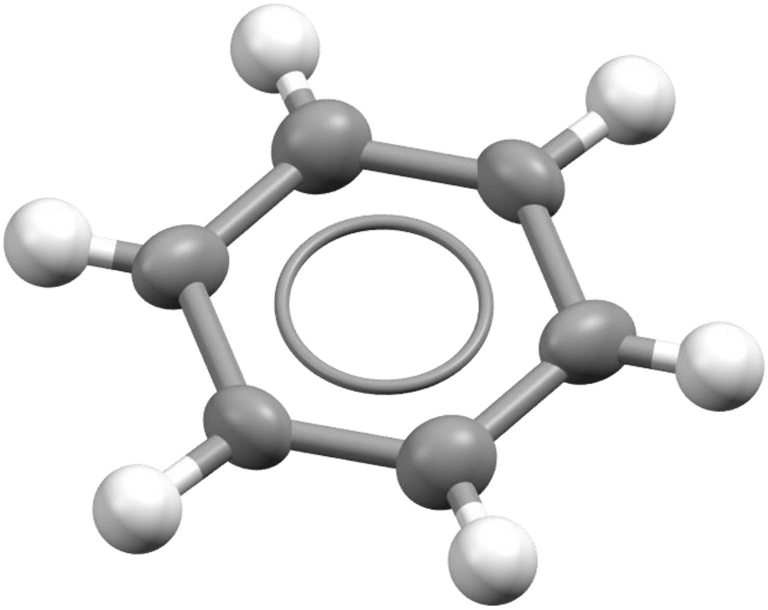
Aromaticity

Table of Contents



CCDC
advancing structural science

1. Introduction

This teaching module introduces you to the concept of aromaticity and uses entries in the Cambridge Structural Database (CSD) to show the structural characteristics of aromatic molecules. You will use the aromatic molecule benzene to identify distinctive features of aromatic molecules. You will make comparisons with the cyclic polyene cyclooctatetraene and examine structural changes that appear upon reduction.

1.1 Learning outcomes

At the end of this module, you will:

- understand the concept of aromaticity and its structural manifestations
- know the conditions that need to be met to classify a molecule as aromatic
- understand the reason for the stability of benzene in terms of the molecular orbital description of bonding
- be able to predict whether a given compound is aromatic

1.2 Materials

The structures needed to complete this module are available from the online Web service Access Structures.

https://www.ccdc.cam.ac.uk/structures/

This provides you with all the features required to complete this teaching module. Alternatively, you may prefer to use the structure visualization program Mercury, which you can download for free. Instructions for obtaining this software and links to resources to support you using it are given at the end of this document. This teaching module uses entries in the Teaching Subset; you can find out more about the Teaching Subset here: https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/.

1.3 Pre-required skills

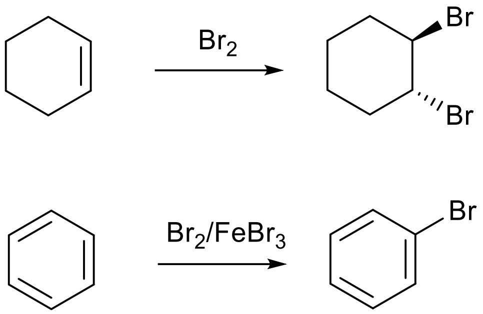
This teaching module assumes no prior experience of crystallography. A basic understanding of valence bond theory and molecular orbital theory is assumed.

2 Introduction to Aromaticity

The word aromatic was used to group molecules based upon smell before their structures and chemistry were well understood; indeed, many aromatic (in the chemical sense) compounds possess a pleasant smell. Examples include benzaldehyde which has the characteristic smell of almonds and toluene, which was extracted from fragrant Tolu balsam (a tree resin containing various aromatic compounds). In the early 19th century, it was recognized that such substances reacted differently from other organic compounds and the term became synonymous with molecules possessing benzene-like functionality. The Cambridge Structural Database (CSD) can be used to explore the structural requirements for aromaticity and in turn help to explain their special stability.

2.1 Examining the structure of benzene

Benzene is unusually stable for an alkene; normally alkenes react with bromine to give dibromoalkane addition products, however, benzene will only react in the presence of a Lewis acid catalysts, and the product is a monosubstituted addition product (see below). Why does benzene behave like this?

