Graphenes – Aromatic Giants

Ivan Gutman and Boris Furtula

Recently, extremely large benzenoid hydrocarbons have been synthesized. These compounds resemble graphite in many ways, and have been named graphenes. Because of their non-standard properties, graphenes have already found numerous applications, especially as special-purpose materials in electronics. In this article we outline the basic chemical facts on graphenes.

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Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (often abbreviated as PAH) are an important class of organic compounds. Students learn about them in any course on organic chemistry. The best known representatives are benzene (which, in fact, is cyclic, not polycyclic), naphthalene, anthracene, phenanthrene and pyrene. Today about 1000 such compounds are known, whereas the number of possible isomers is significantly greater. For instance, there are 'only' 15 stable benzenoid hydrocarbons with 5 six-membered rings, whereas the number of such species with 10 and 14 rings is 14107 and 6031642, respectively [1,2]. There are 'only' 12 benzenoid isomers with formula $C_{22}H_{14}$ (which have all been obtained experimentally), but there are 777 and 14699 possible $C_{36}H_{20}$ and $C_{46}H_{24}$ isomers, respectively. The number of benzenoid isomers with formula $C_{62}H_{34}$ is calculated to be 4799205. Evidently, only a minute fraction of these possible isomers will ever be synthesized in the laboratory.

Polycyclic aromatic hydrocarbons are among the most stable organic compounds [3]. The main sources are tar and pitch [4], especially coal-tar. Coal-tar is a by-product in the manufacturing process of coke, and is produced in millions of tons annually.

Keywords
Graphenes, polycyclic aromatic hydrocarbons, polyphenyls, condensed benzenes.

The molecules of PAH consist of condensed six-membered

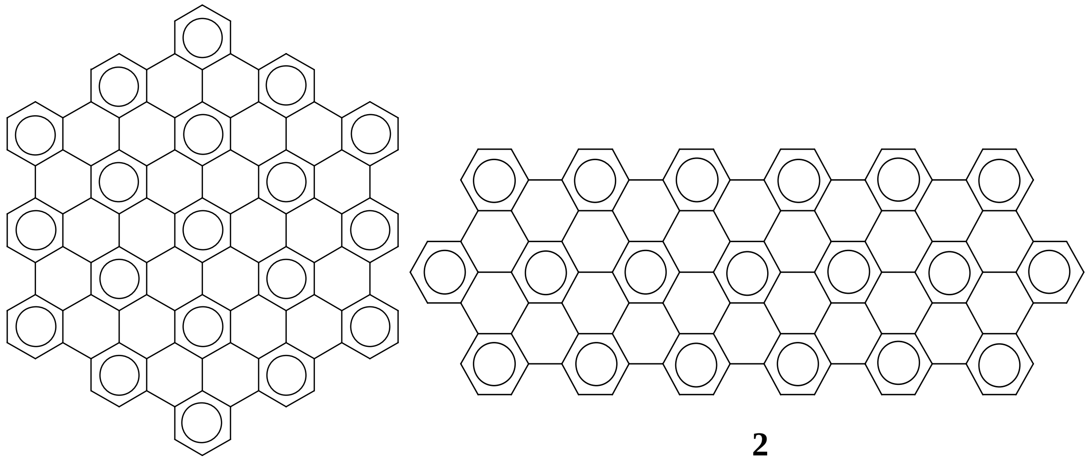

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Figure 1. Two large graphenes, both with 114 carbon atoms: 1 = $C_{114}H_{30}$; 2 = $C_{114}H_{34}$.

(benzene) rings. Until recently it was believed [5] that their chemical investigations are limited to compounds with not more than 15 rings. The reason for this is based on the fact that large PAHs are practically insoluble in water or organic solvents, which makes their purification and chemical characterization nearly impossible. This is especially the problem when separation of isomers (which are very numerous) is needed.

