THE CHEMISTRY OF ACENES AND HELICENES: WHAT CAN AROMATICITY TEACH US?

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INTRODUCTION

Acenes and helicenes are molecules comprised of fused benzene rings that differ only in their connectivity. However, this seemingly trivial difference imparts these two classes of molecules with very distinctive properties. Acenes are comprised of linearly fused benzene rings, such as naphthalene ([2]acene) and anthracene ([3]acene). Helicenes are ortho-fused aromatic rings that adopt a helical conformation to avoid the overlapping of the terminal rings.

Interestingly, helicenes are more stable and persistent than acenes; the longest acene synthesized to date is heptacene ([7]acene),[1] but the longest helicene synthesized to date is [14]helicene.[2] Also, while acenes dimerize in solution and oxidize in the presence of dioxygen, helicenes do not undergo either reaction.

The difference in thermodynamic stability and reactivity is believed to be due to their differences in aromaticity even though they are both fused benzene rings. Can the concept of aromaticity really be used to explain the difference between these two systems that have the same number of electrons?

AROMATICITY

The concept of aromaticity was first used to describe the additional 36 kcal/mol stability of benzene compared to the theoretical "1,3,5-cyclohexatriene" due to the delocalization of the π-electrons.[3] Many attempts were then made to expand this concept to larger cyclic conjugated hydrocarbons, heterocyclic aromatics, and even three-dimensional aromatics such as fullerenes. However, for such a fundamental concept, aromaticity is difficult to define precisely.

Hückel [4*n*+2] Rule

The Hückel [4*n*+2] rule is based on Hückel Molecular Orbital theory[4] which predicts three occupied orbitals where the top two are degenerate for benzene. The lowest orbital is occupied by two π-elections while the next highest level contains two pairs of electrons. The four electrons in the higher orbital would represent the "4n" in the equation and the two electrons in the lowest orbital are the "+2" electrons. This theory measured extra stabilization energy due to the delocalization of the electrons. Hückel expanded the benzene system and predicted that all planar, cyclic molecules with [4*n*+2] π-elections would observe similar stabilization effects and therefore be aromatic.[5]

Although the Hückel [4*n*+2] rule was fundamental for understanding the aromaticity of benzene, it is valid only for monocyclic conjugated systems. Many attempts have been made to extend the rule to polycyclic aromatic systems.[6-11]

Clar's Aromatic Sextet

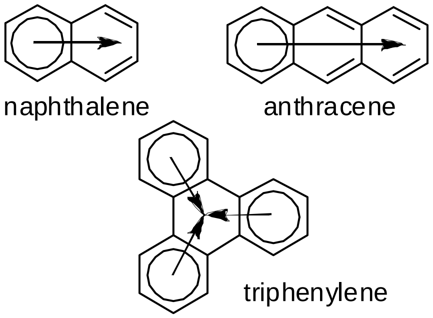


Figure 1. Clar's aromatic sextet.

Clar's aromatic sextet rule,[7] modified from Robinson's aromatic sextet,[6] is the most successful in predicting the reactivity of polycyclic aromatic systems. Robinson introduced a circle inside the hexagon to symbolize the mobility of the 6 π-electrons in benzene. Clar proposed that there can only be one Robinson-type aromatic sextet in naphthalene and an arrow is used to show the migration of the sextet through the conjugated system (Figure 1). On the basis of this theory, the stability of fully benzenoid hydrocarbons or polycyclic aromatic hydrocarbons that only contain sextets can also be explained (Figure 2).

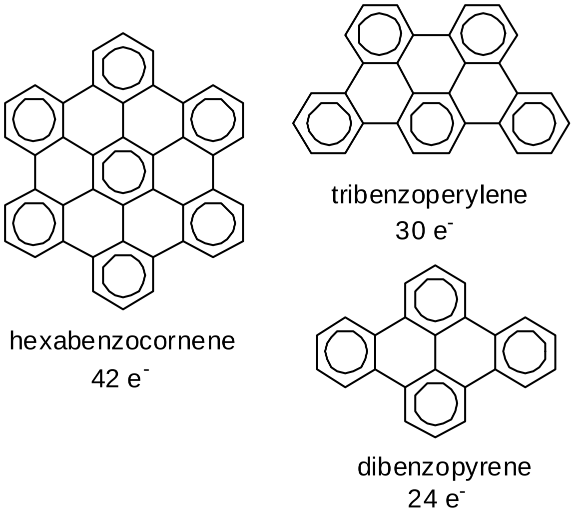


Figure 2. Fully benzenoid hydrocarbons.

