series of benzene and cyclooctatetraene derivatives.
- To understand the reason for the observed stability of benzene in terms of its molecular orbital description.
- To use your findings to predict whether or not certain given compounds are aromatic.

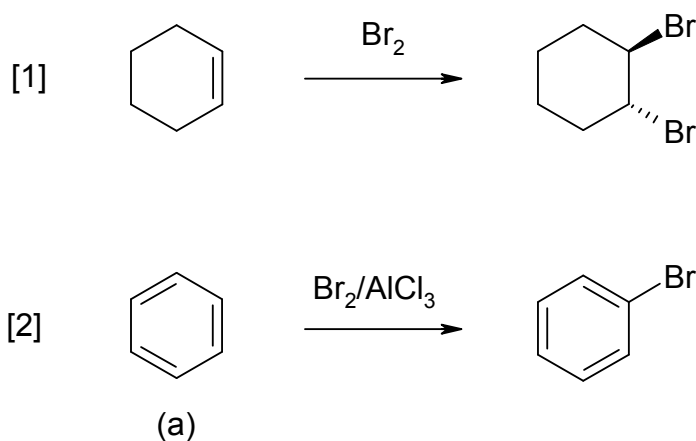
GETTING STARTED

- If you do not subscribe to the Cambridge Structural Database (CSD) System:
 - Open *free* Mercury (the free version of Mercury can be downloaded from http://www.ccdc.cam.ac.uk/free_services/mercury/)
 - Open the free teaching subset of the CSD (downloadable from http://www.ccdc.cam.ac.uk/free_services/teaching/downloads) by selecting **File** from the top-level menu, followed by **Open** in the resulting menu, and then selecting the database file `teaching_subset.ind`
 - Database reference codes (*refcodes*) of the structures in the teaching database will appear in a list on the right hand side of the main Mercury window. To view a structure select the corresponding *refcode* in the list.
- If you subscribe to the Cambridge Structural Database (CSD) System:
 - Open MercuryCSD.
 - The full database should be detected and opened within the *Structure Navigator* on the right hand side of the main Mercury window. To view a structure select, or type in, the corresponding *refcode*.

1 STEPS REQUIRED

1.1 Examine the structure of benzene

- Benzene (a) is unusually stable for an alkene. Normal alkenes readily react with bromine to give dibromoalkane addition products [1]. However, benzene reacts only in the presence of a Lewis acid catalyst and the product is a monosubstituted benzene not an addition product [2]. Why does benzene not behave like other alkenes?



- Display the structure of benzene by clicking on the identifier *BENZEN02* from the *Structure Navigator* on the right hand side of the main Mercury window.
- Inspect the structure. You will notice that benzene is a planar symmetrical hexagon (internal bond angles close to 120 degrees) with six trigonal (sp^2) carbon atoms, each with one hydrogen atom in the plane of the ring.

To manipulate structures in Mercury

1. Structures can be rotated by moving the cursor in the display area while keeping the left-hand mouse button pressed down.
2. To zoom in and out move the cursor up and down in the display area while keeping the right-hand mouse button pressed down.
3. To translate structures hold down the middle mouse button while moving the cursor in the display area (three-button mouse only). Alternatively, move the cursor in the display area while keeping both the left-hand mouse button and the keyboard Ctrl key pressed down.
4. At any stage the display area can be returned to the default view by hitting the **Reset** button at the

bottom of the window.

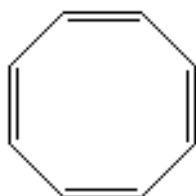
- Next, measure each of the carbon-carbon bond lengths in the structure. You will see that all bond lengths are around 1.38Å. How does this compare to typical carbon-carbon double and single bond lengths? Typical C=C double bonds are 1.33Å and C-C single bonds are 1.46Å.

To measure distances in Mercury

1. Set Picking Mode in the tool bar (near the top of the main Mercury window) to the required parameter type, viz. **Measure Distance**, **Measure Angle** or **Measure Torsion**
2. Geometrical measurements (intramolecular or intermolecular) can now be made by clicking on e.g., two atoms for a distance, three atoms for an angle or four atoms for a torsion angle.
3. To remove all geometrical measurements from the display click on the **Clear Measurements** button in the tool bar near the top of the main Mercury window.

