

M.Sc. 1st sem., Department of Chemistry
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Topic: Homoaromaticity

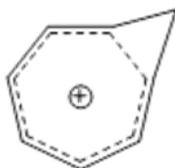
Topics of discussion:

- ☞ Homoaromaticity
- ☞ Criterion for Homoaromaticity
- ☞ Types with examples

Key points:

Homoaromaticity

Homoaromaticity in organic chemistry refers to a special case of aromaticity in which conjugation is interrupted by a single sp³ hybridized carbon atom. Although this sp³ center disrupts the continuous overlap of p-orbitals, traditionally thought to be a requirement for aromaticity, considerable thermodynamic stability and many of the spectroscopic, magnetic, and chemical properties associated with aromatic compounds are still observed for such compounds. This formal discontinuity is apparently bridged by p-orbital overlap, maintaining a contiguous cycle of π electrons that is responsible for this preserved chemical stability



The homoaromatic Homotropylium cation (C₈H₉⁺)

Criterion for Homoaromaticity

The criterion for aromaticity has evolved as new developments and insights continue to contribute to our understanding of these remarkably stable organic molecules.[5] The required characteristics of these molecules has thus remained the subject of some controversy. Classically, aromatic compounds were defined as planar molecules that possess a cyclically delocalized system of $(4n+2)\pi$ electrons, satisfying Huckel's rule. Most importantly, these conjugated ring systems are known to exhibit enormous thermochemical stability relative to predictions based on localized resonance structures. Succinctly, three important features seem to characterize aromatic compounds:

1. molecular structure (i.e., coplanarity: all contributing atoms in the same plane)
2. molecular energetics (i.e., increased thermodynamic stability)

3. spectroscopic and magnetic properties (i.e., magnetic field induced ring current)

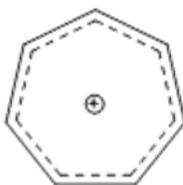
A number of exceptions to these conventional rules exist, however. Many molecules, including Möbius $4n\pi$ electron species, pericyclic transition states, molecules in which delocalized electrons circulate in the ring plane or through σ (rather than π) bonds, many transition-metal sandwich molecules, and others have been deemed aromatic though they somehow deviate from the conventional parameters for aromaticity.

Types

Cationic Homoaromatic: The most established and well-known homoaromatic species are cationic homoaromatic compounds. As stated earlier, the homotrophenylium cation is one of the most studied homoaromatic compounds. Many homoaromatic cationic compounds use as a basis a cyclopropenyl cation, a tropylium cation, or a cyclobutadiene dication as these compounds exhibit strong aromatic character.



Cyclopropenyl cation

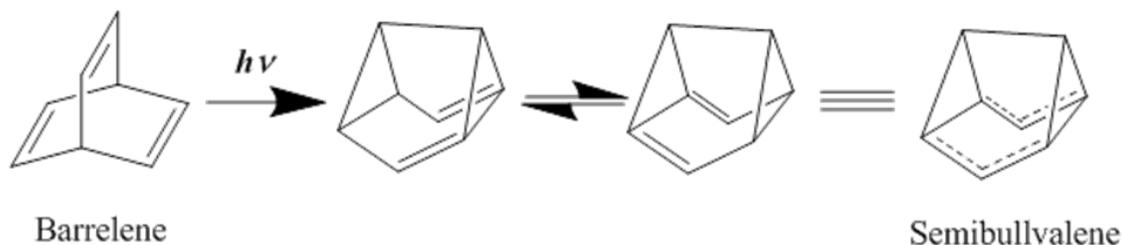


Tropylium cation

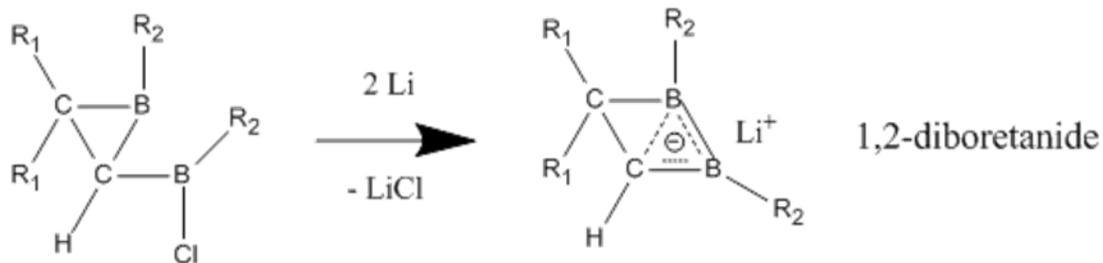


Cyclobutadiene dication

Neutral Homoaromatic: One class of neutral homoaromatic are called monohomoaromatic, one of which is cycloheptatriene, and numerous complex monohomoaromatic. One particular example is a 60-carbon fulleroid derivative that has a single methylene bridge. UV and NMR analysis have shown that the aromatic character of this modified fulleroid is not disrupted by the addition of a homoconjugate linkage, therefore this compound is definitively homoaromatic. Bishomoaromatic is considered that the best examples of neutral homoaromatics. It includes barrelene and semibullvalene. Semibullvalene has a structure that should lend itself well to homoaromaticity although there has been much debate whether semibullvalene derivatives can provide a true delocalized, ground state neutral homoaromatic compound or not. In an effort to further stabilize the delocalized transition structure by substituting semibullvalene with electron donating and accepting groups, it has been found that the activation barrier to this rearrangement can be lowered, but not eliminated. However, with the introduction of ring strain into the molecule, aimed at destabilizing the localized ground state structures through the strategic addition of cyclic annulations, a delocalized homoaromatic ground-state structure can indeed be achieved.



Anionic Homoaromatic: Anionic homoaromatics are widely accepted to exhibit "true" homoaromaticity. These anionic compounds are often prepared from their neutral parent compounds through lithium metal reduction. 1,2-diboretanide derivatives show strong homoaromatic character through their three-atom (boron, boron, carbon), two-electron bond, which contains shorter C-B bonds than in the neutral classical analogue.[25] These 1,2-diboretanides can be expanded to larger ring sizes with different substituents and all contain some degree of homoaromaticity.



Anionic homoaromaticity can also be seen in dianionic bis-diazene compounds, which contain a four-atom (four nitrogens), six-electron center. Experiment results have shown the shortening of the transannular nitrogen-nitrogen distance, therefore demonstrating that dianionic bis-diazene is a type of anionic bishomoaromatic compound. Peculiar feature of these systems is that the cyclic electron delocalization is taking place in the σ -plane defined by the four nitrogens.

Exercise

1. Write a short note on homoaromaticity?
2. Differentiate between cationic and anionic homoaromaticity?