1

Introduction

Ever since the dawn of man, humans have been chemists of one form or another. One of the first chemical reactions primitive man discovered was that certain materials could be burnt and the resultant heat released used to cook food and warm dwellings. As time progressed other chemistries were discovered, ranging from the smelting of metals to brewing to the use of plant extractions for dyeing textiles.

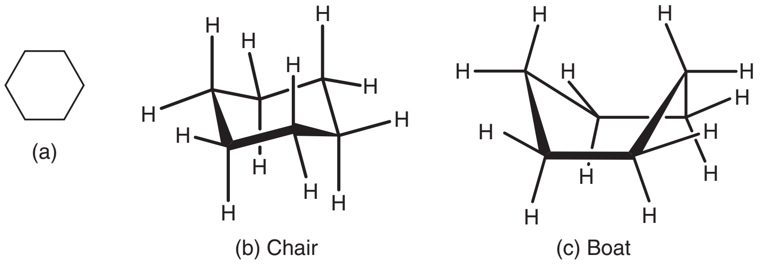
The ancient Greek philosopher Democritus proposed an atomistic theory of matter, which became popular again in the sixteenth and seventeenth centuries AD with the work of some of the great chemists of that time such as Boyle, Cavendish, Lavoisier and Priestley. Many elemental compounds were discovered by these and other workers, and later workers such as Kekulé and Frankland introduced concepts such as valence and molecular structure. One of the results of this work was the discovery of the tetravalence of carbon. Molecular structures for compounds such as alkanes, alcohols, acids and so on were also deduced around this time.

1.1 Simple Ring Compounds

Many early ring compounds were discovered and isolated and had their properties determined long before their actual physical structures were known. Once valency and the concept of the chemical bond were introduced, the structures of some alkanes were deduced to be cyclic, such as the simple hydrocarbon compound cyclohexane (Figure 1.1a). There are a huge number of simple ring carbons, ranging from the simple cyclopropane ring, the smallest of all hydrocarbon ring compounds, through to huge cyclic structures. These large structures are often termed 'macrocycles' to reflect their large size; it is with these compounds that this work is concerned.

There are many aliphatic hydrocarbon ring compounds, with cyclopropane being the smallest, followed by cyclobutane, cyclopentane, cyclohexane and so on. These simple cycloalkanes are similar to the corresponding linear alkanes in their general physical properties, but have higher melting/boiling points and densities. This is due to stronger intermolecular forces, since the ring shape allows for a larger area of contact between molecules. As chemical synthesis methods have improved, the number and ring size of these compounds have increased dramatically, as demonstrated by consideration of, for example, the crystal structures obtained for the cycloalkane $C_{288}H_{576}$.[1]

Macrocycles: Construction, Chemistry and Nanotechnology Applications, First Edition. Frank Davis and Séamus Higson.



(a)

(b) Chair

(c) Boat

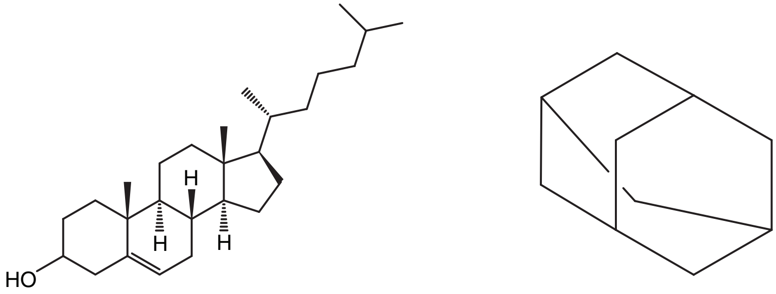
Figure 1.1 Schematic, chair and boat structures of cyclohexane

Of course, the formation of large rings is in no way limited to carbon. Many other elements can be incorporated into ring structures: sulfur for example usually exists as a cyclic S_8 compound, although other ring sizes from 6–20 and polymeric forms have been synthesised.[2] Se_8 is also known, although selenium tends to form polymeric chains. Cyclic siloxanes (with Si—O— chain repeat units) contain a variety of ring sizes and are common industrial chemicals.

Many other elements, although not capable of forming stable ring structures by themselves, can be incorporated into carbon-based rings. Typical examples include tetrahydrofuran, piperidine and ethylene sulphide. The incorporation of heteratoms into hydrocarbon rings has led to the development of several classes of macrocycles such as crown ethers and cryptands (see Chapter 2).

