Chapter 3

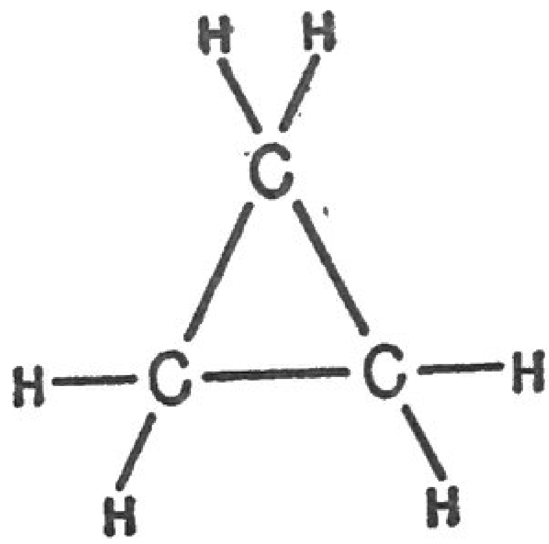
Rings, One and Many

The Battle Against Pain

What is to prevent the two ends of a carbon chain from joining to form a closed ring? Nothing at all. It happens all the time.

The simplest ring, one with three carbons only, has a structural formula that is easily drawn, thus:

Figure 8—Cyclopropane



The ordinary three-carbon hydrocarbon is propane, as you may remember. With the carbon atoms joined in a ring, the molecule is called *cyclopropane.* (The prefix "cyclo" shows that the carbon atoms in the molecule have formed a cycle, or circle.) In general, compounds containing rings of atoms are called *cyclic compounds.* Those without rings are *acyclic compounds.* (The prefix "a" is taken from Greek and means "not.")

Cyclopropane is an *anesthetic* (from a Greek word meaning "no feeling"). That is, when it is inhaled under the proper conditions, it will cause a person to lose the ability to feel pain. Usually, he loses consciousness, too.

The anesthetic does this by acting upon our nerves. Each nerve is surrounded, in part, by a *myelin sheath.* This is composed of molecules that are fairly similar to hydrocarbons in their electrical properties. The nerve fiber, when in action, carries a very small electric current, and the myelin sheath acts as an insulator.

When the lungs are filled with hydrocarbons (or similar compounds), some of the hydrocarbon molecules are absorbed into the bloodstream. From the bloodstream, they enter the various tissues of the body. They mix most easily with those parts of the body made up of molecules that resemble the hydrocarbons electrically. Therefore, the myelin sheaths are ideal. The hydrocarbon molecules accumulate in the myelin sheath. Once the myelin sheath is loaded with these molecules, nerve action stops. The nerve is, somehow, short-circuited. The brain no longer receives impulses such as pain which are carried by the nerves.

The use of anesthetics can be risky. For one thing, when inhaling an anesthetic, a patient must also inhale oxygen or he will suffocate. He must therefore be given just the proper mixture of anesthetic and oxygen to inhale. This mixture is usually highly explosive. For that reason, no smoking is allowed nearby, sparks must be guarded against, and so on.

Also, there must be neither too much nor too little anesthetic. The heart, lungs, and other vital organs are run by nerve impulses. Too much anesthetic will mean that the nerves that control those organs may also be short-circuited. If the situation is not corrected immediately, the patient will die.

On the other hand, once the patient is unconscious and is allowed to breathe ordinary air, the anesthetic slowly leaks out of the myelin sheaths, back into the lungs, and out of the body. After a while, the myelin sheaths are back to normal and the patient revives. If the operation is not over, he must be given additional anesthetic.

For all these reasons, anesthetics are administered in modern hospitals only by trained people who must use great skill and caution.

Hydrocarbon gases of different types vary in their anesthetic properties. Ethylene and acetylene are fairly strong anesthetics, stronger than the straight-chain saturated hydrocarbons. The hydrocarbon which is the strongest anesthetic of all, however, is cyclopropane, which I mentioned at the beginning of this section. It was first used as an anesthetic in 1929 and has stayed in use ever since.

