Objectives

After completing this section, you should be able to draw the resonance contributors for polycyclic aromatic compounds, such as naphthalene, anthracene, etc.

Key Terms

Make certain that you can define, and use in context, the key term below.

- polycyclic aromatic compounds

Study Notes

As their name indicates, polycyclic aromatic hydrocarbons are aromatic hydrocarbons which contain more than one benzenoid (i.e., benzene-like) ring. This section deals only with those compounds in which the benzenoid rings are fused together; in other words, compounds in which at least one carbon-carbon bond is common to two aromatic rings. Another type of polycyclic aromatic hydrocarbon contains two or more benzenoid rings joined by a carbon-carbon single bond. The simplest compound of this type is biphenyl, the compound from which PCBs (polychlorinated biphenyls) are derived.

biphenyl and 2,4,2',5'-tetrachlorobiphenyl

*Figure 15.3: Structures of biphenyl and a typical PCB*

Aromatic Compound with a single ring

**Unstable Planar Configurations**

- transannular crowding in trans-isomer
- angle strain (240° total) in cis-isomer

Aromatic Compounds with more than one ring

Benzene rings may be joined together (fused) to give larger polycyclic aromatic compounds. A few examples are drawn below, together with the approved numbering scheme for substituted derivatives. The peripheral carbon atoms (numbered in all but the last three examples) are all bonded to hydrogen atoms. Unlike benzene, all the C-C bond
lengths in these fused ring aromatics are not the same, and there is some localization of the pi-electrons.

The six benzene rings in coronene are fused in a planar ring; whereas the six rings in hexahelicene are not joined in a larger ring, but assume a helical turn, due to the crowding together of the terminal ring atoms. This helical configuration renders the hexahelicene molecule chiral, and it has been resolved into stable enantiomers.

Figure 2: Examples of Polycyclic Aromatic Hydrocarbons (PAHs).

Exercises

Questions

Q15.6.1

This is an isomer of naphthalene. Is it aromatic? Draw a resonance structure for it.

Q15.6.2

The following molecule is adenine. It has a purine core. Of the nitrogen in the core, how many electrons are donated into the pi system?
Solutions

S15.6.1

Yes, it is aromatic. 4n+2 pi-electrons.

\[
\begin{align*}
\text{[Diagram of cyclic conjugated system with nitrogen atoms]} \\
\text{[Diagram of cyclic conjugated system with nitrogen atoms]} \\
\end{align*}
\]

S15.6.2

There is only one nitrogen of the core that contributes to the pi-system (in red). With this one lone pair the core is aromatic with 10 electrons in the pi-system.

\[
\begin{align*}
\text{[Diagram showing nitrogen atom and pi-electron system]} \\
\text{[Diagram showing nitrogen atom and pi-electron system]} \\
\end{align*}
\]

Contributors and Attributions

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If we extend the structure of corannulene by adding similar cycles of five benzene rings, the curvature of the resulting molecule should increase, and eventually close into a sphere of carbon atoms. The archetypical compound of this kind (C_{60}) has been named buckminsterfullerene because of its resemblance to the geodesic structures created by Buckminster Fuller. It is a member of a family of similar carbon structures that are called fullerenes. These materials represent a third class of carbon allotropes. Alternating views of the C_{60} fullerene structure are shown on the right, together with a soccer ball-like representation of the 12 five and 20 six-membered rings composing its surface. Precise measurement by Atomic Force Microscopy (AFM) has shown that the C-C bond lengths of the six-membered rings are not all equal, and depend on whether the ring is fused to a five or six-membered neighbor. By clicking on this graphic, a model of C_{60} will be displayed.

Although C_{60} is composed of fused benzene rings its chemical reactivity resembles that of the cycloalkenes more than benzene. Indeed, exposure to light and oxygen slowly degrade fullerenes to cage opened products. Most of the reactions thus far reported for C_{60} involve addition to, rather than substitution of, the core structure. These reactions include hydrogenation, bromination and hydroxylation. Strain introduced by the curvature of the surface may be responsible for the enhanced reactivity of C_{60}.

. Larger fullerenes, such as C_{70}, C_{76}, C_{82} & C_{84} have ellipsoidal or distorted spherical structures, and fullerene-like assemblies up to C_{240} have been detected. A fascinating aspect of these structures is that the space within the carbon cage may hold atoms, ions or small molecules. Such species are called endohedral fullerenes. The cavity of C_{60} is relatively small, but encapsulated helium, lithium and atomic nitrogen compounds have been observed. Larger fullerenes are found to encapsulate lanthanide metal atoms.

Interest in the fullerenes has led to the discovery of a related group of carbon structures referred to as nanotubes. As shown in the following illustration, nanotubes may be viewed as rolled up segments of graphite. The chief structural components are six-membered rings, but changes in tube diameter, branching into side tubes and the capping of tube ends is accomplished by fusion with five and seven-membered rings. Many interesting applications of these unusual structures have been proposed.