

# Handbook of POLYCYCLIC AROMATIC HYDROCARBONS

edited by

Alf Bjørseth

# HANDBOOK OF POLYCYCLIC AROMATIC HYDROCARBONS

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**POLYCYCLIC**  
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## Preface

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During recent years, it has become increasingly evident that cancer in man is linked to environmental factors. In particular, attention has been focused on the importance of chemical carcinogens in the environment.

One of the largest classes of environmental carcinogens known today is the polycyclic aromatic hydrocarbons (PAH). These compounds have their main sources in fossil or synthetic fuels or from combustion or high-temperature reactions of organic materials. Since these sources are ubiquitous in an industrialized society, there are a large number of stationary as well as mobile sources of PAH. In less developed countries PAH from fires may also represent a pollution problem. Furthermore, PAH are subject to considerable aerial transport. This makes PAH one of the most widespread environmental contaminants known today. Since many PAH compounds exhibit carcinogenic or cocarcinogenic properties, the environmental concern for these compounds is well justified.

A prerequisite for the control of PAH in the environment is an understanding of the chemical and physical properties of PAH as well as the methodologies for their sampling, sample handling, and analysis. I have for a long time seen the need for a comprehensive and systematic treatise describing our present knowledge in these areas in such a way that it might be of value to active researchers as well as people involved in regulatory actions, monitoring work, etc. Furthermore, a handbook giving a state-of-the-art review and at the same time providing hints for the practical application of methods would be extremely valuable for those researchers beginning work in this area. It is also useful to show how modern-day analytical techniques are applied to various environmental problems.

This handbook consists of contributions from selected authors who are authorities in their subject areas and provides a description of the state of the art in these areas of research. It is my hope that it will encourage and motivate further research on PAH in order to provide a clearer understanding of sources and distributions of PAH in the environment.

I want to express my warm thanks to all the contributors to this handbook for their cooperation, their hard work, and their patience while their manuscripts were being prepared for the press. I also wish to express my indebtedness to Dr. Peter W. Jones for helpful discussions in the early planning stage and to my colleagues at the Central Institute for Industrial Research, Oslo, for their valuable advice and encouragement. Finally, I wish to thank my wife, Eva, and my daughter, Tone, for their understanding and patience when I occasionally gave higher priority to my professional life than to my family life.

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## Abbreviations and Acronyms

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Anthr	Anthracene
ASTM	American Society for Testing and Materials
BaA	Benz[a]anthracene
BaP	Benzo[a]pyrene
BkF	Benzo[k]fluoranthene
EPA	Environmental Protection Agency
FID	Flame-ionization detector
GC	Gas chromatography
GC/MS	Gas chromatography/mass spectrometry
CGC/MS	Capillary gas chromatography/mass spectrometry
GLC	Gas-liquid chromatography
GSC	Gas-solid chromatography
HPLC	High-performance (or high-pressure) liquid chromatography
HMO	Hückel molecular orbital
HRMS	High-resolution mass spectrometry
IR	Infrared
LC	Liquid chromatography
MOs	Molecular orbitals
Nap	Naphthalene
NMR	Nuclear magnetic resonance
PAH	Polycyclic aromatic hydrocarbons
Phen	Phenanthrene
ppb	Parts per billion
ppm	Parts per million
ppt	Parts per trillion
TLC	Thin-layer chromatography
Py	Pyrene
RE	Resonance energy
UV	Ultraviolet



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## Physical and Chemical Properties of Polycyclic Aromatic Hydrocarbons

MAXIMILIAN ZANDER / Rütgerswerke AG, Castrop-Rauxel,  
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### I. Structural Principles of PAH

This chapter deals exclusively with PAH that are composed solely of six-membered or six- and five-membered rings and in which interlinked rings have at least two carbon atoms in common, i.e., bi- and polyaryls are not taken into consideration.

The entire group of PAH can be divided into kata-annellated and peri-condensed systems. In kata-annellated PAH, the tertiary carbon atoms are centers of two interlinked rings (e.g., tetracene [1]), whereas in peri-condensed PAH some of the tertiary C atoms are centers of three interlinked rings (e.g., pyrene [2]). Annellation can be linear (the six-membered rings are located on one straight line) or angular (the six-membered rings are located on different straight lines, with the angle between the lines always being 120°). Tetracene [1] is an example of a PAH with linear annellation, and triphenylene [3] that of a PAH with angular annellation.