One of the advantages of both cyclopropane and ethylene is that they can be mixed with considerable oxygen without losing strength. This reduces the chances of suffocating the patient. On the other hand, it makes the mixture particularly explosive.

Hexagons

You can have a ring of four carbon atoms (*cyclobutane*), five carbon atoms (*cyclopentane*), six carbon atoms (*cyclohexane*), or more. Carbon atoms form rings of five or six atoms (particularly six) most often. For instance, most of the terpene hydrocarbons contain six-carbon rings as part of the molecule. Carotene has six-carbon rings at each end of its long molecule.

The most important six-carbon ring is that which makes up the molecule of *benzene*. Compare its formula (on the right) with that of cyclohexane (on the left):

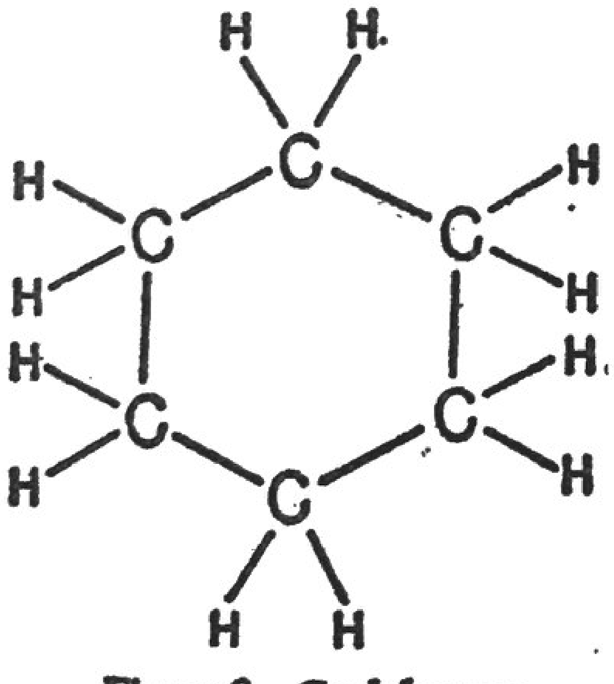


Figure 9—Cyclohexane

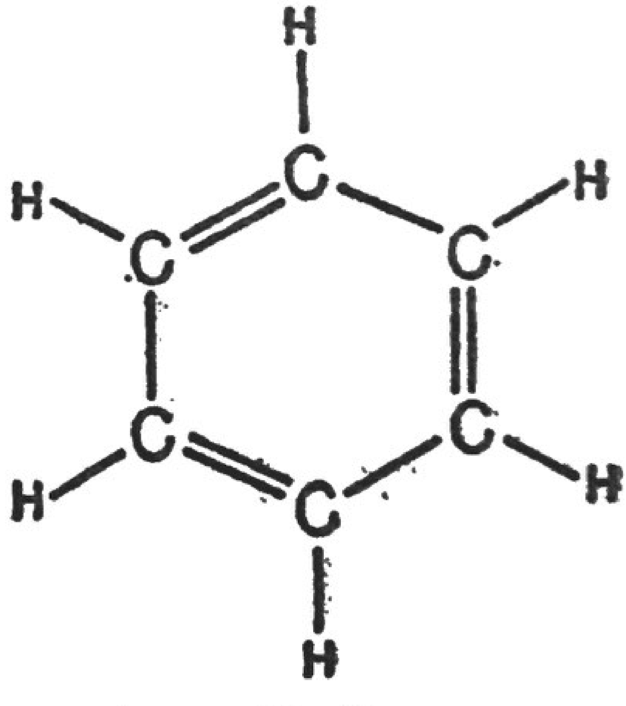


Figure 10—Benzene

Benzene has three double bonds. These alternate with single bonds so that benzene contains conjugate double bonds. This makes benzene rather inactive; less active than cyclohexane, for instance.[1] The benzene ring takes less energy to form. The result is that a great many organic compounds contain the benzene ring as part of their molecules. So many compounds do, in fact, that chemists usually place all such compounds in a special class and call them *aromatic compounds.* The first few natural compounds found to belong to this class had a definite, fairly pleasant aroma; hence the name. However, that should not be taken too seriously. It is impossible to tell aromatic compounds from other organic compounds just by the smell.