Computational Methods

Extensive computational studies have been directed to understand the aromaticity of fused benzene ring systems. The common aromaticity indicators used are the harmonic oscillator model of aromaticity index (HOMA), the nucleus independent chemical shift (NICS), and the para-delocalization index (PDI), which cover the geometric, magnetic, and electronic consequences of aromaticity, respectively.

The HOMA index was defined by Kruszewski and Krygowski[8] (equation 1)

$$HOMA = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}(R_{opt} - R_i)^2 \qquad (1)$$

where n is the number of bonds considered, R_{opt} is defined as the ideal bond length of an aromatic molecule. Here, R_{opt} is 1.388 Å for C-C bonds. R_i is the actual bond length, and α is an empirical constant fixed to give HOMA = 0 for antiaromatic systems and HOMA = 1 for aromatic systems. In this case, α = 257.7 for C-C bonds. Thus, more aromatic compounds have values closer to 1.

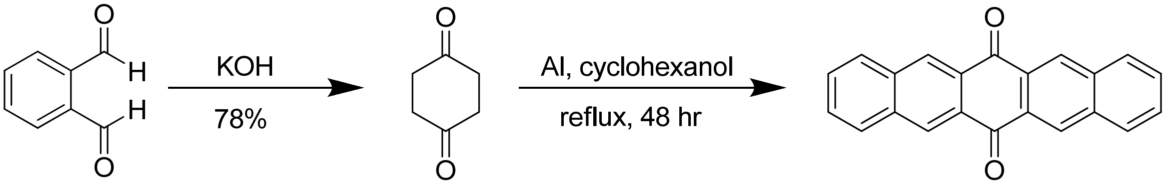
NICS is one of the most widely employed indicators of aromaticity. It is defined by Schleyer[9] as the negative value of the absolute electron shielding computed at the ring center or at some other interest point of the system. According to this definition, the more negative NICS values correspond to the greater aromaticity of the rings.

PDI is derived from the delocalization index (DI) which gives a quantitative idea of the number of electrons delocalized or shared between atoms.[10] Tthe para-related carbon atoms are more relevant than the meta-related carbon atoms when discussing aromaticity.[11] Therefore, PDI is defined as the average of all DI of para-related carbon atoms in a given six-membered ring system. Hence, the larger PDI values correspond to greater aromaticity of the rings.

ACENES

With the increasing number of fused benzene rings, the reactivity of acenes increases. The small acenes, naphthalene and anthracene, are readily available because they can be isolated from petroleum sources. Pentacene was first synthesized by Clar in 1929 who also synthesized tetracene and hexacene in 1942.[12] Clar's synthesis of pentacene involved a vigorous Friedel-Crafts reaction of m-xylophenone to yield 4,6-dibenzoyl-1,3-dimethylbenzene which was then heated with copper to give the dihydropentacene. Dehydrogenation was accomplished by boiling the dihydro-derivative in nitrobenzene with the phananthraquinone. A milder synthetic route to pentacene was developed in 1960 by the reduction of its bis-quinone derivative (Scheme 1),[13] which is now the most common method used to synthesize and functionalize pentacene.[14] Although syntheses of heptacene were reported by several groups in the 1950s,[15] because of the lack of characterization and reproducibility, the validity of these preparations was questionable. In 2006, Neckers unequivocally generated and characterized heptacene in a polymer matrix.[1]

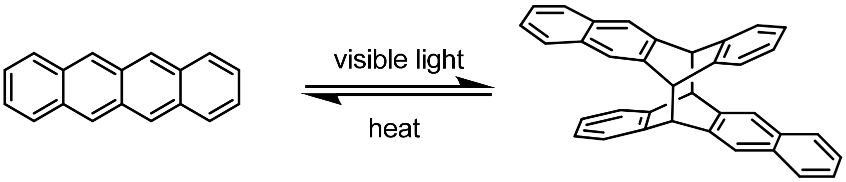
Scheme 1. Synthesis of pentacene from its bis-quinone derivative.