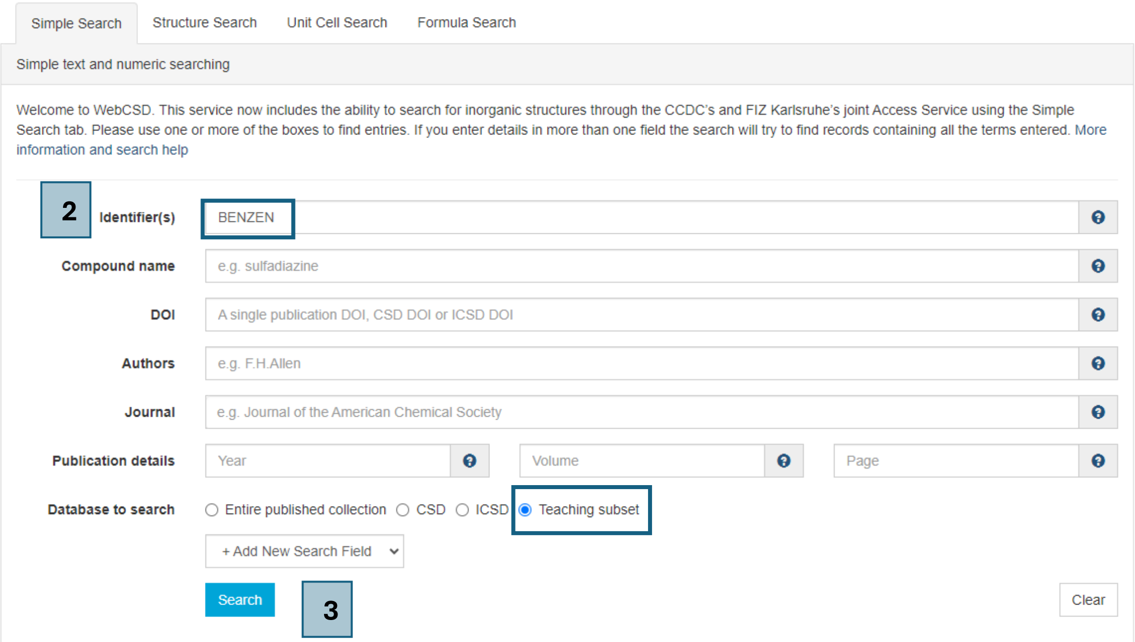


The reaction of cyclohexene with bromine(top) and the reaction of benzene with bromine in the presence of Lewis acid catalyst $FeBr_3$*(bottom).*

1. To get started, navigate to Access Structures at https://www.ccdc.cam.ac.uk/structures/.
2. In the *Identifiers* field, enter “BENZEN”. The six-letter code BENZEN is known as a *refcode*; it is used to identify database entries in the CSD.

Note: you could also search for “benzene” in the *Compound name* field, though more results will be returned.

