# 3.13 MOLECULES WITH MULTIPLE AROMATIC RINGS

**Naphthalene** was formerly used in some brands of mothballs because the crystals slowly evaporated (sublimed) and the pungent smell of naphthalene vapor repelsed moths from woolens. Concern about flammability have resulted in 1,4 dichlorobenzene being used instead. The chlorination reduces the flammability of the compound.

Naphthalene:



## **Polychlorinated Biphenyls(PCBs)**



**Polychlorinated biphenyls** are a group of aromatic compounds with two ore more Cl atoms substituted on 2 benzene rings, as shown in the structure above. The number of Cl atoms and the position of those Cl atoms on the two benzene rings can vary considerably and that is indicated in the above structure by having the Cl bonding into the center of the ring and with the  $(Cl)_n$  indicating a variable number of Cl's.

Polychlorinated biphenyl compounds (PCBs) are very stable (unreactive) nonflammable compounds that were used to absorb heat in electrical transformers and lubricants from 1929 until about 1977.





Sales of PCBs stopped in 1977, but disposal of PCB's has been a major problem. They are not readily destroyed. They require extremely high temperatures to decompose to harmless compounds and it has been difficult to find organisms that metabolize them effectively.

Unfortunately these compounds were sometimes dumped in landfills or streams when the transformers were replaced and PCB's have contaminated soils and waters throughout the world. Since these are non-polar compounds and are not metabolized, they tend to accumulate in fat and neural tissue at increasing concentrations as they work up the food chain (alga/small fish/big fish/eagle) Experimental laboratory data on animals (most commonly rats and monkeys) suggests that these compounds are carcinogens and that they can disrupt immune system and neurological systems. They may also disrupt the reproductive system and hormonal system (i.e. they may act as **endocrine disruptors**). Epidemiological data on humans exposed to PCBs suggest that humans are likewise at risk.

A substantial leak occurred from a powerhouse transformer near the Dalles, Oregon in January 2004 and PCBs have been found in sturgeon in the Columbia River near the US Army Corp of Engineers dumpsite.



## Dioxin

Like the PCBs, the terms dioxin refers to a mixture of compounds containing varying amounts of Cl atoms on a basic 3-ring dibenzodioxin molecule.



Dibenzodioxin



2,3,7,8-tetrachlorodibenzoparadioxin (TCDD)

The most toxic dioxin is the tetrachlorinated structure shown above whose full chemical name is 2,3,7,8-tetrachlorodibenzoparadioxin, abbreviated **TCDD**. Dioxin is a contaminant that is formed from the synthesis of certain chlorinated herbicides (particularly 2,4,5 trichlorophenoxyacetic acid or 2,4,5 T ), bleaching of paper pulp, and incineration of chlorinated plastics. It is a fairly nonpolar molecule (C-Cl bonds are only slightly polar) and accumulates in the fat, being metabolized only slowly. One estimate has the half life of TCDD in fat as 8 years.

TCDD was a contaminant in **Agent Orange** defoliant (herbicide) that was widely sprayed (estimated 11 million gallons on 6 million acres) over tropical forests in Viet Nam from 1962 to 1971 to kill all vegetation and reduce the forest cover used by the Viet Cong guerilla fighters. Its toxicity is the subject of a great deal of controversy and has been the subject of lawsuits by veterans of the Viet Nam war.









# AGENT ORANGE



Many veterans of the Viet Nam war alleged that dioxin was the cause of a variety of health problems, including skin rashes, neurological and psychological problems, and birth defects. In 1996 a National Academy of Science committee concluded there was suggestive evidence for slightly increased risk of Hodgkin's disease, soft-tissue sarcoma, and non-Hodgkin's lymphoma among American veterans heavily exposed to Agent Orange. It has been difficult to gather data, given the lack of quantitative information about the level of Agent Orange exposure and the possibility that other factors besides Agent Orange and its dioxin contaminant might be involved.

The small town of Time Beach, Missouri was evacuated in 1985 when oil made out of chemical wastes from a plant making Agent Orange was used for dust control on the town's streets. Sixty two horses died when oil was used to control dust in a horse stable. Eventually the whole town was evacuated, and compensated by the federal government to relocate elsewhere. The contaminated soil was incinerated (at a cost of \$110 million) in an on-site incinerator which was then dismantled and removed. The former town is now a state park..

Incineration of urban waste containing chlorinated plastics (such as PVC and Saran and other compounds) can produce small quantities of dioxin that are released into the air and this has been a concern about waste incineration. Changes in the combustion conditions has greatly reduced the amount of dioxin produced in this manner.

Soldiers claim war zone contractors exposed them to toxins Nashville lawsuit one of several over 'burn pits' in Iraq and Afghanistan alleged to contain dioxin, asbestos and human corpses

Email | Print By E. Thomas Wood

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Contractors working for the military in Iraq and Afghanistan are fouling the nests of U.S. soldiers with pollution, poisoning the troops in the very bases meant to be their sanctuaries.

That's the central allegation in a new set of lawsuits filed in Nashville and elsewhere across the country. The legal actions name as defendants the controversial contracting firm KBR Inc. (formerly Kellogg Brown and Root), as well as Halliburton Co., of which KBR used to be a subsidiary, and a Turkish general contracting firm, ERKA Ltd.



## Chloracne

Acute exposure to large amounts of dioxin can cause a wide variety of symptoms including an unusual form of acne called **chloracne**. This got major media attention in 2004 in the case of Viktor Yushchenko, a presidential candidate in the Ukraine in 2004.

In September 2004 Yushchenko became ill during a very heated political campaign. He became very weak and was in great pain. Blood tests showed a high white blood cell count and elevated liver enzymes, but nothing specific. Disfiguring **chloracne** developed several weeks later and was the key to discovering the source of his health problems. His health has gradually improved and he won the election, but his face is very scarred and may remain so for years.



**Graphite** is a large sheet of benzene rings that extend in large 2 dimensional sheets. It is a black powder with a greasy feeling and is used in "lead" pencils. (Although the Romans did use lead to make marks on papyrus, the discovery of pure deposits of graphite in 1564 gradually led to graphite replacing lead for this purpose. Graphite is often mixed and baked with clay to increase its hardness and then inserted into a wood or plastic/metal pencil to make it efficient to use.) Graphite is also used as a dry lubricant in machinery. Its lubricant properties result from the graphite sheets easily sliding over each other. It is also used in structural materials such as "high end" golf clubs, fishing rods, and bicycle frames.





Single layers of graphite are referred to as **graphene** and are a subject of intense research interest for potential technical applications such as a component of integrated circuits.



Andre Geim and Konstantin Novoselov won the physics Nobel Prize in 2010 for their work studying grapheme.

