Polycyclic aromatic hydrocarbon

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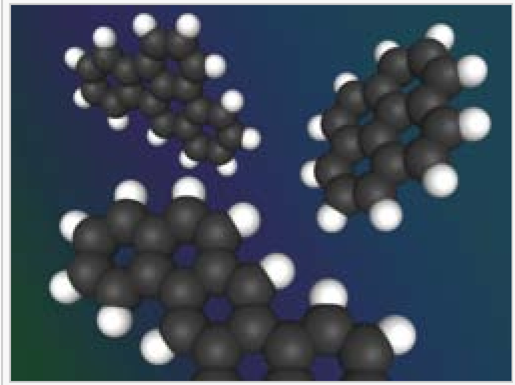
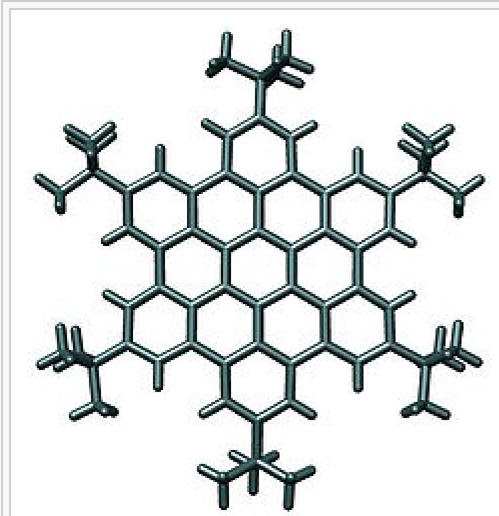
Polycyclic aromatic hydrocarbons (**PAHs**), also known as **poly-aromatic hydrocarbons** or **polynuclear aromatic hydrocarbons** are chemical compounds that consist of fused aromatic rings and do not contain heteroatoms or carry substituents.[1] PAHs occur in oil, coal, and tar deposits, and are produced as byproducts of fuel burning (whether fossil fuel or biomass). As a pollutant, they are of concern because some compounds have been identified as carcinogenic, mutagenic, and teratogenic. PAHs are also found in foods. Studies have shown that most food intake of PAHs comes from cereals, oils and fats. Smaller intakes come from vegetables and cooked meats.[2][3][4]



An illustration of typical polycyclic aromatic hydrocarbons. Clockwise from top left: benz[e]acephenanthrylene, pyrene and dibenz[a,h]anthracene

They are also found in the interstellar medium, in comets, and in meteorites and are a candidate molecule to act as a basis for the earliest forms of life. In graphene the PAH motif is extended to large 2D sheets.



Crystal structure of a hexa-t-butyl derivatized hexa-peri-hexabenzo[bc,ef,hi,kl,no,qr]coronene, reported by Müllen and coworkers in Chem. Eur. J., 2000, 1834-1839. The t-butyl groups make this compound soluble in common solvents such as hexane, in which the unsubstituted PAH is insoluble.

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Occurrence and pollution [edit]

Polycyclic aromatic hydrocarbons are lipophilic, meaning they mix more easily with oil than water. The larger compounds are less water-soluble and less volatile (i.e., less prone to evaporate). Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or air. However, they are also a component of concern in particulate matter suspended in air.

Natural crude oil and coal deposits contain significant amounts of PAHs, arising from chemical conversion of natural product molecules, such as steroids, to aromatic hydrocarbons. They are also found in processed fossil fuels, tar and various edible oils.[5]

PAHs are one of the most widespread organic pollutants. In addition to their presence in fossil fuels they are also formed by incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, and incense.[6] Different types of combustion yield different distributions of PAHs in both relative amounts of individual PAHs and in which isomers are produced. Thus, coal burning produces a different mixture than motor-fuel combustion or a forest fire, making the compounds potentially useful as indicators of the burning history. Hydrocarbon emissions from fossil fuel-burning engines are regulated in developed countries.[7]

Human health [edit]

PAHs toxicity is very structurally dependent, with isomers (PAHs with the same formula and number of rings) varying from being nontoxic to being extremely toxic. Thus, highly carcinogenic PAHs may be small or large. One PAH compound, benzo[*a*]pyrene, is notable for being the first chemical carcinogen to be discovered (and is one of many carcinogens found in cigarette smoke). The EPA has classified seven PAH compounds as probable human carcinogens: benzo[*a*]anthracene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene.

PAHs known for their carcinogenic, mutagenic and teratogenic properties are benzo[*a*]anthracene and chrysene, benzo[*b*]fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, benzo[*ghi*]perylene, coronene, dibenz(a,h)anthracene ($C_{20}H_{14}$), indeno(1,2,3-cd)pyrene ($C_{22}H_{12}$) and ovalene.[8]

High prenatal exposure to PAH is associated with lower IQ.[9]

Chemistry [edit]

The simplest PAHs, as defined by the International Union on Pure and Applied Chemistry (IUPAC) (G.P Moss, IUPAC nomenclature for fused-ring systems), are phenanthrene and anthracene, which both contain three fused aromatic rings. Smaller molecules, such as benzene, are not PAHs.