Properties of Acenes

As the number of fused benzene rings increases, the HOMO-LUMO gap decreases substantially.[16] This property has been exploited in organic field-effect transistors (OFETs) and organic solar cells. High quality OFET devices made from thin films of pentacene ([5]acene) typically show hole mobilities (positive charge) greater than 1.5 $cm^2/(V\cdot s)$,[17] which is higher than the 1 $cm^2/(V\cdot s)$ mobility of the prototypical semiconductor, hydrogenated amorphous silicon.[18] Rubrene, a tetraphenyl subsituted tetracene with hole mobilities up to 8 $cm^2/(V\cdot s)$, possesses the highest mobility measured for an organic semiconductor.[19] Pentacenes can also be used as the positive charge carrying material in organic solar cells. Together with C_{60} as the negative charge carrying material, the yielding power conversion for pentacene is as high as 2.7%,[20] which while high for organic solar cells, is still far from the efficiencies of silicon-based solar cells with power conversions typically around 22%.[21] Polyacenes are believed to have a zero band gap similar to graphene and behave as one-dimensional organic conductors.[22] Consequently, the reactivity of acenes increases as the number of six-membered rings increases. In pentacene, intermolecular [4+4] cycloaddition reactions occur so quickly that monomeric pentacene has a half-life of a few minutes in solution.[23] Tetracene, the first reported photochromic molecule, is reactive in solution where it dimerizes upon irradiation to a colorless "butterfly dimer."[38] The retro cycloaddition can be induced by heating (Scheme 2). Pentacene can also be photodimerized; however, the reaction is irreversible. Furthermore, the formation of endoperoxides upon exposure to dioxygen is also facile with pentacene and longer acenes. The sensitivity of these molecules to light and air is a major obstacle to the development of these materials.

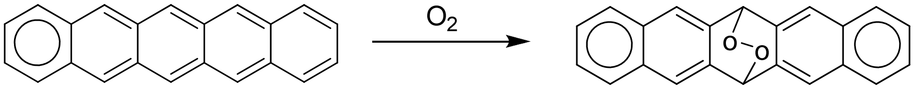
Scheme 2. The photochormism of tetracene.



Aromaticity of Acenes

According to Clar's sextet rule, naphthalene can only have one sextet, and the other ring has two π-bonds. Similarly with anthracene, the π-sextet can only be drawn in one of the six-membered rings, which means the "aromaticity" is shared among the three rings (Figure 2). Therefore, as the number of rings increases, the level of aromaticity gradually decreases, explaining the increase in reactivity. It has also been shown that the center ring is the most reactive ring of an acene.[39] Clar's sextet rule can explain this from a thermodynamic perspective. Breaking the conjugation of the middle ring cuts the acene into two smaller acenes, each with more sextet character than the parent acene. For example, when pentacene reacts with dioxygen to give an endoperoxide, it is converted from a pentacene to two more stable naphthalenes on either side (Scheme 3).

Scheme 3. Formation of an endoperoxide.



The aromaticity calculations performed on acenes from benzene to nonacene ([9]acene) indicate that the terminal rings are "less" aromatic than the inner rings.[24] However, whereas the HOMA and PDI values show that the overall aromaticity decreases as the number of rings increases, as expected, NICS demonstrates the opposite trend. The PDI also shows that the largest difference between the most and least aromatic ring decreases with the increasing number of carbons, suggesting that the reduction of aromaticity in the central ring is more important than in the peripheral ring. Conversely, the NICS values show the difference between the most and least aromatic ring increasing with the number of carbons. These two findings support the claim that NICS often overestimates aromaticity.[25]

The calculations described above assume that acenes have a closed-shell singlet state.[24] Bendikov et al. proposed that the ground states of larger acenes are open-shell singlets, suggesting that they have partially filled orbitals.[26] In this case, the aromaticity calculations give drastically different results.[27] The PDI values show the outer ring to be the most aromatic, which is opposite to what is observed in the closed-shell singlet state. In addition, as the aromaticity of the outer ring stays somewhat constant with the increasing number of rings, the aromaticity of the most inner ring decreases drastically. Although the HOMA values show a slight decrease in aromaticity from the outer ring to the inner ring, the difference is not significant, but the NICS values agree strongly with the PDI values. According to the weight average values of NICS, there is a reduction of aromaticity when going from the closed-shell to the diradical singlet state. However, the PDI and HOMA values indicate no change in overall aromaticity.