In writing formulas, chemists often save time by representing rings of carbon atoms as simple geometrical figures. For instance, cyclohexane is written as a six-sided figure (called a hexagon), thus:

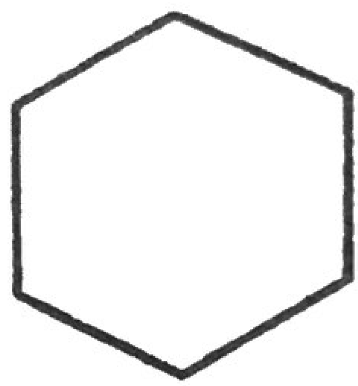


Figure 11—
Cyclohexane (schematic)

and benzene is a hexagon with the double bonds marked, thus:

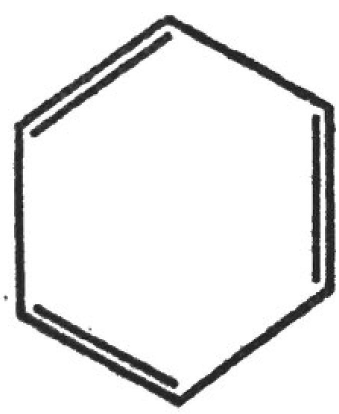


Figure 12—
Benzene (schematic)

[1] Ever since the formula for benzene was first worked out (by Kekulé), organic chemists have puzzled over its details. In many ways, the benzene molecule behaves as though the double bonds aren't really there. (After all the double bonds ought to make benzene *more,* not less, active than cyclo-hexane.) Modern theories of atomic behavior have finally given chemists a fairly satisfactory answer. The theories are too complicated to go into here but they involve notions of partial or fractional bonds. Thus, the six carbon atoms of the benzene ring can be looked upon as being connected by six equal "one-and-a-half" bonds which are less active than either single or double bonds.

If you ever have to make sense out of formulas containing these hexagons, or other figures like them, just remember two simple rules:

First: a carbon atom must be placed at each angle of the figure;

Second: any spare bonds not involved in forming the ring must be filled with hydrogen atoms. (If any atoms other than hydrogen atoms are involved, they are shown in the geometrical formulas so that you know they are there.)

It is these geometric figures that make most organic formulas look so complicated and frightening to people who aren't used to them. Actually, if you remember the two rules, you have no trouble with them. Still, as far as this book is concerned, I will use geometrical figures only when I absolutely have to.

More Power in Gasoline

A carbon atom (or a chain of carbon atoms) can be attached to one or more of the atoms making up a ring. Such an attached atom or atoms is called a *side-chain*. The simplest of such aromatic compounds is one in which a single carbon is attached to a benzene ring, as follows:

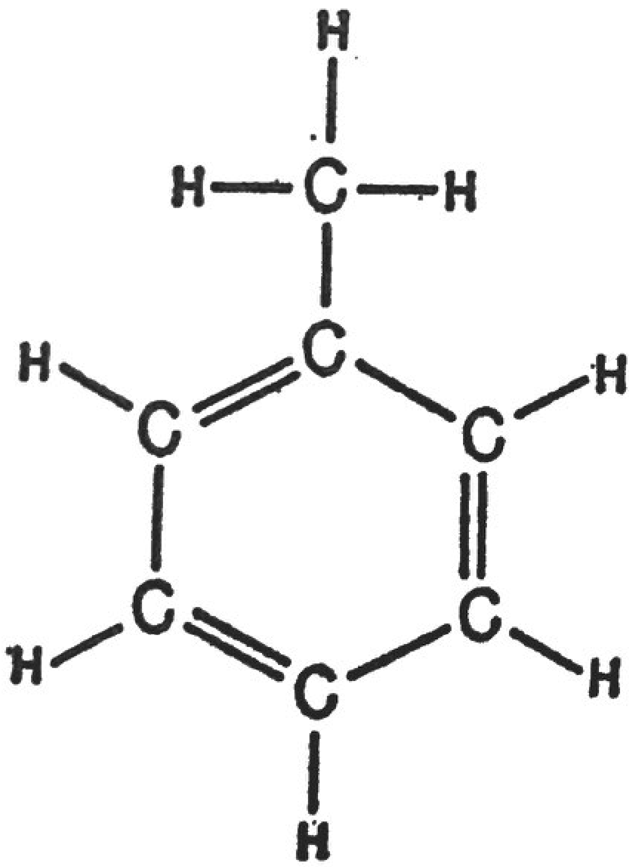


Figure 13—Toluene

The side-chain in this compound consists of a carbon atom to which three hydrogen atoms are attached. It is, so to speak, a methane molecule with one hydrogen atom missing. Such a side-chain is therefore called a methyl group. A benzene ring with a methyl group attached is called toluene.

What if there are two methyl groups attached to a benzene ring? Here there is an opportunity for isomerism, since there are three different ways in which two methyl groups can be attached to a benzene ring. The easiest way to show this to you is to use a hexagon to represent the benzene ring and attach little dashes to indicate the two methyl groups, thus:

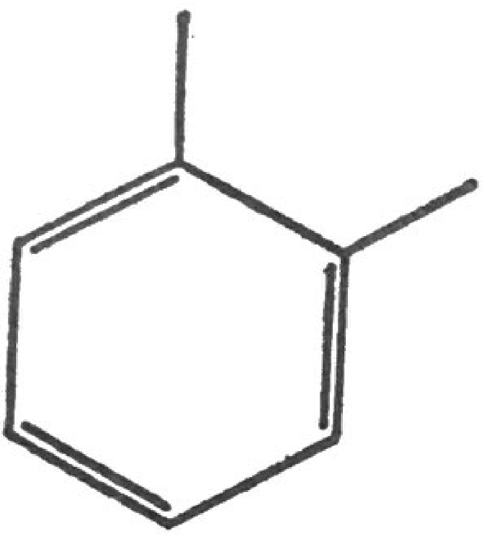


Figure 14—
Ortho-xylene

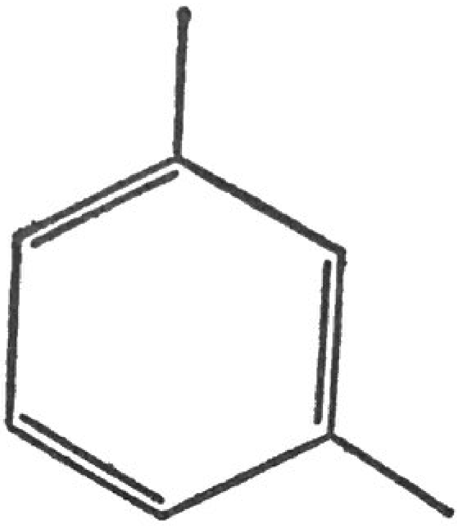


Figure 15—
Meta-xylene

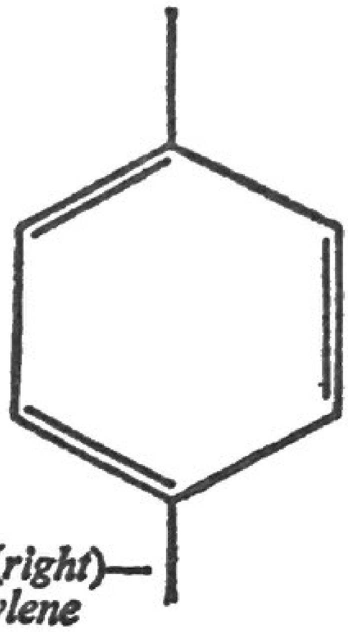


Figure 16 (right)—
Para-xylene

Any compound with a molecule consisting of a benzene ring and two methyl groups is called *xylene*.[2] In order to show the exact position of the two methyl groups, however, certain prefixes are attached to the name. For instance, when the two methyl groups are attached to neighboring carbon atoms, as in the hexagon on the left, we have *ortho-xylene*. If they are on opposite ends of the benzene ring, as in the hexagon on the right, we have *para-xylene*. If they have an intermediate arrangement, as in the hexagon in the middle, we have *meta-xylene*.

Sometimes, to save space, the prefixes are abbreviated and the names are written: *o*-xylene, *m*-xylene, and *p*-xylene, with the initials written in italics as shown.

These simple aromatic hydrocarbons—benzene, toluene, and the xylenes—increase the octane rating of gasoline.

[2] Chemical names starting with "x" are pronounced as though they start with a "z." This is "zylene," therefore; not "ksylene" or "exylene."

Gasoline containing them is sometimes called *aromatic fuel* and sometimes *aviation gasoline* because it is used for airplanes. The "aromatics" are now also used in the new "super-premium" gasolines on the market for use in late-model automobiles.

Petroleum usually contains aromatic hydrocarbons along with the other varieties. The exact amount varies according to the area in which the oil well is located. Some samples of petroleum from Borneo have as much as 40 per cent of aromatic hydrocarbon.

Aromatic hydrocarbons can also be obtained from bituminous coal. Such coal, commonly called "soft coal," is 70 to 80 percent carbon. The remaining 20 to 30 percent is hydrogen and organic compounds (the latter being mostly hydrocarbon). If such coal is heated in the absence of air (to keep it from burning) everything but the carbon is driven off. The carbon that remains is called *coke.*

The material driven off from bituminous coal by the heat is partly in the form of a gas called *coke-oven gas.* This is made up mostly of hydrogen and methane. However, a small percentage of it consists of vapors of more complicated molecules. These can be separated out as a liquid called *light oil.* This is mostly benzene, toluene, and the xylenes. Every ton of bituminous coal will yield nearly three gallons of this light oil.

More benzene, in fact, is derived from coal than from petroleum. Benzene is produced in enough quantity so that it serves as a very important starting material for chemists who wish to build up more complicated molecules.

Moth Balls and Cancer

Two or more rings of carbon atoms can join up like the cells in a honeycomb. Such combinations are said to consist of *fused rings.*

A simple fused-ring compound is *naphthalene.* Its molecule is made up of a combination of two benzene rings. I will show you the formula here, both in full and in geometrical shorthand.

Unlike benzene, toluene, and the xylenes, which are liquids at ordinary temperatures, naphthalene is a white solid. Its most familiar use, at one time, was to keep moths away from clothes. It was placed among the clothes in closed trunks and closets, usually in the form of small, white spheres called mothballs. These gave off vapors that slowly filled the air within those trunks and closets. Apparently, moths found such vapors unpleasant and stayed away. Nowadays, naphthalene has been replaced by more effective compounds.