Larger PAH may contain peri-condensed molecular regions in addition to linear and angular annellated regions (e.g., dibenzo[a,n]perylene [4]).

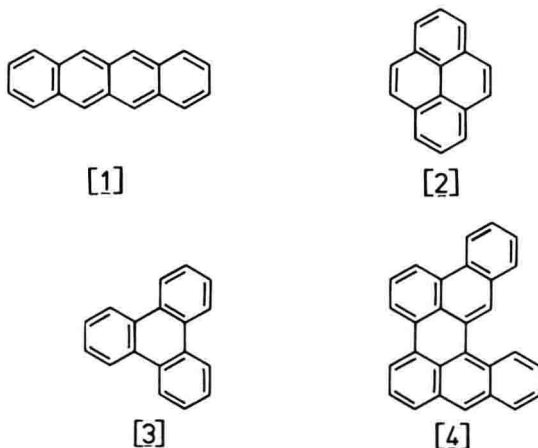


Table 1 shows the number of possible isomeric PAH which consist exclusively of six-membered rings, as a function of the number  $n$  of six-membered rings [1]. It will be seen that the sum total of possible PAH with two to eight rings comes to as much as 1896. There are 683,101 theoretical possibilities for the linking of 12 rings alone [2].

## II. Fundamental Aspects Concerning the Correlation of Structure and Properties of PAH

In their ground state, PAH with an even number of carbon atoms are systems with "closed shells," i.e., all bonding  $\pi$ -orbitals are occupied by two electrons with opposite spin, and all antibonding orbitals are unoccupied.

The pairing theorem applies to alternant PAH (systems comprising six-membered rings only) [3]: the  $\pi$ -molecular orbitals (MOs) appear in pairs  $\psi_{\mu}^{+}$  and  $\psi_{\mu}^{-}$  with energies  $\alpha + E_{\mu}$  and  $\alpha - E_{\mu}$ , where  $\alpha$  is the Coulomb integral (energy of a carbon-2p<sub>z</sub> orbital), i.e., bonding and antibonding  $\pi$ -MOs are in symmetry with one another. The MO diagram of an even-alternant PAH is shown in Fig. 1. The energies of the frontier orbitals, the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital), are particularly significant for the physical and chemical properties of PAH.

The properties of PAH depend on the *size* and *topology* of the systems. Here "size" is understood to mean the number of carbon centers, i.e., number of  $\pi$  electrons, while "topology" denotes the type of ring linkage (see Sec. I). Since the energies of the frontier orbitals determine the properties of PAH in decisive degree, the significance of the size of the systems is understandable: the number of occupied MOs increases in step with the growing total number of  $\pi$  electrons—it is always half the number of  $\pi$  electrons—and the energies of the frontier orbitals increase accordingly.

For PAH, correlations between topology and properties can be demonstrated in a variety of ways and frequently by very simple means. Figure 2 shows the characteristic graphs [1] of the isomeric, i.e., isoelectronic, kata-

**Table 1.** Number of PAH with  $n$  Six-Membered Rings

$n$	Kata-annellated PAH	Peri-condensed PAH	$\Sigma$
1	1	0	1
2	1	0	1
3	2	1	3
4	5	2	7
5	12	10	22
6	37	45	82
7	123	210	333
8	446	1002	1448

Source: Ref. 4.

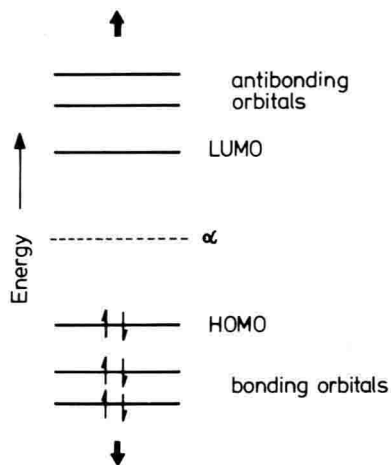


Figure 1. MO diagram of an even-alternant PAH.