1.2 Examine the structure of cyclooctatetraene.

- Cyclooctatetraene (shown below) has four double bonds in a ring, what do you think its 3D structure will be?

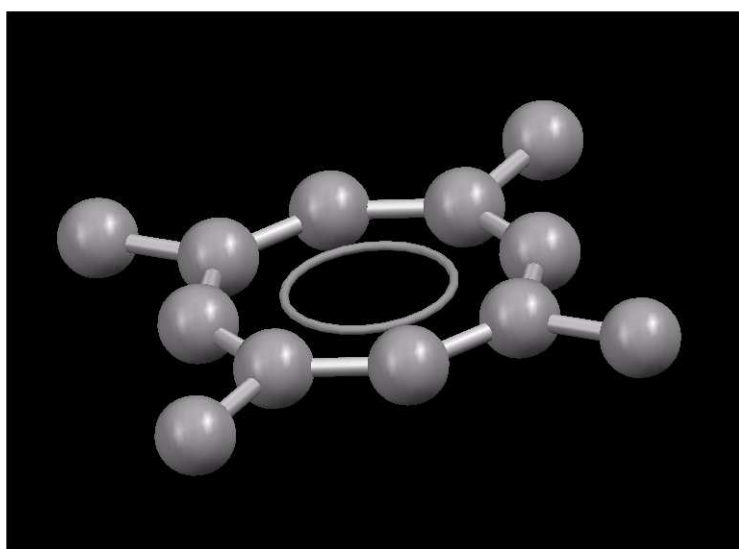
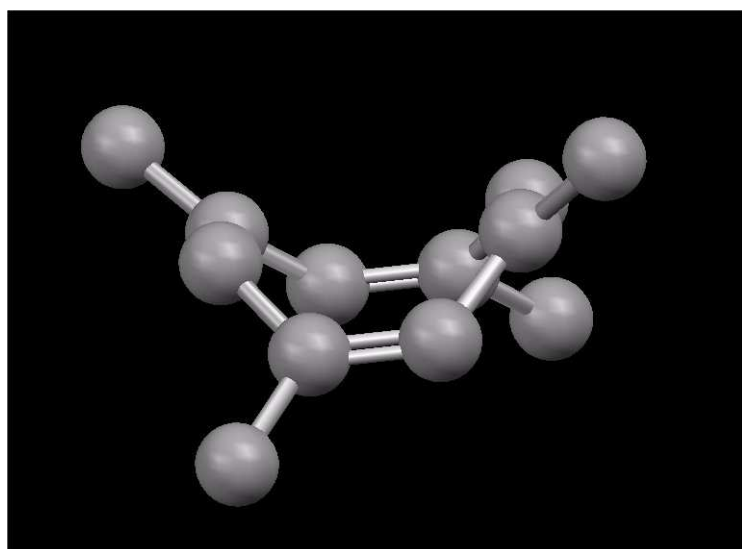


- Display the structure of cyclooctatetraene by selecting the identifier *ZZZSAE01* from the *Structure Navigator*.
- Inspect the structure. You will notice that unlike benzene, cyclooctatetraene is not planar, instead it adopts a “*tub*” shape. The reason for this lack of planarity is that a regular octagon has internal angles of 135 degrees, while sp^2 angles are most stable at 120 degrees. To avoid the strain the molecule therefore adopts a nonplanar geometry.
- Measure each of the carbon-carbon bond lengths in the structure. There are two carbon-carbon bond lengths: 1.46Å and 1.33Å. These are typical for double and single carbon-carbon bonds.
- Chemically speaking, cyclooctatetraene behaves like an alkene not like benzene e.g. it does not form a substitution product with bromine, but an addition product.
- Why is benzene so different from other alkenes and why is cyclooctatetraene different from

benzene?