Recently, these problems were overcome by Klausa Müllen (working at the Max Planck Institute for Polymer Research in Mainz, Germany). He discovered a chemical reaction (see *Figure* 4a) by means of which PAHs of unprecedentedly large size can be obtained, with just a single isomer each! In addition to this, Müllen discovered a laboratory trick (which is outlined in *Figure* 6) by means of which these compounds can be converted into easily soluble forms. The formulas of a few largest (obtained so far) PAHs are shown in *Figures* 1–3.

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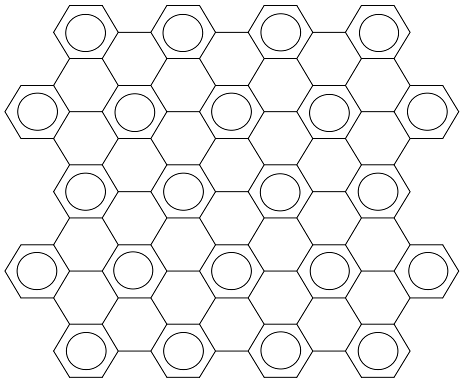
Synthesis of Graphenes

The synthesis of graphenes, elaborated by Müllen and coworkers, [6,7] consists of two phases. In the first, by standard methods of organic chemistry, one obtains polyphenyls – compounds having



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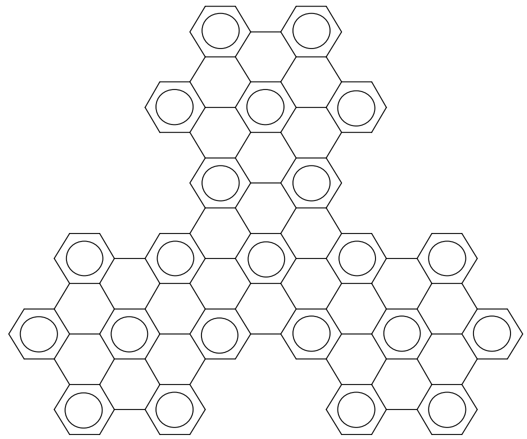

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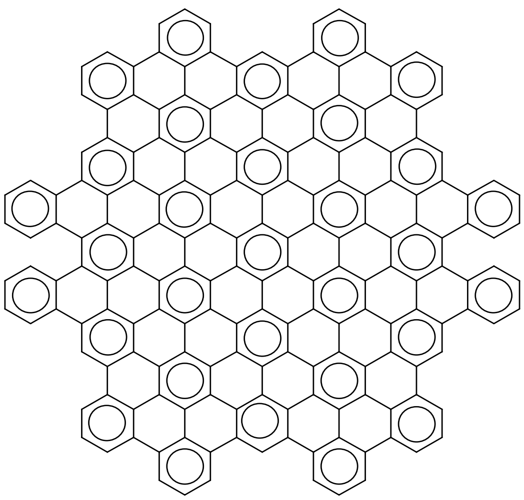

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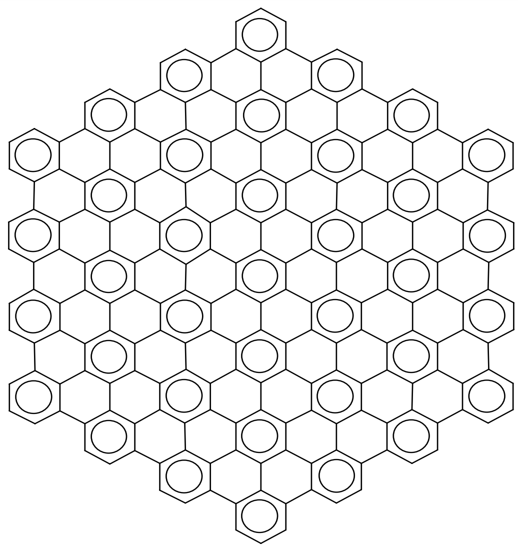