3. For *Database to search*, select **Teaching Subset** and press **Search.**



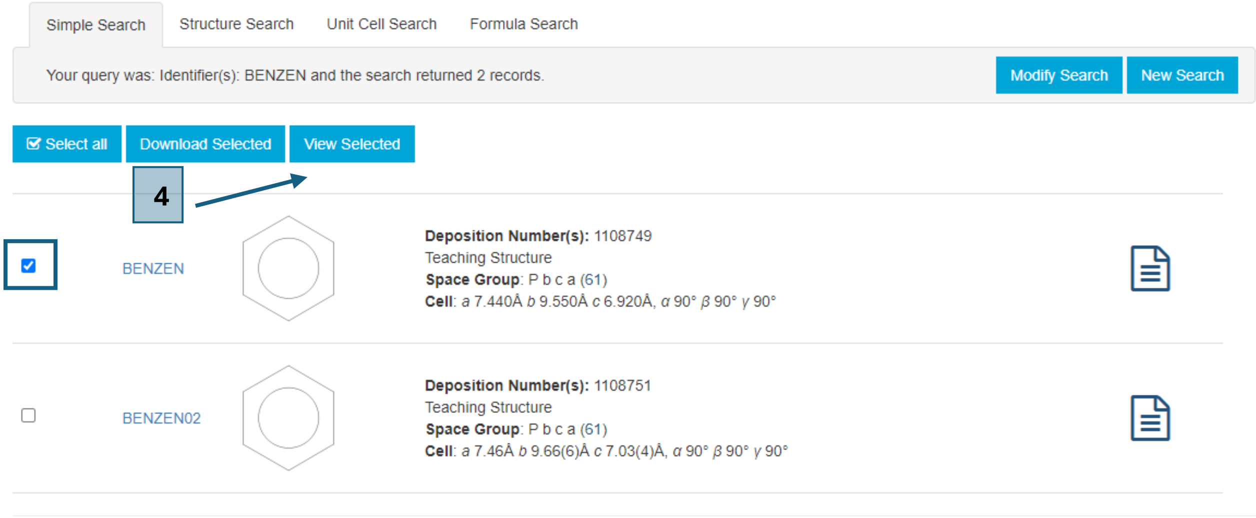
Simple text and numeric searching

Welcome to WebCSD. This service now includes the ability to search for inorganic structures through the CCDC's and FIZ Karlsruhe's joint Access Service using the Simple Search tab. Please use one or more of the boxes to find entries. If you enter details in more than one field the search will try to find records containing all the terms entered. More information and search help

Identifier(s) BENZEN

Database to search ○ Entire published collection ○ CSD ○ ICSD ● Teaching subset

4. The search may return more than one result. Deselect all except *BENZEN* and click **View Selected.**

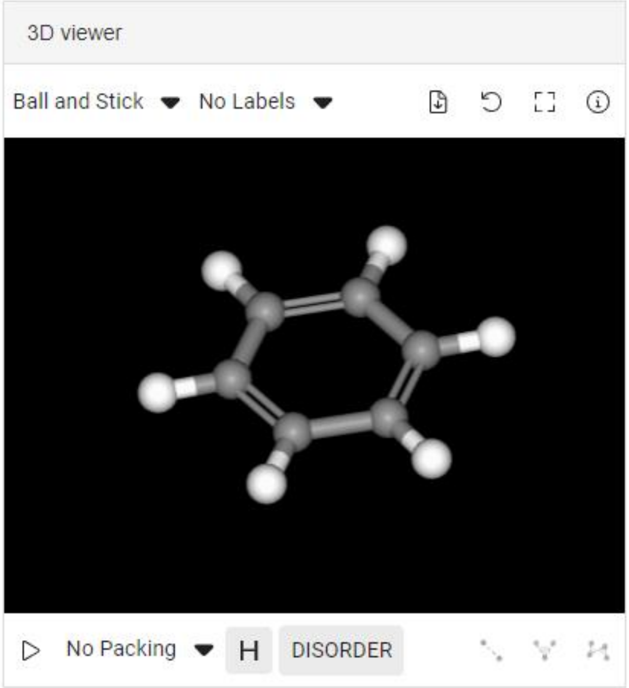


Your query was: Identifier(s): BENZEN and the search returned 2 records.

☑ BENZEN
Deposition Number(s): 1108749
Teaching Structure
Space Group: P b c a (61)
Cell: *a* 7.440Å *b* 9.550Å *c* 6.920Å, *α* 90° *β* 90° *γ* 90°

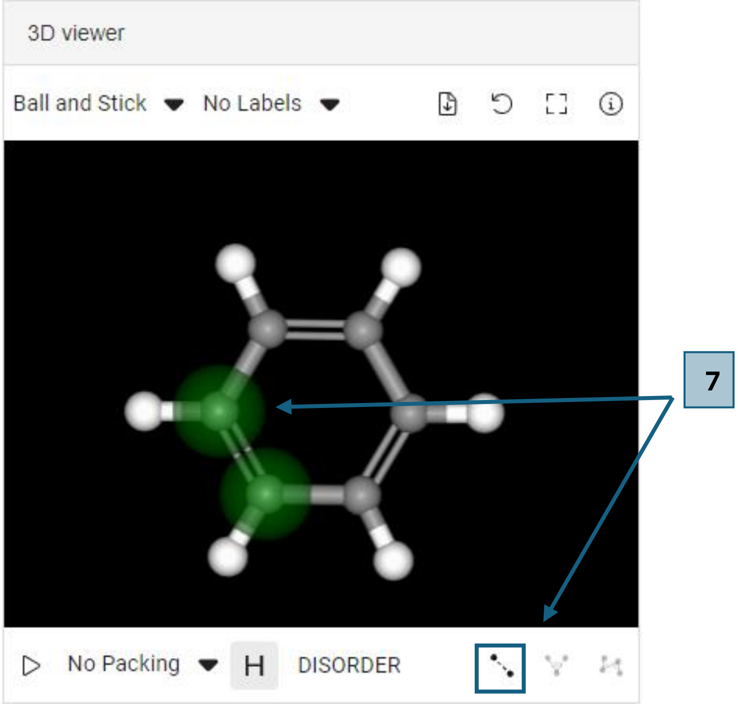
☐ BENZEN02
Deposition Number(s): 1108751
Teaching Structure
Space Group: P b c a (61)
Cell: *a* 7.46Å *b* 9.66(6)Å *c* 7.03(4)Å, *α* 90° *β* 90° *γ* 90°