PAHs may contain four-, five-, six- or seven-member rings, but those with five or six are most common. PAHs composed only of six-membered rings are called alternant PAHs. Certain alternant PAHs are called "benzenoid" PAHs. The name comes from benzene, an aromatic hydrocarbon with a single, six-membered ring. These can be benzene rings interconnected with each other by single carbon-carbon bonds and with no rings remaining that do not contain a complete benzene ring.

The set of alternant PAHs is closely related to a set of mathematical entities called polyhexes, which are planar figures composed by conjoining regular hexagons of identical size.

PAHs containing up to six fused aromatic rings are often known as "small" PAHs, and those containing more than six aromatic rings are called "large" PAHs. Due to the availability of samples of the various small PAHs, the bulk of research on PAHs has been of those of up to six rings. The biological activity and occurrence of the large PAHs does appear to be a continuation of the small PAHs. They are found as combustion products, but at lower levels than the small PAHs due to the kinetic limitation of their production through addition of successive rings. In addition, with many more isomers possible for larger PAHs, the occurrence of specific structures is much smaller.

PAHs possess very characteristic UV absorbance spectra. These often possess many absorbance bands and are unique for each ring structure. Thus, for a set of isomers, each isomer has a different UV absorbance spectrum than the others. This is particularly useful in the identification of PAHs. Most PAHs are also fluorescent, emitting characteristic wavelengths of light when they are excited (when the molecules absorb light). The extended pi-electron electronic structures of PAHs lead to these spectra, as well as to certain large PAHs also exhibiting semi-conducting and other behaviors.

Naphthalene ($C_{10}H_8$ constituent of mothballs), consisting of two coplanar six-membered rings sharing an edge, is another aromatic hydrocarbon. By formal convention, it is not a true PAH, though is referred to as a bicyclic aromatic hydrocarbon.

Aqueous solubility decreases approximately one order of magnitude for each additional ring.

PAH compounds

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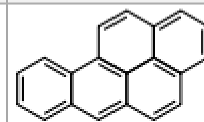
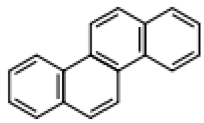
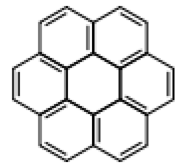
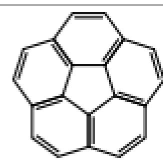
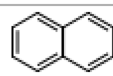
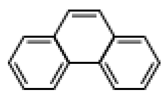
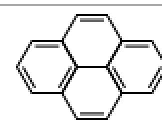
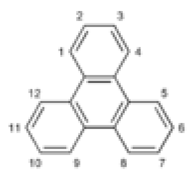
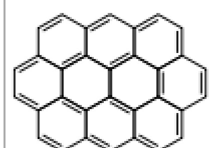
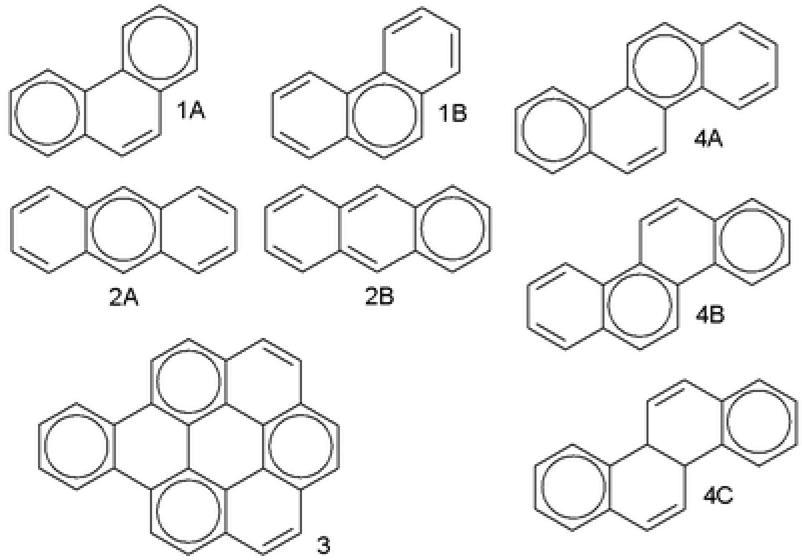
Chemical compound		Chemical compound	
Anthracene		Benzo[*a*]pyrene	
Chrysene		Coronene	
Corannulene		Tetracene	
Naphthalene		Pentacene	
Phenanthrene		Pyrene	
Triphenylene		Ovalene	

The U.S. EPA has designated 32 PAH compounds as priority pollutants. The original 16 are listed. They are naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene, and indeno[*1,2,3-cd*]pyrene. This list of the 16 EPA priority PAHs is often targeted for measurement in environmental samples.