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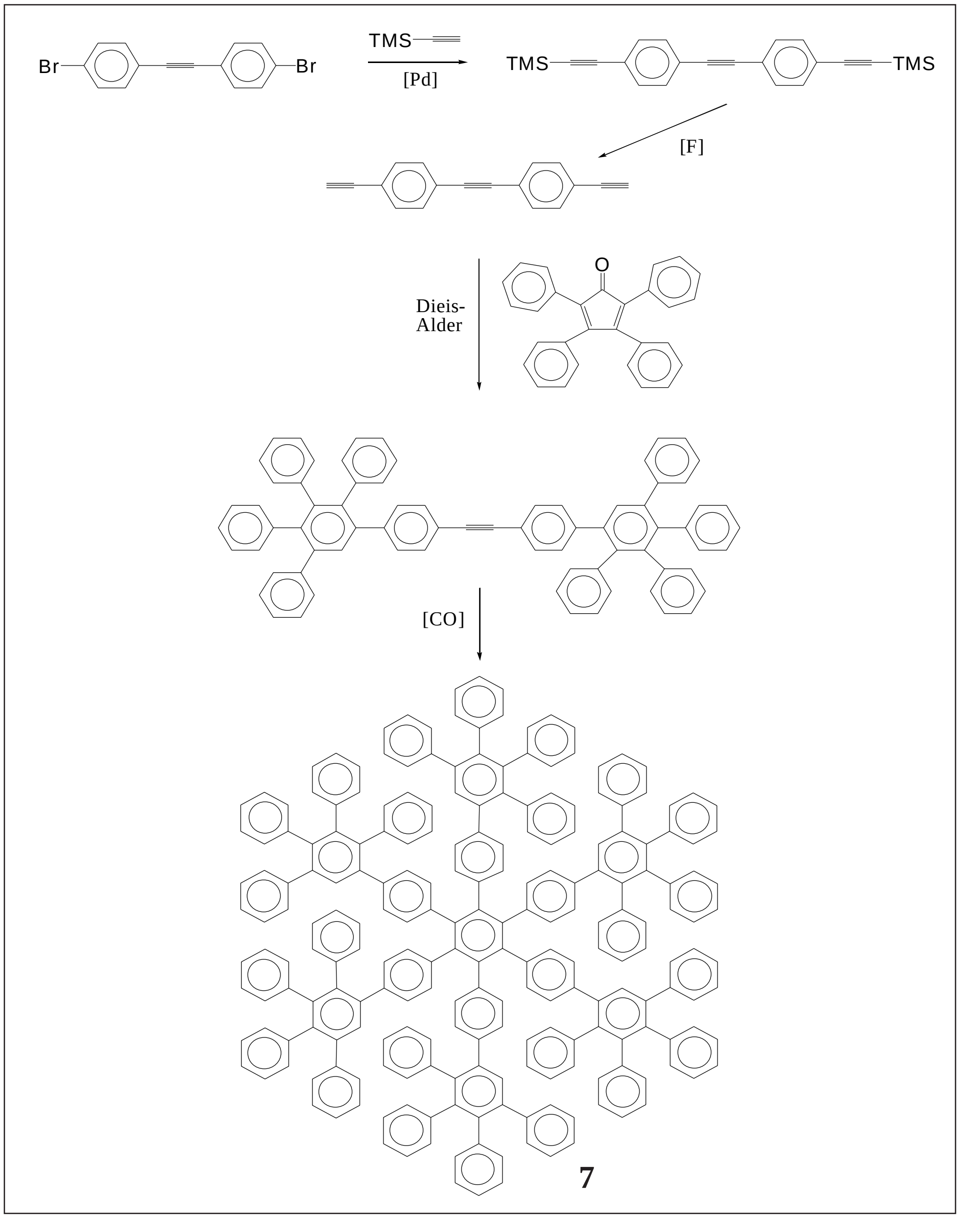
Figure 2 (top). Two still bigger graphenes, both with 132 carbons atoms: 3 = $C_{132}H_{34}$, 4 = $C_{132}H_{42}$.
Figure 3 (bottom). The two biggest graphenes synthesized so far:: 5 = $C_{186}H_{46}$, 6 = $C_{222}H_{40}$. It is worth noting that compound 6 contains only 1.48% hydrogen, whereas the rest is carbon.