5. Inspect the structure in the **3D Viewer**. You will see that it is a planar six-membered ring containing trigonal (*sp*^{2}) carbon atoms, each of which has one attached hydrogen atom.



6. To manipulate the structure:
    - Left click and drag to rotate the structure.
    - Right click and drag to translate the structure.
    - Scroll up/down with the mouse wheel to zoom in/out.
    - At any time, hit ⟲ to reset the viewer.

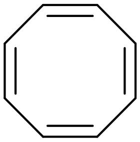
7. Next, measure the C–C bond lengths in the structure. To do so, click on two adjacent C atoms in benzene (they will be highlighted green) and click the measure distance symbol.



8. Repeat the process for all 6 C–C bonds. You should find that they are all 1.39 Å. The values for single and double bonds, which are 1.46 Å and 1.33 Å, respectively. What does this suggest about the bond order of the C–C bonds in benzene?

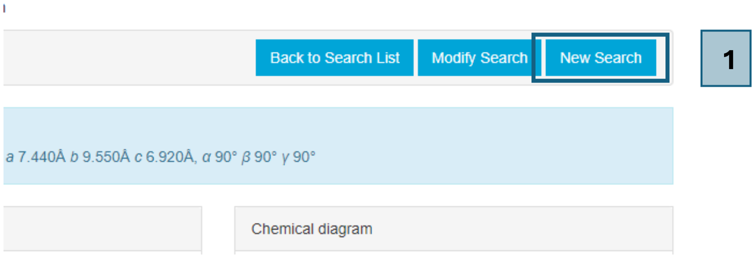
2.2 Examining the structure of cyclooctatetraene

Cyclooctatetraene (C_8H_8) has four alternating pairs of single and double bonds in a ring. What do you think the structure will be in 3D?



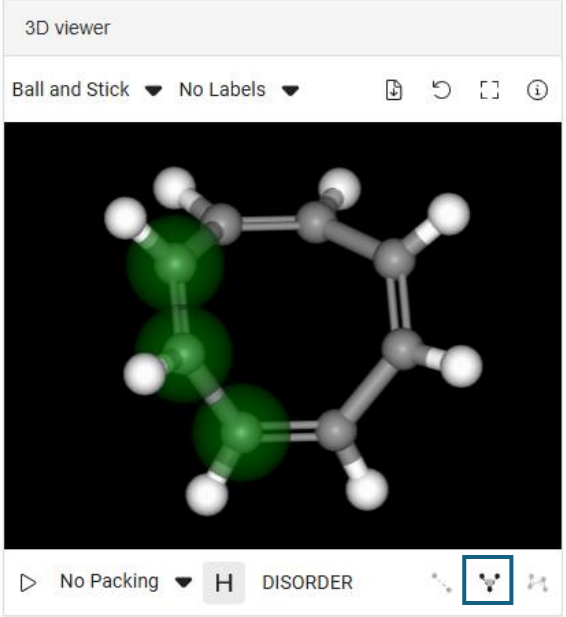
The cyclooctatetraene molecule.

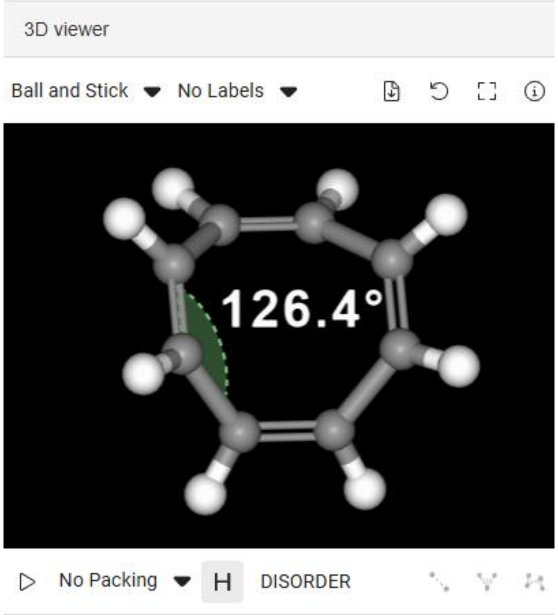
1. In the Access Structures results page, press **New Search**.