1.3 Consider what happens when we treat cyclooctatetraene with a powerful reducing agent

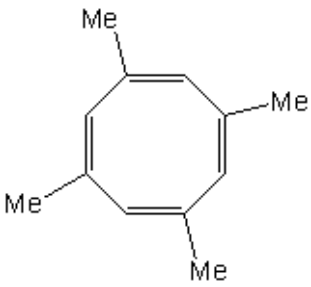
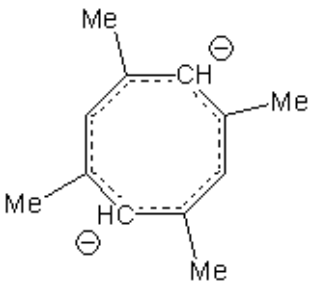
- If 1,3,5,7-tetramethylcyclooctatetraene (refcode *TMCOTT*) is treated with alkali metals a dianion is formed (refcode *TMOCKE*).
- Look closely at the structures of 1,3,5,7-tetramethylcyclooctatetraene (refcode *TMCOTT*) and the resultant dianion (refcode *TMOCKE*). How do these two compounds differ structurally?
- The dianion is planar and all bonds lengths are equivalent (within experimental error). Whereas the neutral compound is non-planar (“*tub*” shaped) with alternate double and single bonds lengths of 1.48Å and 1.33Å.



left: “*tub*” shape of 1,3,5,7-tetramethylcyclooctatetraene (refcode *TMCOTT*); right: the resulting planar dianion (refcode *TMOCKE*)

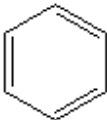
- By reducing 1,3,5,7-tetramethylcyclooctatetraene we are adding electrons. The difference between the anion and the neutral compound is therefore the number of electrons in the π system. The following table summarises what we have discovered so far:

Compound and CSD Refcode	Diagram	π Electrons	Geometry
cyclooctatetraene <i>ZZZSAE01</i>		8	non-planar

Compound and CSD Refcode	Diagram	p Electrons	Geometry
1,3,5,7-tetramethyl cyclooctatetraene <i>TMCOTT</i>		8	non-planar
1,3,5,7-tetramethyl cyclooctatetraene dianion <i>TMOCKE</i>		10	planar

1.4 Consider what happens if we treat benzene with oxidizing or reducing agents

- Treatment of benzene with strongly oxidising $\text{SbF}_5/\text{SO}_2\text{ClF}$ has no effect. However, it is possible to oxidise substituted derivatives. Hexakis(dimethylamino)benzene (refcode *GENFAG*) can be oxidised with iodine to give the dication (refcode *GENFEK*).
- Compare these two structures. This time you will notice that, unlike the neutral compound, the cation is nonplanar and all carbon-carbon bonds lengths are not the same.
- Similar results are obtained when we reduce hexakis(trimethylsilyl)benzene (refcode *KELVOM*) to the dianion (refcode *KINFUI*). Again, compare these two structures, how do they differ?
- Clearly the number of p electrons is important in determining whether or not cyclic alkenes adopt a planar geometry. Complete the table below with your findings:

Compound and CSD Refcode	Diagram	p Electrons	Geometry
benzene <i>BENZEN02</i>		6	planar

Compound and CSD Refcode	Diagram	p Electrons	Geometry
hexakis(dimethylamino) benzene <i>GENFAG</i>		6	
hexakis(dimethylamino) benzene dication <i>GENFEK</i>			
hexakis(trimethylsilyl) benzene <i>KELVOM</i>			planar
hexakis(trimethylsilyl) benzene dianion, <i>KINFUI</i>			

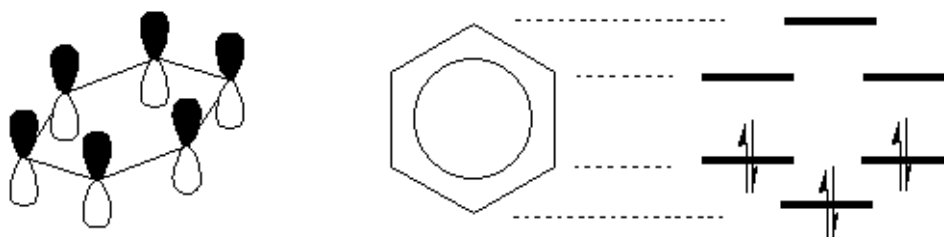
1.5 Do you see a pattern forming?