a large number of benzene rings connected by single carbon-carbon bonds. A typical reaction of this kind is shown in *Figure* 4a. The six-membered rings in polyphenyls (for instance, in the polyphenyl **7** shown in *Figure* 4a) have a complicated spatial arrangement, and do not lie in a single plane. In the second phase, the polyphenyl is treated with a mild oxidizing agent. Müllen discovered that if one uses iron(III)-chloride, $FeCl_3$, as an oxidant, then the polyphenyl is transformed into a graphene *in a single chemical reaction*. This reaction runs fast and with very high yield. *Figure* 4b shows how graphene **6** is obtained from

Figure 4a. The first phase of synthesis of graphene: Polyphenyl 7 is obtained by standard procedures.



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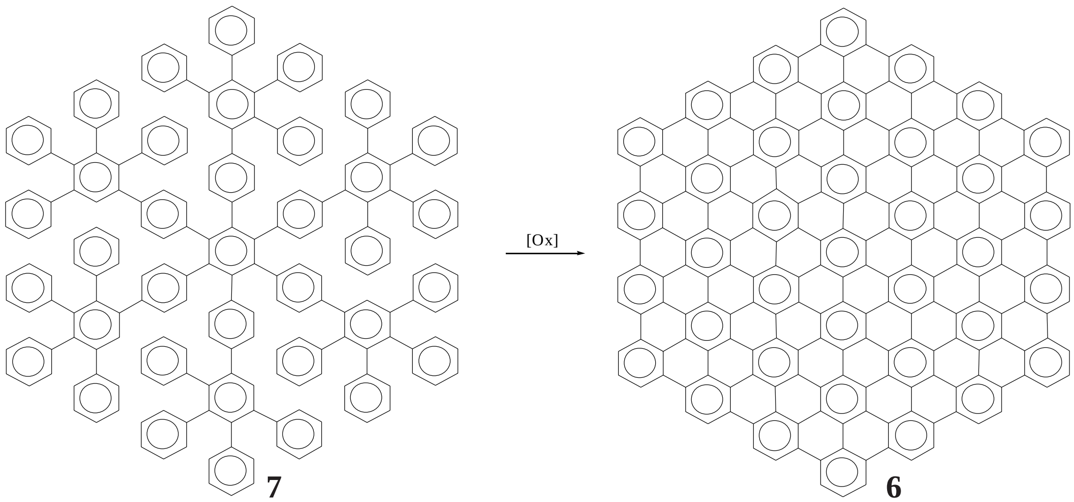

Figure 4b. The second phase of synthesis of graphene: By a single-step oxidation of the polyphenyl 7, graphene 6 is gained in high yield. $FeCl_3$ is used as the oxidizing agent.

polyphenyl **7**. It is worth noting that in this way a non-planar polyphenyl is transformed into a graphene, whose molecules are almost perfectly planar, that is all atoms of the graphene molecule lie in the same plane.

In *Figure* 5 is shown another, but in essence very similar, synthesis of a graphene [6,7]. For this synthesis it is characteristic that first a mixture of several isomeric polyphenyls is obtained, all yielding (by oxidation) the same end product. We leave to the readers to recognize how great an advantage this is for a successful and efficient laboratory synthesis.

Soluble Graphite

The problem of low solubility of graphenes has been resolved by Müllen in an ingenious manner. The readers of this article may think that this was something 'obvious' and 'very easy'. However, the fact is that nobody came up with such an idea prior to Müllen. The idea is the following [6,7]:

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By minor modifications of the synthesis procedure, using compounds with appropriate side groups as starting reactants, one arrives at graphenes to which these side groups are attached.