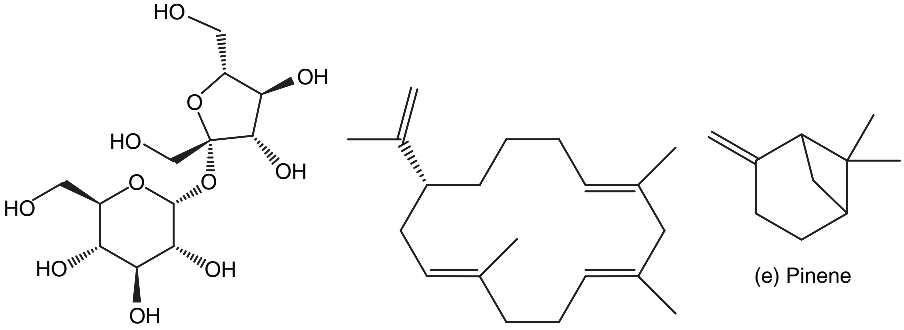
As drawn in Figure 1.1, the structure of cyclic alkanes such as cyclohexane appears to be a simple flat ring. However the real structures of these systems are far more complex. Since three points define a plane, cyclopropane is by definition flat. In cyclobutane however the carbon atoms adopt a puckered conformation, with three atoms in a plane and the fourth at an angle of about 25°. Cyclohexane, if it existed as a flat hexagon, would undergo considerable angle strain and as a consequence exists in a 'chair-like' conformation (Figure 1.1), with a carbon–carbon bond angle of 109.5°. A second, less energetically-favoured conformation is the 'boat' conformation, which cannot be isolated; there are also a number of other potential structures, such as the twist conformation. Substituted cyclohexanes can exist in the chair conformation with substituents which are either 'equatorial' or 'axial'; these two isomers tend to interconvert rapidly at room temperature. In the case of large substituents, these are mostly in the equatorial position, since this conformation is energetically more stable. Large ring structures have a multitude of possible conformers.

Multiple ring systems are also possible, either linked as in bicyclohexyl or fused as in decalin. Within the field of natural product chemistry, there are many examples of fused multiple aliphatic ring systems. A review of this is far beyond the scope of this work, but these include for example the steroid family of molecules such as cholesterol with fused cyclohexane and cyclopentane rings, as well as the multiple ring systems of adamantane. There are also a huge number of carbohydrates based on linked cyclic furanose and pyranose systems, such as sucrose. Within natural product chemistry, the five- and six-membered ring compounds tend to dominate, although there are many exceptions such as the terpenes, pinene with fused six- and four-membered rings, cembrene A with a 14-membered ring, and the penicillins, which contain a four-membered ring. An extreme example is the family of compounds known as ladderanes, which are formed by certain bacteria, an example of which is pentacycloammoxic acid,[3] with five fused cyclobutane rings. Figure 1.2 shows the structure of these compounds.



(a) Cholesterol

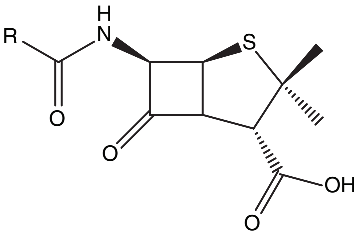
(b) Adamantane



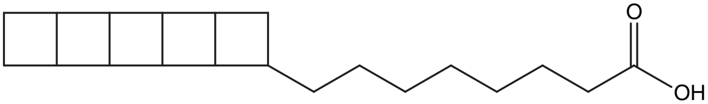
(c) Sucrose

(d) Cembrene A

(e) Pinene



(f) Penicillins

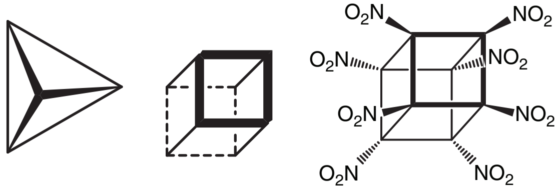


(g) Pentacycloammoxic acid

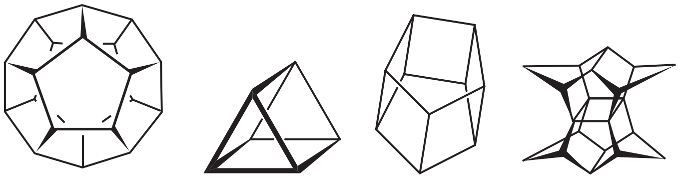
Figure 1.2 *Examples of multi-ring aliphatic compounds*

1.2 Three-Dimensional Aliphatic Carbon Structures

There is an aesthetic desire amongst chemists to synthesise molecules with a symmetry and artistic beauty. This can be seen in the amount of effort that has gone into the synthesis of numerous three-dimensional structures from carbon and a wide range of heteroatoms. Often the high degree of strain in these compounds



(a) Tetrahedrane (b) Cubane (c) Octanitrocubane



(d) Dodecahedrane (e) Prismane (f) Pentaprismane (g) Pagodane

Figure 1.3 *Platonic and other strained hydrocarbons*

can lead to unusual forms of bonding and novel chemistries. Some of these small molecules will be detailed below.