a 7.440Å b 9.550Å c 6.920Å, α 90° β 90° γ 90°

2. In the Identifier(s) box, type “ZZZSAE01” and press **Search**.
3. Inspect the structure in the visualizer. Unlike benzene, this molecule in non-planar; it adopts a “tub” shape. The reason for this is that the internal angles of an octagon are 135°, whereas the ideal angle for a *sp*^{2} hybridised atom is 120°. Such a ring would be highly strained; therefore, the molecule distorts from planar to alleviate this. You can measure angles in the viewer by clicking on three atoms and pressing the angle button.





4. Measure each of the C–C bond lengths in the structure. You should find there are two different bond lengths, 1.47 Å and 1.33 Å. These are close to typical values for single and double bonds, respectively. Observe that this contrasts with benzene in Section 2.1, where the bond length suggests a bond order of 1.5.

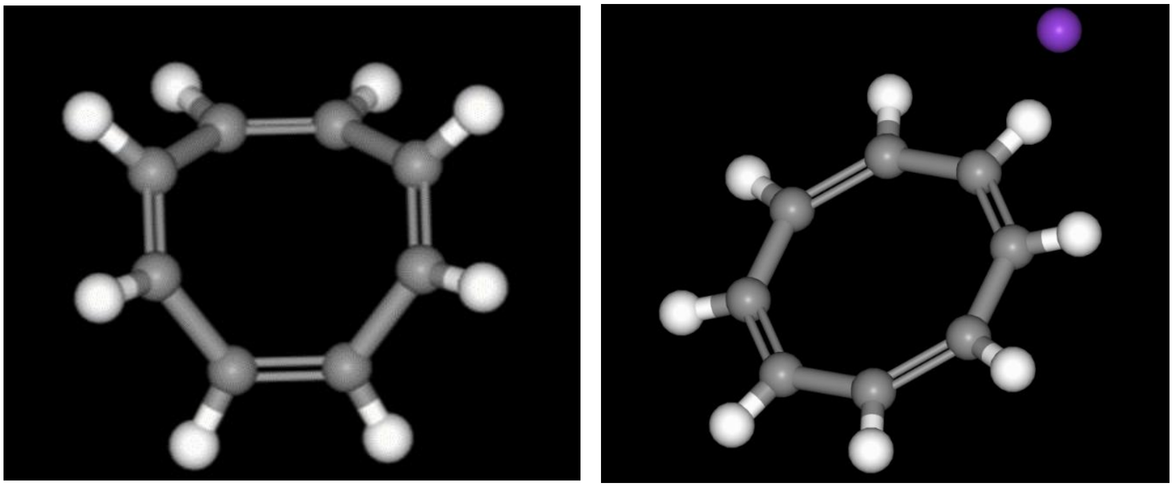
Chemically speaking, cyclooctatetraene behaves like an alkene, i.e. it does not form a substitution product on reaction with bromine; rather, it forms an addition product. Why is benzene so different from other alkenes, and why is cyclooctatetraene different from benzene?

2.3 Reduction of cyclooctatetraene

If cyclooctatetraene is treated with potassium in a suitable solvent, $K_2C_8H_8$ is formed. The $C_8H_8^{2-}$ ion, formed by reduction, can be compared to the neutral molecule.

1. Start a new search for *Identifier(s)* “XINGIM”.
2. Inspect the structure of this entry in the visualizer and focus on the $C_8H_8^{2-}$ anion.
3. You should find that whereas the neutral alkene (ZZZSAE01) is tub-shaped, the dianion (XINGIM) is planar.

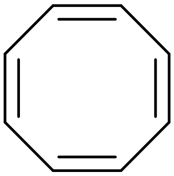
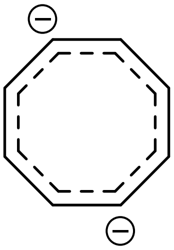
4. Measure the bond lengths in the anion. You should find they are 1.41–1.42 Å. How does this compare with bond lengths in neutral cyclooctatetraene and what does this suggest about the nature of the bonding in the dianion? How do their molecular structures compare (see below).