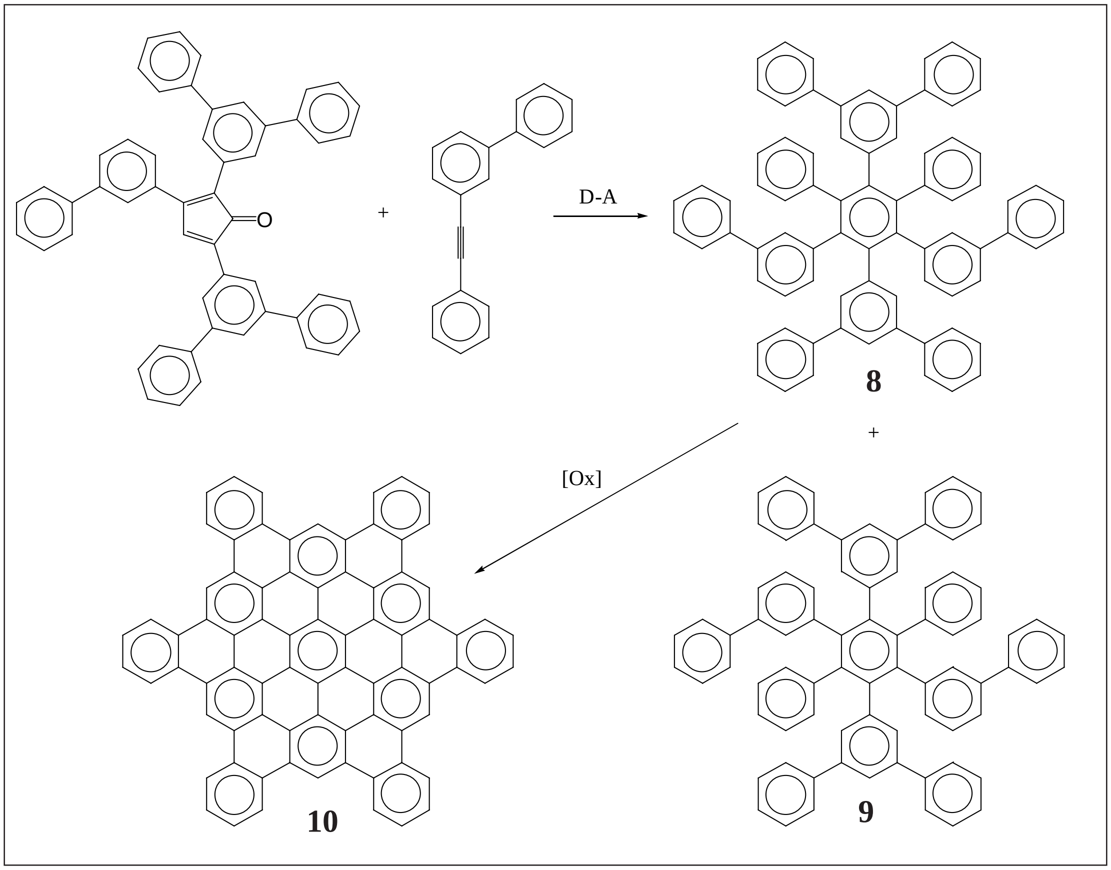


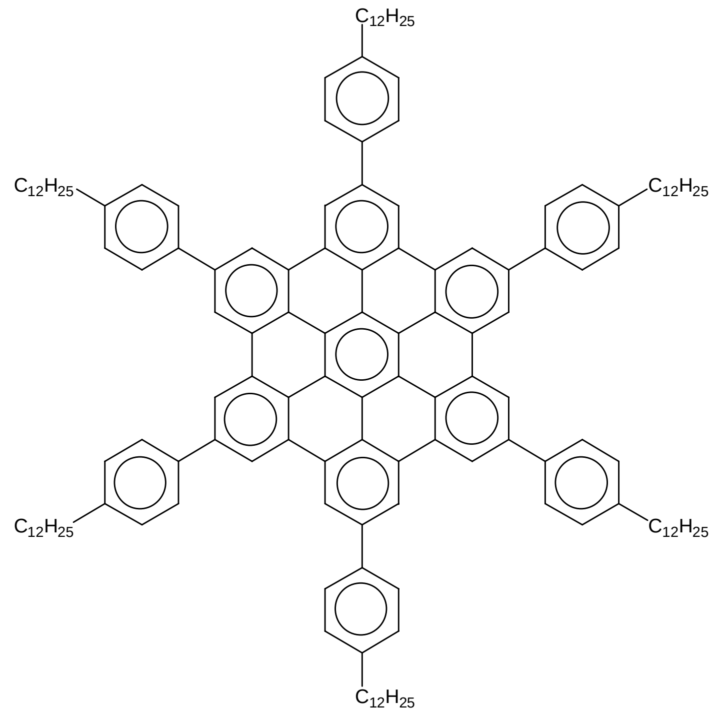
Figure 5. Another example of how a graphene is obtained. In the first phase a mixture of isomeric polyphenyls 8 + 9 is obtained. In the second phase, this mixture is oxidized (in a one-step reaction) into a unique end product – the graphene 10 .

