# Nomenclature, Isomerism and Aromaticity Involved in Cyclic Compounds

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## Commentary

## DESCRIPTION

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The naming of cyclic structures, both as core structures and as substituents appended to alicyclic structures is governed by strict rules in IUPAC nomenclature. When a ring-containing compound has a ring of 12 or more atoms, it is referred to as a macrocycle. When more than one ring appears in a single molecule, the term polycyclic is used. Naphthalene is classified as a bicyclic compound rather than a polycyclic compound. The final gallery below contains several examples of macrocyclic and polycyclic structures. The atoms that make up the ring structure are known as annular atoms.

#### Isomerism

Closing atoms into rings may lock specific atoms with distinct substitution by functional groups, resulting in stereochemistry and chirality of the compound, including some manifestations unique to rings (e.g., configurational isomers).

**Conformational isomerism**: The three-dimensional shapes of specific cyclic structures-typically rings of 5-atoms and larger-can vary and interconvert depending on ring size, resulting in conformational isomerism. Indeed, the history of this important chemical concept can be traced back to cyclic compounds.

The chair conformation is the preferred configuration because it minimizes the steric strain, eclipsing strain, and angle strain that would otherwise be possible. Which of the possible chair conformations predominates in cyclohexanes with one or more substituents depends on the substituents and where they are located on the ring; generally, "bulky" substituents-those with large volumes or groups that are otherwise repulsive in their interactions-prefer an equatorial location. The interaction between the two methyl groups in cis-1,4-dimethylcyclohexane is an example of a molecule interaction that would cause steric strain, resulting in a shift in equilibrium from boat to chair.

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#### Aromaticity

Cyclic compounds can be aromatic or non-aromatic; benzene is an aromatic cyclic compound, whereas cyclohexane is not. Aromaticity is a term used in organic chemistry to describe a cyclic (ring-shaped), planar (flat) molecule that has unusual stability when compared to other geometric or connective arrangements of the same set of atoms. Because of their stability, aromatic molecules are extremely difficult to break apart and react with other substances. Aliphatic compounds are organic compounds that are not aromatic-they may be cyclic, but only aromatic rings have especial stability (low reactivity).

Because one of the most common aromatic systems of compounds in organic chemistry is based on derivatives of the prototypical aromatic compound benzene (an aromatic hydrocarbon found in petroleum and its distillates), the term "aromatic" is sometimes used informally to refer to benzene derivatives, and this is how it was first defined. Nonetheless, many aromatic compounds other than benzene exist. The most common aromatic rings in living organisms, for example, are the double-ringed bases in RNA and DNA. An aromatic functional group or other substituent is referred to as an aryl group.

The term "aromatic" was first used in an article by August Wilhelm Hofmann. Unlike pure saturated hydrocarbons, Hofmann used the term to refer to a class of benzene compounds that have odors (aromas). Today, there is no general relationship between aromaticity as a chemical property and the olfactory properties of such compounds, although in 18<sup>th</sup> century, before the structure of benzene or organic compounds was understood, chemists like Hofmann were beginning to understand that odiferous molecules from plants, such as terpenes, had chemical properties similar to unsaturated petroleum hydrocarbons like benzene.

Aromaticity describes a conjugated system made up of alternating single and double bonds in a ring in terms of the electronic nature of the molecule. The electrons in the molecule's ( $\pi$ ) system can be delocalized around the ring in this configuration, increasing the molecule's stability. The molecule cannot be represented by a single structure, but rather by a resonance hybrid of multiple structures, such as the two benzene resonance structures. These molecules cannot be found in either of these representations, with the longer single bonds in one and the shorter double bonds in the other. Rather, the molecule has bond lengths that fall somewhere between single and double bonds. August Kekulé developed this widely accepted model of aromatic rings, namely the idea that benzene was formed from a six-membered carbon ring with alternating single and double bonds (cyclohexatriene). The benzene model is made up of two resonance forms, which correspond to double and single bonds superimposing to form six one-and-a-half bonds. Without accounting for charge delocalization, benzene is a more stable molecule than would be expected.