A comparison of non-planar cyclooctatetraene (left) and the planar cyclooctatetraene dianion (right).

By reducing cyclooctatetraene, electrons are added and the electronic difference between these molecules is therefore the number of electrons in the π-system. Table 1 summarises the findings of this section.

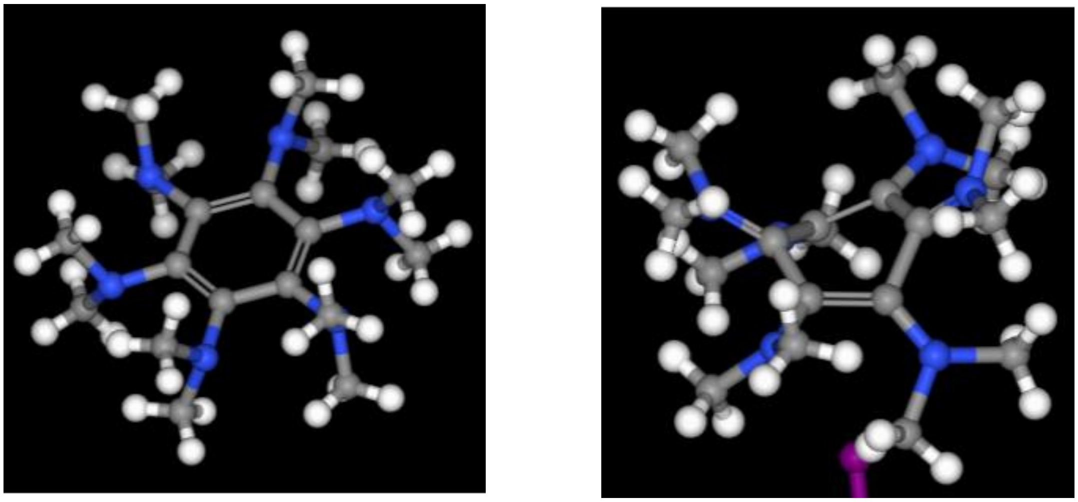
Table 1. Comparison of the structures and π electron counts of cyclooctatetraene and derivatives.

Name and CSD Refcode	**Diagram**	**Number of π electrons**	**Geometry**
Cyclooctatetraene *ZZZSAE01*		8	Non-planar
Cyclooctatetraene dianion (also called cyclooctatetraenediide) from *XINGIM*		10	Planar

2.4 Oxidation and reduction of benzene and related aromatic compounds

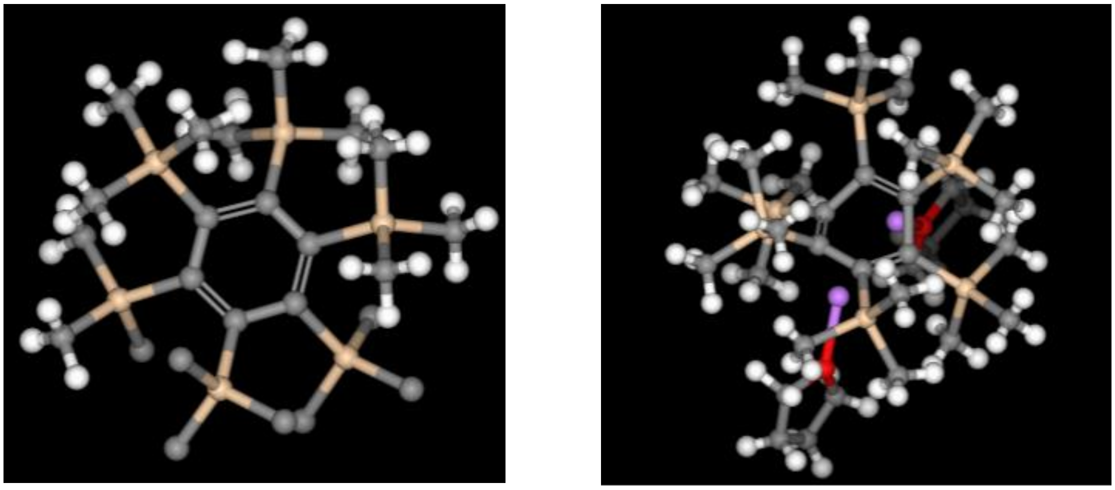
Benzene is inert to the strongly oxidising mixture SbF_5/SO_2ClF but substituted derivatives, such as hexakis(dimethylamino)benzene (CSD entry GENFAG) can be oxidised with iodine to give a dication (CSD entry GENFEK)

1. Start a new search for *Identifier(s)* "*GENFAG, GENFEK*".
2. Inspect their structures using the visualizer and examine the C–C bond lengths. You should find that the neutral species is planar, with equal C–C bond lengths, whereas the dication is non-planar with unequal bond lengths.