These side groups may be long hydrocarbon chains (as in compound **11** in *Figure* 6) or methoxy groups (as in compound **12**) or any other substituent.

Thanks to the side groups, the substituted graphenes become easily soluble in organic solvents. Then it is much easier to work with them. We illustrate this by a simple example. If a drop of a dilute solution of a graphene (for instance, in ether) is put on some surface (for instance, of an insulating plastic), and if the solvent is evaporated, then an extremely thin layer of graphene is obtained, whose electrical behaviour is similar to that of graphite.

Graphenes, same as graphite, possess easily movable electrons (so-called π-electrons) that are responsible for their characteristic electric properties. However, instead of being true conductors (like graphite), graphenes are semiconductors. This feature is of

Figure 6. Graphenes with side groups. Thanks to these substituents the graphenes become easily soluble in organic solvents (for instance, 11 is soluble in ether, and 12 in alcohol). There are also water-soluble graphenes. Such solutions have many, especially electric, properties similar to graphite and are called "liquid graphite" or "soluble graphite".



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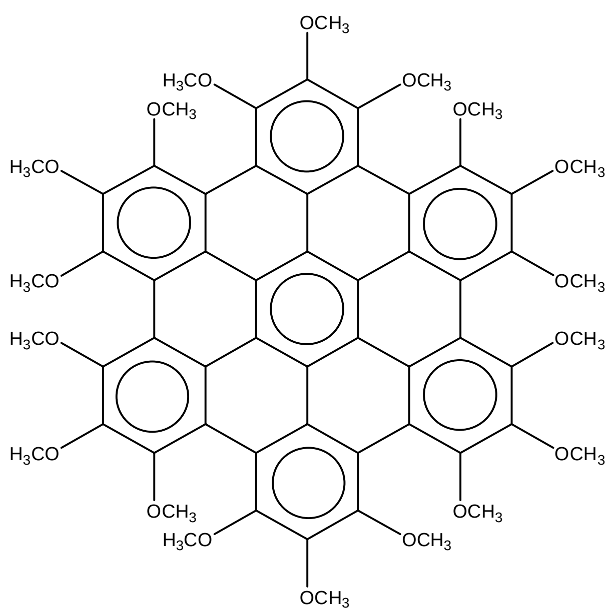

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great value in electrical engineering (for instance, for designing transistors), because the semiconducting properties of graphenes depend on the size and shape of the aromatic core of the molecule, as well as on the nature of its side groups. All these structural details a chemist can modify according to the customer's wish.

Substituted graphenes, known as '*soluble graphite*' or '*liquid graphite*' have become highly valued materials in electronics. Nowadays these compounds are used in various 'high-tech' devices, mainly in those in which light and electricity are interconverted (photo cells, solar cells, light detectors, light-emitting diodes, colour photocopying). Details of these applications are not easy to get because these are usually treated as industrial secrets. In particular, in the two extensive, recently published review articles [6,7], the technical applications of graphenes are mentioned in only a few lines, without saying anything concrete.

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Suggested Reading

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