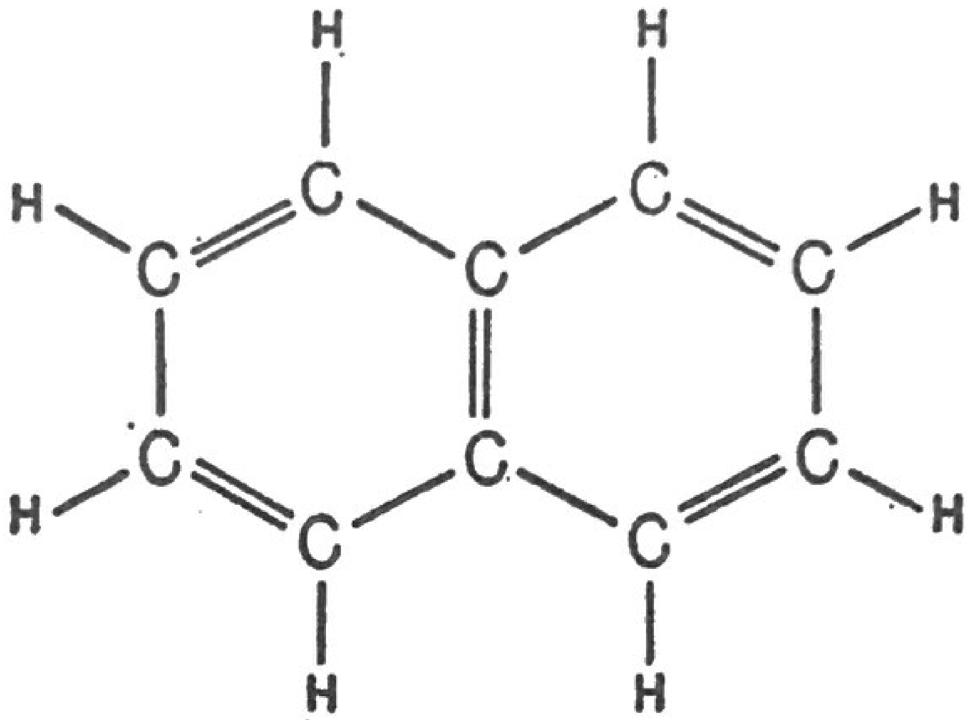


Figure 17—Naphthalene

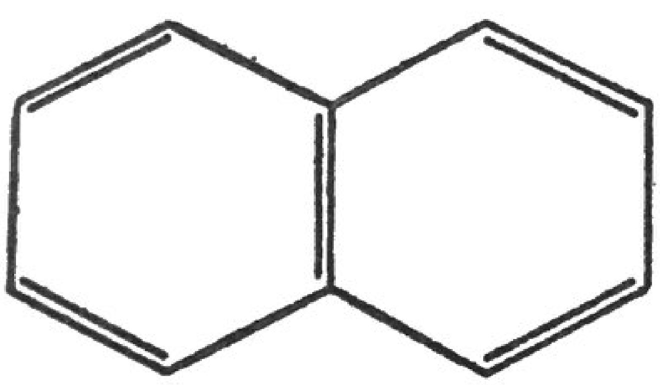


Figure 18 Naphthalene (schematic)

Some naphthalene is found in the light oil fraction of bituminous coal. More of it, however, is found in another fraction of that same coal. After the coal has been heated and the coke-oven gas fraction has been driven off, some organic material still remains in the coal. Still stronger heating drives this off, too, and it is collected as a thick black liquid called *coal tar*. A ton of bituminous coal will yield about sixty pounds of coal tar.

This coal tar is about ten percent napthalene. The rest is largely made up of other hydrocarbons with rather complicated fused-ring compounds. Compounds with three, four, five, or even more fused rings have been isolated from coal tar and some of these are quite dangerous.

In 1914 Japanese chemists first found that certain portions of the coal-tar mixture of compounds could produce cancer in animals if the coal-tar was applied to their skin for a long enough time. In 1930, British chemists discovered a particular hydrocarbon, made up of five fused benzene rings, which could be obtained from coal tar and which could cause cancer. Such a cancer-causing compound is called a *carcinogen*. Since 1930, dozens of carcinogens have been discovered in coal-tar and elsewhere.

(Recently, small amounts of carcinogens have been found in the smoke of burning tobacco. Doctors are wondering if there is a connection between cigarette-smoking and lung cancer, because lung cancer has become a good deal more common than it used to be.)