A comparison of planar hexakis(diimethylamino)benzene (left) and the non-planar cation derived from it (right).

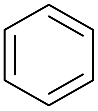
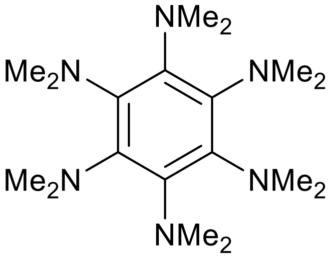
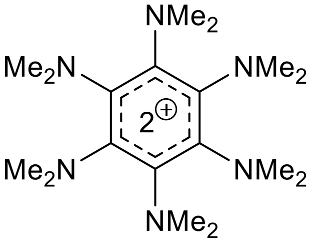
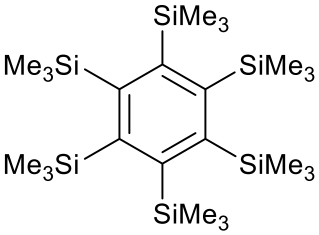
3. Repeat this procedure for hexakis(trimethylsilyl)benzene, CSD entry KELVOM, and its dianion, CSD entry KINFUI, and compare their structures. (You may find it interesting to compare the C–C bond length in KELVOM with those in BENZEN).

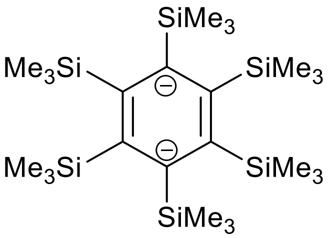


A comparison of planar hexakis(trimethylsilyl)benzene (left) and the non-planar dianion derived from it (right).

The number of π electrons is important in determining whether a cyclic alkene adopts a planar geometry; the results are summarized in Table 2.

Table 2. Summary of the π electron counts and ring geometries of selected structures.

Compound and CSD Refcode	**Diagram**	**Number of π electrons**	**Geometry**
Benzene *BENZEN*		6	Planar
Hexakis(dimethyl amino) benzene *GENFAG*		6	Planar
Hexakis(dimethyl amino) benzene dication from *GENFEK*		4	Non-planar
Hexakis(trimethylsilyl) benzene *KELVOM*		6	Planar

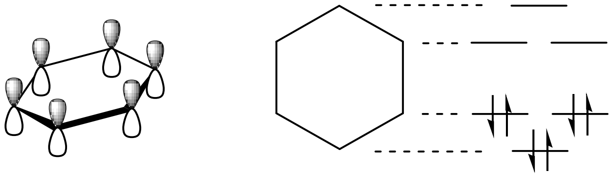
Hexakis(trimethylsilyl) benzene dianion, from *KINFUI*		8	Non-planar

2.5 Conclusions

Do you see a pattern forming? The number of π electrons in the system is crucial: when there are 4 or 8 π electrons, both cyclooctatetraene and benzene derivatives adopt non-planar geometries; when 6 or 10 π are electrons are present, as in benzene and cyclooctatetraenediide (CSD entry XINGIM), a planar geometry is preferred. It should be remembered that the planar ring in cyclooctatetraenediide is still considerably strained, therefore the other stabilizing influence (the 10 π electron count) outweighs the strain caused by planarity. This extra stabilizing effect is called aromaticity.