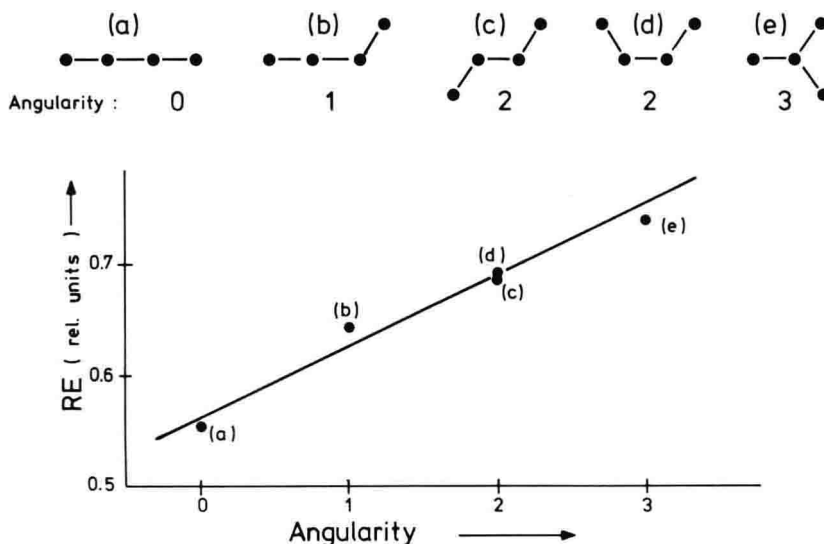


Figure 2. Correlation between resonance energy (RE) and angularity of isoelectronic PAH. (From Ref. 4.)

annellated PAH with four rings. The points mark rings; the lines, the edges of annellated rings. The characteristic topological property is the *angularity*, which is the sum of the  $120^\circ$  angles in the graphs. As an example of correlations between angularity and molecular properties, the resonance energy (RE) as the quantity characterizing the stability of PAH is plotted against the angularity in the figure. Note that the linear correlation is quite satisfactory [4].

The pronounced dependence of most PAH properties on the topology of the systems explains why all quantum-mechanical approximation methods, which are topological methods, reproduce PAH properties well. Methods using Kekulé structures are explicitly topological. These also include the methods developed using elements of graph theory [5-7]. The Hückel molecular orbital (HMO) method is also topological, since the HMO secular determinant reproduces the topology of the  $\pi$ -electron system [8]. The fact that the resonance theory (not strictly proven in physics [9]), which operates with structures, supplies results for PAH that coincide with HMO results is based on a correspondence conditioned by the topological character of both methods.

### III. Clar's $\pi$ -Sextet Model

A structural-chemical model introduced by Clar more than 20 years ago is eminently suitable for systematizing PAH topologies and representation of correlations between topology and properties of PAH [10]. Figure 3 gives formulas for pyrene (a) and benzo[ghi]perylene (d). The dots represent carbon- $2p_z$  electrons, whose interaction leads to the formation of  $\pi$  MOs. Clar's proposal is to divide the quantity of carbon- $2p_z$  electrons into sub-

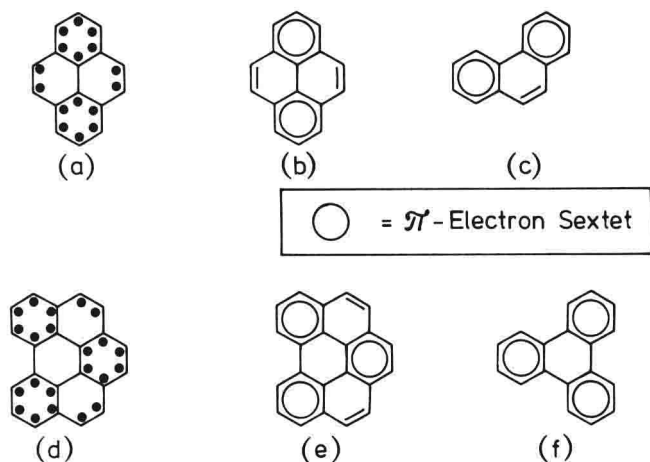


Figure 3. Clar's  $\pi$ -sextet model of PAH. (From Ref. 4.)

quantities in which  $\pi$  electrons are assigned to particular rings. This is accomplished in such a way that the maximum possible number of subquantities consisting of six  $\pi$  electrons, i.e., (benzoid)  $\pi$ -electron sextets, is obtained. Thus, Clar's formulas *b* and *e* are formed from the initial formulas *a* and *d*. Formulas *c* and *f* are Clar's models for two kata-annellated PAH.