Platonic solids are regular convex polyhedra in which all angles and side lengths are identical. The simplest of the five Platonic solids is the tetrahedron. Attempts have been made to synthesise tetrahedrane (Figure 1.3), C_4H_4, but with no success, and it seems unlikely that this molecule is stable enough to exist under normal laboratory conditions. However, derivatives of tetrahedrane where the hydrogen atoms are replaced by larger stabilising groups have been successfully synthesised. Derivatives of tetrahedrane substituted with either four tertiarybutyl[4] or four trimethylsilyl[5] groups have been successfully isolated as stable solids. In the case of the trimethylsilyl derivative, the C—C bonds were significantly shorter than typical C—C bonds and this compound could also be dimerised to form a ditetrahedrane with an extremely short (144 pm) bond connecting the two tetrahedra.[5]

Tetrahedral molecules also exist for other elements. White phosphorus is made up of P_4 tetrahedra, and As_4 tetrahedra are also known. A synthesis of a substituted silicon version of tetrahedrane with an Si_4 tetrahedron substituted with stabilising silyl groups has also been reported.[6]

The second of the Platonic solids is the cube, and its chemical equivalent, cubane C_8H_8, has been known[7] since 1964. Cubane (Figure 1.3) is a stable solid melting at 131 °C and has a very high density (1.29) for a hydrocarbon. The same group demonstrated the rich chemistry of cubane by synthesising nitrated versions with between four and all eight hydrogen atoms replaced by nitro groups;[8] this is a highly energetic compound with potential for use as a high explosive. Cubane-type structures do exist in nature, such as for example a number of iron-sulfur proteins containing cubane-type structures with Fe and S atoms at alternating corners.

A third Platonic solid is the dodecahedron. Dodecahedrane ($C_{20}H_{20}$) was first synthesised[9] in 1982. The structure was confirmed by NMR spectra, which showed that all carbon and hydrogen atoms were equivalent (Figure 1.3). When a sample of dodecahedrane was bombarded with helium ions, a small fraction of the dodecahedrane molecules were shown to form a so-called $He@C_{20}H_{20}$ compound, where the helium is not bound by a chemical bond (since it is a noble gas) but rather is encapsulated in the carbon cage and physically unable to escape.[10]

Two other Platonic solids exist, the octahedron and the icosahedron. However, octahedrane (which would have the formula C_6) is thought to be too highly strained to exist, especially as stabilising groups cannot be attached. A carbon icosahedron cannot exist since it would require each carbon to bind to five neighbouring carbons, which is ruled out by the tetravalency of carbon.

Apart from the platonic solids, a series of other symmetrical hydrocarbons also exists. Benzene has the formula C_6H_6, which would normally require a combination of multiple bonds and ring systems, but much of the chemistry of benzene does not fit with the presence of unsaturated groups. One proposed structure was that of Ladenburg, which had the carbon atoms forming a prism (Figure 1.3). Although later proved not to be the structure of benzene, the compound was eventually synthesised and named prismane.[11] Prismane is stable at room temperature but decomposes to benzene upon heating.[11] A wide range of other esoteric hydrocarbons have also been synthesised, including pentaprismane[12] and pagodane.[13]

1.3 Annulenes

Many compounds have been found to have properties which are not in keeping with their predicted structures. One such is benzene, for which a formula C_6H_6 was deduced from Faraday's work in 1825, which discovered the empirical formula and molecular weight of benzene. However, if the classical valencies of carbon and hydrogen were to be maintained, this would require the incorporation of multiple rings or bonds within the structure. A number of possible structures were proposed but the one that became most prevalent was that of Kekulé, who suggested that benzene was in fact cyclohexa-1,3,5-triene (Figure 1.4a), with a six-membered ring structure containing alternating double and single bonds.[14] This explained some of the properties of benzene, such as the fact that there was only one isomer for singly-substituted benzenes but three isomers of disubstituted rings.[15] Twenty-five years later at a meeting in his honour, Kekulé apparently spoke of how he had realised the structure of benzene during a dream in which he saw a snake biting its own tail.

However, it soon became obvious that benzene could not be the simple hexatriene originally postulated. First it was realised that there should be more isomers of disubstituted compounds than could be isolated. The three isomers of, for example, dimethyl benzene are the 1,2, 1,3 and 1,4 substituted derivatives. However, there should be two isomers of 1,2-dimethylbenzene, as shown in Figure 1.4b. These compounds ought to be separable, but only one isomer could be isolated. One possible explanation for this could be that benzene and substituted benzenes are mixtures of two rapidly equilibrating cyclohexatrienes.

