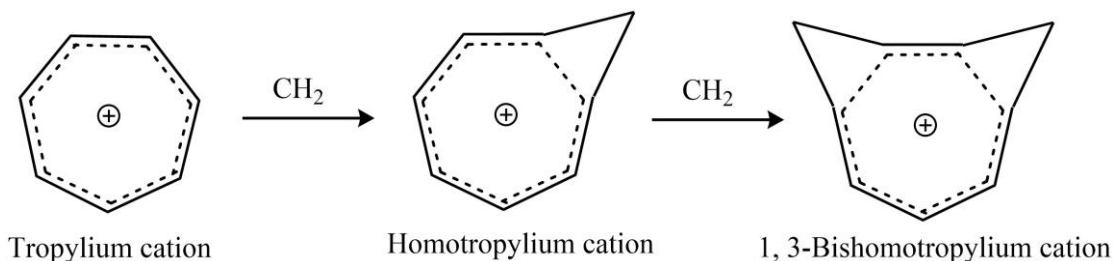


❖ Homoaromaticity

The homoaromaticity in organic chemistry may simply be defined as a special case of aromatic behavior where the normal conjugation is interrupted by a single sp^3 -hybridized carbon atom.

Though this sp^3 center disturbs the continuity of overlap between p -orbitals, conventionally thought to be a primary need for aromaticity, substantial thermodynamic stability, and many of the magnetic, spectroscopic, and chemical properties related to aromatic compounds are still observed for such molecules. This official discontinuity is bypassed by p -orbital overlap, preserving a contiguous cycle of π -electron density that is accountable for its extra stability. The idea of homoaromaticity was proposed by S. Weinstein in 1959, encouraged by his analysis of the “tris-homocyclopropenyl” ion. After Weinstein's publication, abundant research has been dedicated to the understanding of these molecules, which embody an additional class of aromatic compounds included broadening the definition of aromatic behavior. Up to the present time, homoaromatic molecules are quite well-known to exist as anionic and cationic species, and some reports support the presence of neutral homoaromatic compounds, nonetheless, these are not so common. It seems that the 'homotropylium' cation ($C_8H_9^+$) is the most studied case of a homoaromatic system.

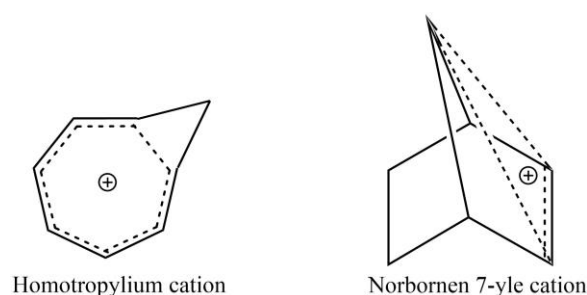
The label "homoaromaticity" originates from the similar structural profile of homoaromatic compounds with analogous homo-conjugated alkenes observed previously. The IUPAC Gold Book needs that bis-, tris-, etc. type prefixes to be used to define homoaromatic compounds where two, three, etc. sp^3 centers separately interrupt the phenomenon of conjugation of the aromatic molecules.



The homoaromatic compounds can simply be divide into three different categories, depending on the nature of the charge on them. A general discussion on all three types is given below.

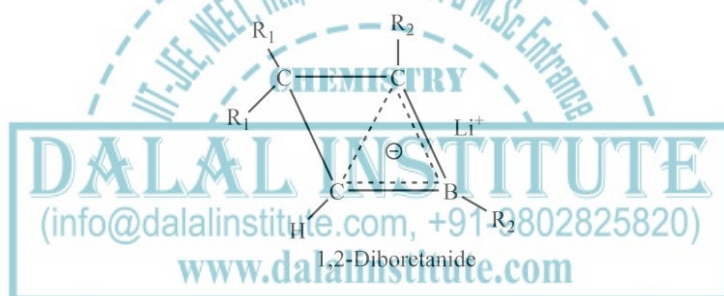
➤ Cationic Homoaromatic Compounds

The most well-known and proven homoaromatic species are cationic entities. As we have earlier mentioned, the homotropylium cation is the most studied homoaromatic compound. Numerous homoaromatic cationic species act as a basis for a tropylium cation, cyclopropenyl cation, or a cyclobutadiene dication because these species have very strong aromaticity. Additionally, another well-known cationic homoaromatic compound is the norbornen-7-yl cation, which is quite strongly homoaromatic, proven both experimentally and theoretically.



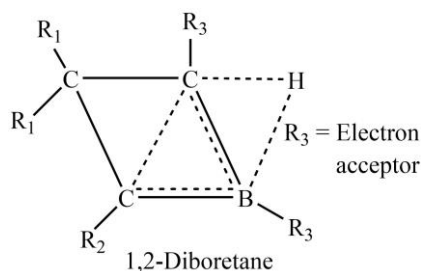
➤ Anionic Homoaromatic Compounds

The homoaromatic anions are widely accepted to have "true" homoaromaticity. These anionic species are frequently obtained from their neutral parent molecules via Li-based reduction. 1,2-diboretanide derivatives display strong homoaromatic behavior via their 3-atom (B, B, and C), 2-electron bond, which contains shorter carbon-boron bonds than in the neutral analog. These 1,2-diboretanides can be expanded to bigger ring sizes with different groups and all have some degree of homoaromaticity.



➤ Neutral Homoaromatic Compounds

Numerous classes of neutral homoaromatic compounds have been observed though there is a debate whether they are truly homoaromatic or not. One class of the type of neutral homoaromatics is called monohomoaromatics, including cycloheptatriene. One more example is a 60-carbon fulleroid derivative that has only one methylene bridge. The NMR and UV-visible study has proven that the aromatic character of this modified fulleroid is not disturbed by the addition of a homoconjugate bond, and therefore, this molecule is homoaromatic for sure.



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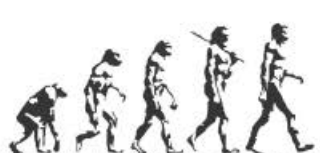
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

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