A particularly important combination of fused rings forms what we may call the *steroid nucleus*. I won't draw the detailed arrangement of atoms, but only the geometric pattern of the rings:

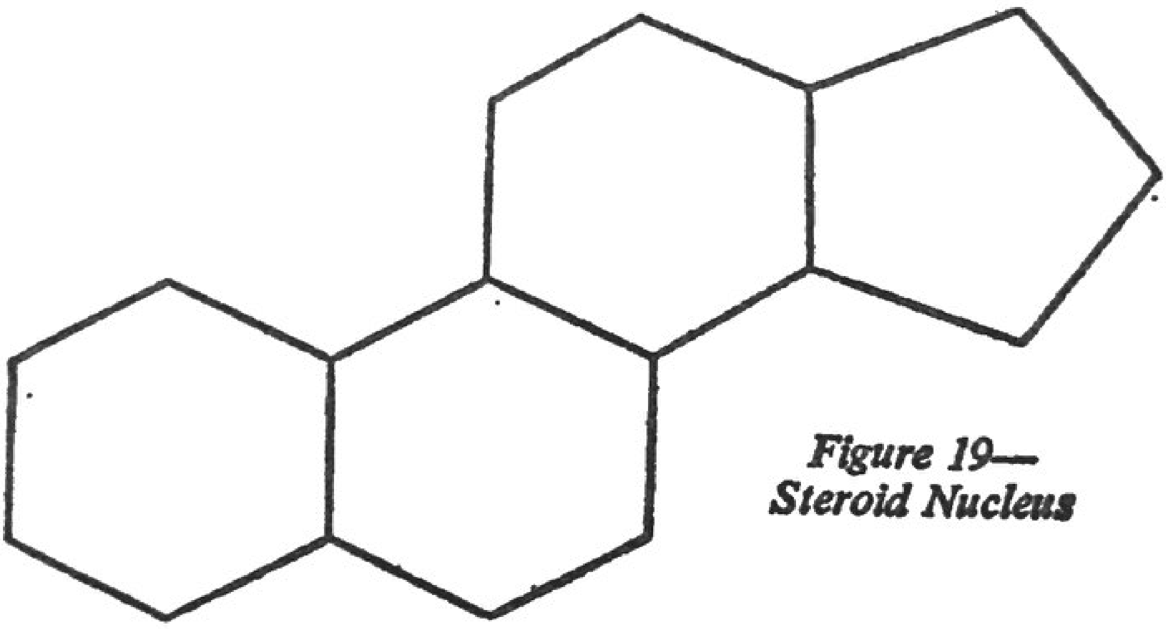


Figure 19—Steroid Nucleus

There are four rings. Three of them are six-carbon rings arranged in a bent line. (Three six-carbon rings so arranged form a *phenanthrene* group.) The fourth ring, the one on the upper right, contains only five carbon atoms. A large number of compounds containing this pattern of rings have been found in living tissue. Some are exceptionally important, too. This class of compounds is referred to as the *steroids*.

An example of a steroid hydrocarbon is *20-methylcholanthrene*. This has a molecule containing the steroid nucleus, plus an additional ring, nine double bonds, and a methyl side-chain.[8] The interesting thing about methylcholanthrene is that it is one of the most dangerous carcinogens known. Since some of the important compounds of the body also have a steroid nucleus as part of their molecules, chemists wonder if these might not be converted, occasionally, to something like 20-methyl-cholanthrene. They wonder if this might account for the development of cancer in a person. It seems unlikely, but they have not yet entirely ruled out the possibility.

[8] The Geneva nomenclature provides a system for numbering the carbon atoms in chains and rings. A name such as 20-methylcholanthrene indicates that the methyl group is attached to carbon atom number 20. Of course, you have to learn the numbering system in order to understand the formula from the name and, frankly, I have seen even experienced chemists grow confused in their numberings. We won't have to bother much with the numbers in this book.