- The number of p electrons in the system is crucial: when they have 4 or 8 p electrons both cyclooctatetraene and benzene adopt non-planar geometries; when they have 6 or 10 p electrons a conjugated planar geometry is preferred.
- Remember: the planar 1,3,5,7-tetramethylcyclooctatetraene dianion (refcode *TMOCKE*) still has

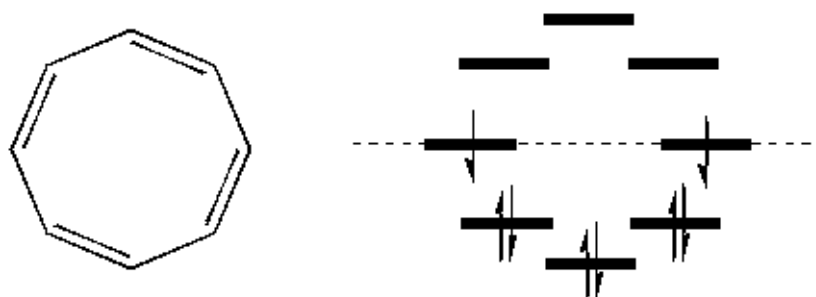
considerable ring strain. The fact that this structure adopt a planar geometry must mean that there is some other form of stabilization (gained as a results of having 10 p electrons) that outweighs the strain of being planar. The extra stability is called aromaticity.

1.6 Molecular orbital description

- The special stability (aromaticity) of benzene comes from having six p electrons. These six electrons fully occupy the three molecular bonding orbitals and are therefore delocalised over the entire conjugated system. This closed shell structure is the reason for the observed stability of benzene.



- By comparison, cyclooctatetraene has eight electrons, six of these fill the molecular bonding orbitals and two occupy the degenerate pair of non-bonding orbitals.



- Cyclooctatetraene must therefore lose or gain 2 electrons in order to have a closed shell structure. We have seen this already: the 1,3,5,7-tetramethyl-cyclooctatetraene dianion is planar, allowing delocalisation over the ring, whereas the neutral structure adopts a nonplanar tub shape with localised bonds.
- Look at the MO level diagrams above. There is always a single low-energy bonding orbital followed by pairs of degenerate orbitals. Since the single orbital will hold two electrons when full and the degenerate pairs four, we will only have a closed shell of electrons in these p orbitals when they contain $4n+2$ electrons.

1.7 Requirements for aromaticity

- We can now summarize what we have discovered: A molecule can only be aromatic if it has a

planar (so that *p*-orbitals can overlap) system of conjugation with $4n+2$ *p* electrons (where $n = 0, 1, 2, 3\dots$) i.e. only molecules with 2, 6, 10, 14, 18... *p* electrons can be aromatic.

- This is the basis for Huckels Rule, which states “Planar, fully conjugated, monocyclic systems with $4n+2$ *p* electrons ($n = 0, 1, 2, 3\dots$) have a closed shell of electrons all in bonding orbitals and are exceptionally stable. Such systems are said to be aromatic”

1.8 Use Huckels rule to predict aromaticity

- Determine which of the following compounds are aromatic. Examine the structures to see whether or not they are planar and fully conjugated. Justify your answers with some electron counting:
 - tetra-*t*-butyl-cyclobutadiene (*TBUCBD10*)
 - naphthalene (*NAPHTA12*)
 - cyclohepta-1,3,5-triene (*CHMOCO01*)
 - cyclopentadienyl anion (*NARGET*)
 - (14)annulene (*FANNUL*)
 - (16)annulene (*ANNUL01*)
 - (18)annulene (*ANULEN*)
 - pyridine (*PYRDNA01*)

SUMMARY OF KEY CONCEPTS

- Benzene is a cyclic, planar, conjugated molecule. All carbon-carbon bonds are equivalent and have a length of 1.38Å, a value between that of normal carbon single- and double-bond lengths.
- Benzene is unusually stable. It reacts slowly with electrophiles to give substitution products in which cyclic conjugation is retained. This stability comes from having $4n+2$ p electrons (where $n = 1$). These six electrons fully occupy the three molecular bonding orbitals and are therefore delocalised over the entire conjugated system. This closed shell structure is the reason for the observed stability of benzene.
- A molecule can only be aromatic if it has a planar (so that *p*-orbitals can overlap) system of conjugation with $4n+2$ p electrons. This is the basis for Huckels rule.
- Other kinds of molecules can also be aromatic according to the Huckel definition. For example, the 1,3,5,7-tetramethyl-cyclooctatetraene dianion (*TMOCKE*) and the cyclopentadienyl anion (*NARGET*) are both aromatic ions. Heterocyclic compounds can also be aromatic, for example pyridine (*PYRDNA01*) is a six-membered nitrogen-containing heterocycle and resembles benzene electronically.