The connection between Clar's model and the graph-theoretical methods employing Kekulé structures [5-7] is evident. Figure 4 shows the Kekulé structures of phenanthrene. Let each double bond be assigned only one ring. Then rings A and B in four of the five structures each contain three double bonds (the rings are "benzoid"), while ring C contains three double bonds in two structures only. Rings A and B are also "benzoid" in character in Clar's phenanthrene formula (six  $\pi$  electrons).

Numerous examples from the chemistry and physics of PAH [11] suggest that Clar's model is more than a useful formalism, i.e., the inherent  $\pi$  sextets postulated may possess physical reality. Only two examples will be discussed

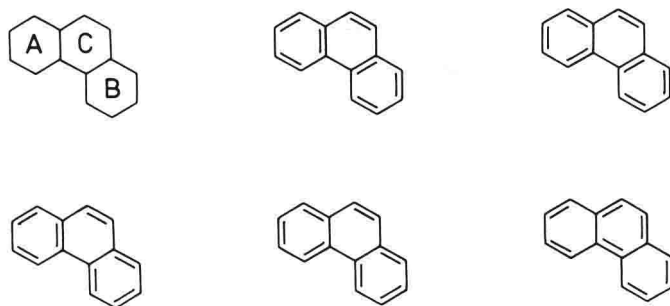
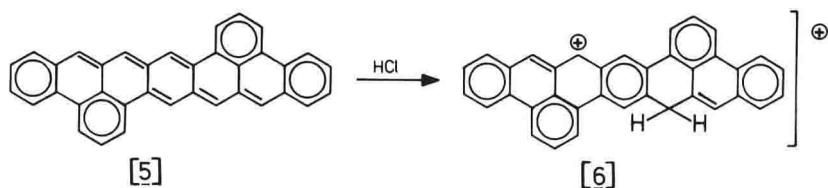


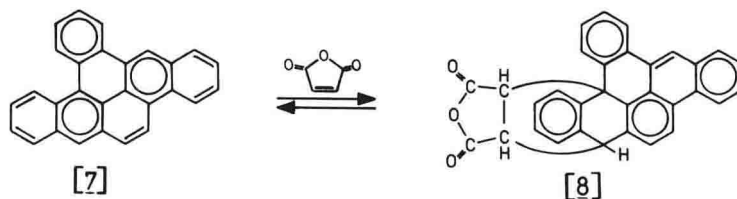
Figure 4. Kekulé structures of phenanthrene.



in detail here: (i) The PAH [5] is surprisingly basic for a hydrocarbon and together with hydrochloric acid forms a hydrochloride. Evidently the carbenium ion [6] formed by the addition of a proton possesses greater stability than the hydrocarbon. Moreover, precisely this result is obtained by writing the PAH and its carbenium ion with the maximum number of  $\pi$  sextets and applying Clar's postulate that the stability of the systems increases with the number of  $\pi$  sextets. (ii) There is a simple correlation between the positions



at which a PAH adds maleic anhydride endocyclically on the lines of a Diels-Alder reaction and the  $\pi$ -sextet formulas. In cases where the addition can lead to several isomeric adducts, the adduct whose formula can be written with the largest number of inherent  $\pi$ -electron sextets is always the only one to be formed [12]. Figure 5 gives a number of examples. A necessary and usually also adequate condition for the endocyclic Diels-Alder reaction of PAH with maleic anhydride is that at least one  $\pi$ -electron sextet be "gained" by the addition, i.e., that the number of sextets in the product be at least one more than in the reactant. The application of this principle has also led to the discovery of the first example of an endocyclic Diels-Alder reaction with a PAH including dearomatization of the pyrene system: the PAH [7] reacts with maleic anhydride to form the Diels-Alder adduct [8] [13]. Recently, the rate constants of the Diels-Alder reaction with maleic anhydride of numerous kata-annellated PAH have been measured under identical conditions and correlated with various experimental and theoretical molecular parameters [14].



Even though Clar's model permits a consistent description of the relationships between structure and properties of PAH (and has enabled many correct predictions to be made [15]), it cannot be utterly precluded that Clar's  $\pi$ -sextet formulas correspond to another parameter—in the model not explicitly expressed—which ultimately determines the structure-property relationships. Of course, the same applies to all graph-theoretical methods that are equivalent to Clar's model [5-7].

#### IV. Correlations among Properties, Size, and Topology of PAH

When considering the properties of PAH, it is useful to separate the effects of size and topology on those properties. Here, Clar's  $\pi$ -sextet model is eminently suitable: the properties of PAH of different sizes but with the same