Aromaticity

[edit]

Although PAHs clearly are aromatic compounds, the degree of aromaticity can be different for each ring segment. According to Clar's rule (formulated by Erich Clar in 1964) for PAHs the resonance structure with the most disjoint aromatic π-sextets—i.e. benzene-like moieties—is the most important for the characterization of the properties.[10]



For example, in phenanthrene the Clar structure 1A has two sextets at the extremities, while resonance structure 1B has just one central sextet. Therefore in this molecule the outer rings are firmly aromatic while its central ring is less aromatic and therefore more reactive. In contrast, in anthracene 2 the number of sextets is just one and aromaticity spreads out. This difference in number of sextets is reflected the UV absorbance spectra of these two isomers. Phenanthrene has a highest wavelength absorbance around 290 nm, while anthracene has highest wavelength bands around 380 nm. Three Clar structures with two sextets are present in chrysene (4) and by superposition the aromaticity in the outer ring is larger than in the inner rings.

Origins of life [edit]

Main article: PAH world hypothesis

In January 2004 (at the 203rd Meeting of the American Astronomical Society), it was reported[11] that a team led by A. Witt of the University of Toledo, Ohio studied ultraviolet light emitted by the Red Rectangle nebula and found the spectral signatures of anthracene and pyrene (no other such complex molecules had ever before been found in space). This discovery was considered as a controversial[12] confirmation of a hypothesis that as nebulae of the same type as the Red Rectangle approach the ends of their lives, convection currents cause carbon and hydrogen in the nebulae's core to get caught in stellar winds, and radiate outward. As they cool, the atoms supposedly bond to each other in various ways and eventually form particles of a million or more atoms. Witt and his team inferred (as cited in Battersby, 2004) that since they discovered PAHs—which may have been vital in the formation of early life on Earth—in a nebula, by necessity they must originate in nebulae.[13]

Detection [edit]

Detection of PAH is allowed by gaschromatographic methods or by using rapid test PAH indicator strips.

References [edit]

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2. ^ "Polycyclic Aromatic Hydrocarbons – Occurrence in foods, dietary exposure and health effects". European Commission, Scientific Committee on Food. December 4, 2002.
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grilled food". *J Agric Food Chem.* 31 (4): 867–873. doi:10.1021/jf00118a049. PMID 6352775.
4. ^ "Polycyclic Aromatic Hydrocarbons (PAHs)". Agency for Toxic Substances and Disease Registry. 1996.
5. ^ Glenn Michael Roy (1995). *Activated carbon applications in the food and pharmaceutical industries*. CRC Press. p. 125. ISBN 1566761980.
6. ^ "Incense link to cancer". *BBC News*. 2001-08-02.
7. ^ For example, EPA regulations for small engines are at 40 CFR §90.103; see emission standard for more information.
8. ^ Luch, A. (2005). *The Carcinogenic Effects of Polycyclic Aromatic Hydrocarbons*. London: Imperial College Press. ISBN 1-86094-417-5.
9. ^ Exposure to Common Pollutant in Womb Might Lower IQ
10. ^ Portella, Guillem; Poater, Jordi; Solà, Miquel (2005). "Assessment of Clar's aromatic π-sextet rule by means of PDI, NICS and HOMA indicators of local aromaticity". *Journal of Physical Organic Chemistry* 18: 785. doi:10.1002/poc.938.
11. ^ Battersby, S. (2004). Space molecules point to organic origins. Retrieved December 11, 2009
12. ^ Mulas, G.; Malloci, G.; Joblin, C.; Toublanc, D. (2006). "Estimated IR and phosphorescence emission fluxes for specific polycyclic aromatic hydrocarbons in the Red Rectangle". *Astronomy and Astrophysics* 446: 537. doi:10.1051/0004-6361:20053738.
13. ^ Mulas, G.; Malloci, G.; Joblin, C.; Toublanc, D. (2006). "Estimated IR and phosphorescence emission fluxes for specific polycyclic aromatic hydrocarbons in the Red Rectangle". *Astronomy and Astrophysics* 446: 537. doi:10.1051/0004-6361:20053738.

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- Fused Ring and Bridged Fused Ring Nomenclature
- Database of PAH structures
- National Pollutant Inventory: Polycyclic Aromatic Hydrocarbon Fact Sheet
- Understanding Polycyclic Aromatic Hydrocarbons NASA Spitzer Space Telescope
- Astrobiology magazine *Aromatic World* An interview with Professor Pascale Ehrenfreund on PAH origin of life. Accessed June 2006
- Oregon State University Superfund Research Center focused on new technologies and emerging health risks of Polycyclic Aromatic Hydrocarbons (PAHs)

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