It is hard to determine whether the ground states of acenes are open or closed-shell since acenes larger than pentacene can not be isolated for experimental study. However, recent studies have shown that the ground states of functionalized hexacenes and heptacenes are closed-shell.[28]

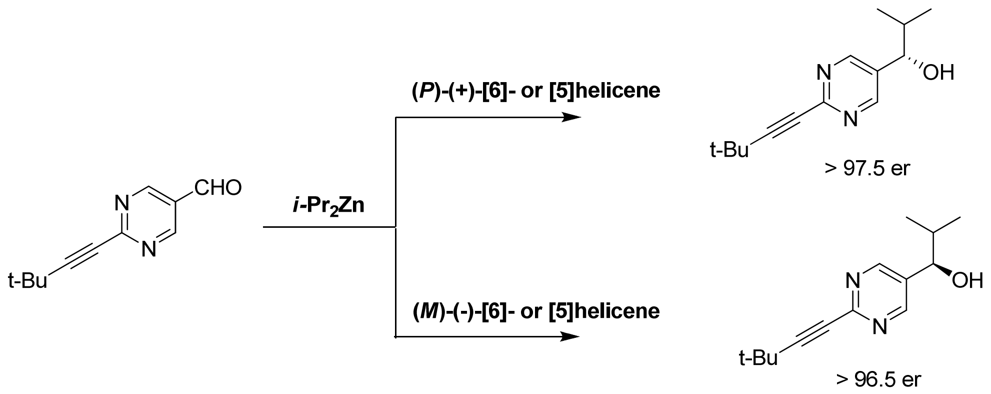
HELICENES

The first synthesis of phenanthro[3,4-c]phenanthrene was reported by Newman[29] in 1956, who proposed the name hexahelicene or [6]helicene referring to the non-planar model. However, the ten-step synthetic route needed to be improved because the overall yield was less than 2%. The key breakthrough for helicene synthesis occurred in 1964 when Mallory[30] was able to cyclize stilbenes photochemically. This chemistry was then used by Martin[31] to successfully prepare hexa-, hepta-, octa-, and nonahelicenes in moderate yields. Since then, many different methods have been developed to improve stereoselectivity[32] or functionality.[33]

Properties of Helicenes

Helicenes have larger HUMO-LUMO gaps compared to acenes[34] and have fewer applications in organic electronic devices. Since helicenes are inherently chiral and their enantiomers can be resolved, they are promising as chiral catalysts[35] and ligands[36] in asymmetric syntheses because of their high stability and resistance to isomerization. Sato et al. have reported using [6]- and [5]helicenes as chiral inducers in the highly enantioselective synthesis of a pyrimidinyl alkanol by the enantioselective addition of diisopropylzinc to 2-(2-tert-butylethynyl)pyrimidine-5-carbaldehyde (Scheme 4).[37]

Scheme 4. The use of helicenes as chiral inducers for highly enantioselective synthesis.



Aromaticity of Helicenes

According to Clar, the most stable resonance form of phenanthrene is represented by π-sextets on the two outer rings and a π-bond on the inner ring. The pattern continues with an increasing number of rings, starting with the terminal rings alternating between a π-sextet ring and a π-bond ring, predicting an alternation of aromaticity proceeding from the terminal to the inner rings (Figure 4). In the Clar depiction of phenanthrene, the two side rings are accorded benzene-like stability, whereas the center ring has a fixed double bond. The localization of this double bond predicts a characteristic olefinic double bond. For example, phenanthrene undergoes dibromination (addition) rather than aromatic substitution (Scheme 5).