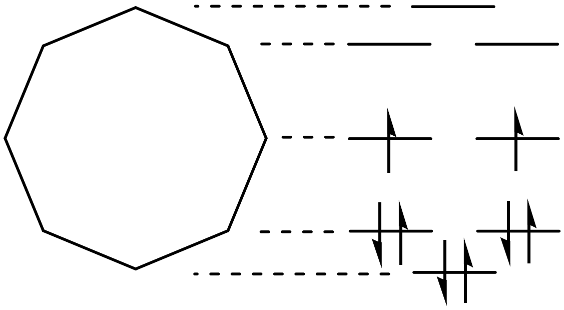
3. Molecular orbital description of aromaticity

The special stability of benzene, called aromaticity, comes from having six π electrons which occupy three bonding π molecular orbitals. The electrons are delocalized across the whole conjugated system and this closed-shell structure is the reason for the observed stability of benzene. The energy level diagram of a monocyclic aromatic molecule can be predicted by drawing the molecule with a vertex at the lowest point and drawing one energy level for each atom at a particular height, parallel to it (see below).



Contiguous ring of p orbitals from sp^2 carbon atoms (left) and an energy level diagram for the π molecular orbitals of benzene (right).

By comparison, cyclooctatetraene has eight π electrons distributed in five molecular orbitals, therefore three bonding molecular orbitals are doubly occupied whilst two degenerate non-bonding orbitals are singly occupied. Theoretical *planar* cyclooctatetraene must therefore lose or gain two electrons in order to have a stable closed-shell structure. We have already seen this in the case of cyclooctatetraenediide; this dianion is planar allowing delocalization over the ring. In contrast, neutral cyclooctatetraene adopts a non-planar tub-shaped conformation to allow a closed-shell structure with alternating double and single bonds. In the figure below, we can see that there will always be one singly-degenerate lowest energy molecular orbital, which can hold two electrons, followed by pairs of doubly degenerate molecular orbitals, which can hold four electrons in total each. A closed-shell arrangement will therefore be achieved when there are 4*n*+2 electrons (*n* is an integer). For benzene, this is realized with *n* = 1 and for cyclooctatetraenediide, *n* = 2.



An energy level diagram for planar cyclooctatetraene.

3.1 Hückels's rule

Our findings so far are summarized in *Hückels's rule*, which states that a cyclic, planar molecule is considered to be aromatic if it has $4n + 2$ π electrons.

3.1.1 Using Hückel's rule to predict aromaticity

Determine if each of the following compounds is aromatic by examining their structures. In each case, check whether the molecules:

- are fully conjugated
- are planar
- conform to Hückel's rule

Table 3. A selection of annulated molecules with the potential for aromaticity.

Name	**CSD refcode**
Tetra-*t*-butyl-cyclobutadiene	TBUCBD10
Naphthalene	NAPHTA12
Cyclohepta-1,3,5-triene	CHMOCO01
Cyclopentadienyl anion	NARGET
[14]annulene	FANNUL
[16]annulene	ANNULE01
[18]annulene	ANULEN
Pyridine	PYRDNA01

4 Summary

In this module, we have explored aromaticity by studying structural features of annulated molecules (ones containing the maximum number of double bonds), including benzene and cyclooctatetraene as well as neutral and ionic derivatives. In benzene, we discovered that all C–C bond lengths are equal to 1.39 Å, a value intermediate between that of a single and a double bond. We noted that benzene is unusually stable and reacts with electrophiles slowly to give substituted aromatic compounds. This unexpected stability was traced to the complete occupancy of all bonding π molecular orbitals and we have seen that this principle can be extended to other ring sizes, leading to the $4n + 2$ rule. Similarly, we observed that a contiguous ring of p orbitals is required and furthermore that the ring must be planar to achieve optimal overlap of the p orbitals. Consequently, aromaticity is observed in other species such as the cyclooctatetraene dianion and the cyclopentadienyl anion.

4.1 Next steps

If you would like to study the structures presented in this teaching sheet further, we suggest viewing them in Mercury, where you can customize the view of the molecules and make more advanced measurements. A free-for academic use version of Mercury is available for educational use. To learn more about Mercury, we recommend trying the online module "Visualization 101 – Visualizing Structural Chemistry Data with Mercury". You can find the structures used in this module in the Teaching Subset, which is pre-loaded into Mercury. See the links below for more information.

https://www.ccdc.cam.ac.uk/solutions/software/free-mercury/
https://www.ccdc.cam.ac.uk/community/training-and-learning/csdu-modules/visualization-101/
https://www.ccdc.cam.ac.uk/community/education-and-outreach/education/teaching-subset/

If you wish to explore the CSD further and search for structures of interest to you, you can find a number of training resources, including self-guided workshops, online courses and videos to you get started from the CCDC's Training and Learning Web pages.

https://www.ccdc.cam.ac.uk/community/training-and-learning/