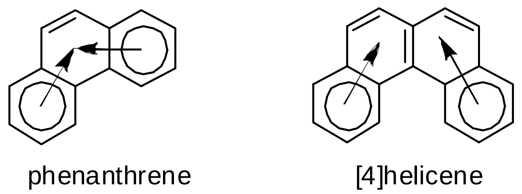
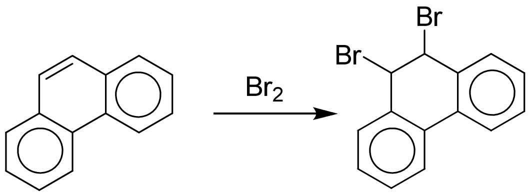


Figure 4. Examples of Clar's sextet rule with helicenes.

Scheme 5. Bromonation of phenanthrene.



The aromaticity calculations for both PDI and HOMA indices display an alternating aromaticity with the terminal rings as the most aromatic. In terms of overall aromaticity, PDI and HOMA values indicate that the aromaticity decreases as the number of rings increases. On the other hand, NICS values show the same trend with local and overall aromaticity until [8] and [9]helicene. The local aromaticity no longer alternates but instead decreases continuously from outer to inner rings, and the overall aromaticity increases. Moreover, while the PDI and HOMA values for the terminal rings are relatively unchanged, the NICS values disagree. Based on the NICS calculations, the aromaticity of the terminal rings increase starting from [5]helicene. This increase is also observed for ring B from [6]helicene, ring C from [7]helicene, and ring D from [8]helicene (Chart 1). This behavior is attributed to the magnetic coupling of the overlapping rings starting from [5]helicene.

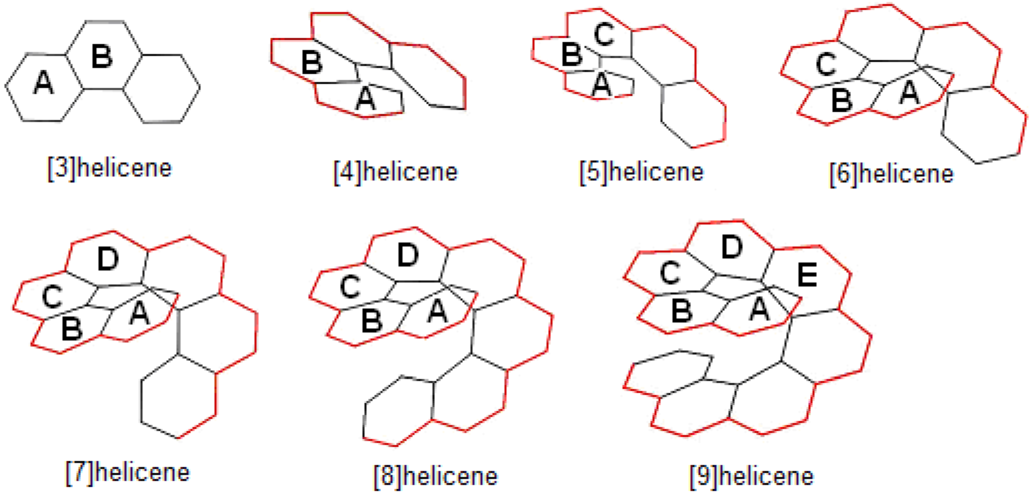


Chart 1. Labels used in calculations for helicenes.

CONCLUSION

Although all computational and experimental studies conclude that the aromaticity of acenes decreases as the oligomer length increases, there are still discrepancies with the discussion of local aromaticity. The three indices discribed for a closed-shell ground state show that the inner rings are more aromatic than the outer ones, even though the former is more reactive. The PDI and HOMA show that the aromaticity per ring decreases with the size of the acene, whereas NICS indicates the opposite trend. This different trend has been attributed to the overestimation by NICS of the local aromaticity of the central rings. If the assumption of a closed-shell ground state for acenes were changed to an open-shell diradical singlet state, the PDI and NICS values show an opposite trend of local aromaticity. In this case, the outer rings would be the most aromatic.

As for helicenes, Clar's sextet theory suggested an alternation of aromaticity from outer to inner ring; this theory can be confirmed using the aromaticity calculations. Helicenes larger than [6]helicene show an increase of local aromaticity in the terminal rings which has been explained by the magnetic couplings with the overlapping six-membered rings.

These data indicate that the difference in aromaticity depends on the definition; therefore conclusions should be drawn with caution.

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