Another fault with the postulated structure was that the chemistry of cyclohexatriene should be that of a highly reactive alkene; cyclohexatriene should for example decolourise bromine water, with the concurrent formation of highly brominated derivatives. However, for benzene this reaction does not occur under conditions under which many other alkenes readily brominate. This required the development of molecular orbital theory and the idea of resonance energy. Instead of alternating single and double bonds, a structure was proposed where the carbon–carbon bonds are intermediate between single and double bonds. Interactions between the p-orbitals lead to the formation of circular delocalised 'clouds' of electrons above

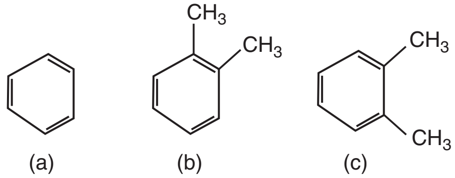


Figure 1.4 *Structures of 'cyclohexatriene' and isomers of 'dimethyl cyclohexatriene'*

and below the plane of the carbon atoms. The convention is to draw the six-membered benzene ring as a hexagon with a circle (symbolising the cyclic delocalised system) inside it (Figure 1.5a). The symmetry of such a structure was finally proved when X-ray crystallography could be utilised to determine the structure of the benzene ring. Work by Kathleen Lonsdale in 1929 on hexamethylbenzene[16] showed it to have a symmetrical flat hexagonal structure, with the C—C bonds of the ring having a length (142 pm) intermediate between those of carbon–carbon single and double bonds. The term 'aromatic' was coined for hydrocarbons of this type.

One consequence of molecular orbital theory was the Huckel $4n + 2$ rule. For a molecule to have aromatic properties it must follow three rules: it must have $4n + 2$ electrons in a circular conjugated bond system (for example, benzene has six, i.e. $n = 1$), it must be capable of assuming a planar (or almost planar) conformation, and finally each atom must be able to participate in the delocalised ring system by having either an unshared pair of electrons or a p-orbital.

Once this rule was formulated, interest was generated in synthesising analogues of benzene with alternating single/double bonds but of different ring sizes. These compounds have been grouped under the name '[n]annulene', where n is the number of atoms in the ring. Therefore benzene could be referred to as [6]annulene. A wide range of other annulenes have been synthesised.

The smallest annulene, cyclobutadiene or [4]annulene (Figure 1.5b), has four electrons available to participate in an aromatic system. This does not follow the $4n + 2$ rule and experimental measurements show that there is no aromaticity. Cyclobutadiene is rectangular rather than square and is highly reactive, forming a dimer with a reaction half-life measurable in seconds. However, metal–cyclobutadiene complexes[17] such as $(C_4H_4)Fe(CO)_3$ display much higher stabilities because the metal atom donates two electrons to the cyclobutadiene ring, giving it six electrons, which enables it to obey the $4n + 2$ rule. Similarly, the dilithium salt of a tetrasilylated cyclobutadiene dianion,[18] $C_4(SiMe_3)_4{}^{2-}$ $2Li^+$, has been shown to be relatively stable at room temperature and to contain a square, planar cyclobutadiene species.

Cyclooctatetraene or [8]annulene (Figure 1.5c) was found not to be aromatic and displayed the chemistry of a conjugated polyene. However, it is much more stable than cyclobutadiene and is available commercially. With eight electrons, cyclooctatetraene was not expected to have an aromatic structure, as confirmed by an X-ray study[19] which showed the molecule adopts a 'tub' shape with alternating single and double bonds. Reaction with potassium metal gives a dianion, however, which is highly stable, obeys the $4n + 2$ rule since it has 10 electrons – and has been shown to be planar and aromatic in nature by X-ray studies.[20]

A large range of higher annulenes have been synthesised and a comprehensive review is beyond the scope of this chapter. Early work has been reviewed by Sondiemer,[21] and much later work has also been reviewed.[22] Within this chapter we will provide a brief summary of work that has been carried out in this field.

[10]annulene has been synthesised. Since this obeys the Huckel $4n + 2$ rule, it would be expected to be aromatic. However, the NMR and reactivity of this compound are typical of a polyene-type structure rather than an aromatic one. This can be explained by the fact that aromatic systems need a high degree of planarity. A simple all-cis ring system such as that shown in Figure 1.5d would have C—C bond angles of 144° rather than the 120° found in benzene. This high degree of strain prevents a planar structure from forming; a possible structure with two trans double bonds would alleviate this but would display a high degree of steric repulsion between the hydrogen atoms shown in Figure 1.5e. This can be alleviated however by removing the two hydrogens and replacing them, for example with a methylene bridge[23] as shown in Figure 1.5f. This compound is still not completely planar but the NMR spectrum indicates considerable delocalisation. A triply bridged system (Figure 1.5g) with increased planarity has also been synthesised[24] and displays considerable aromatic chemistry.

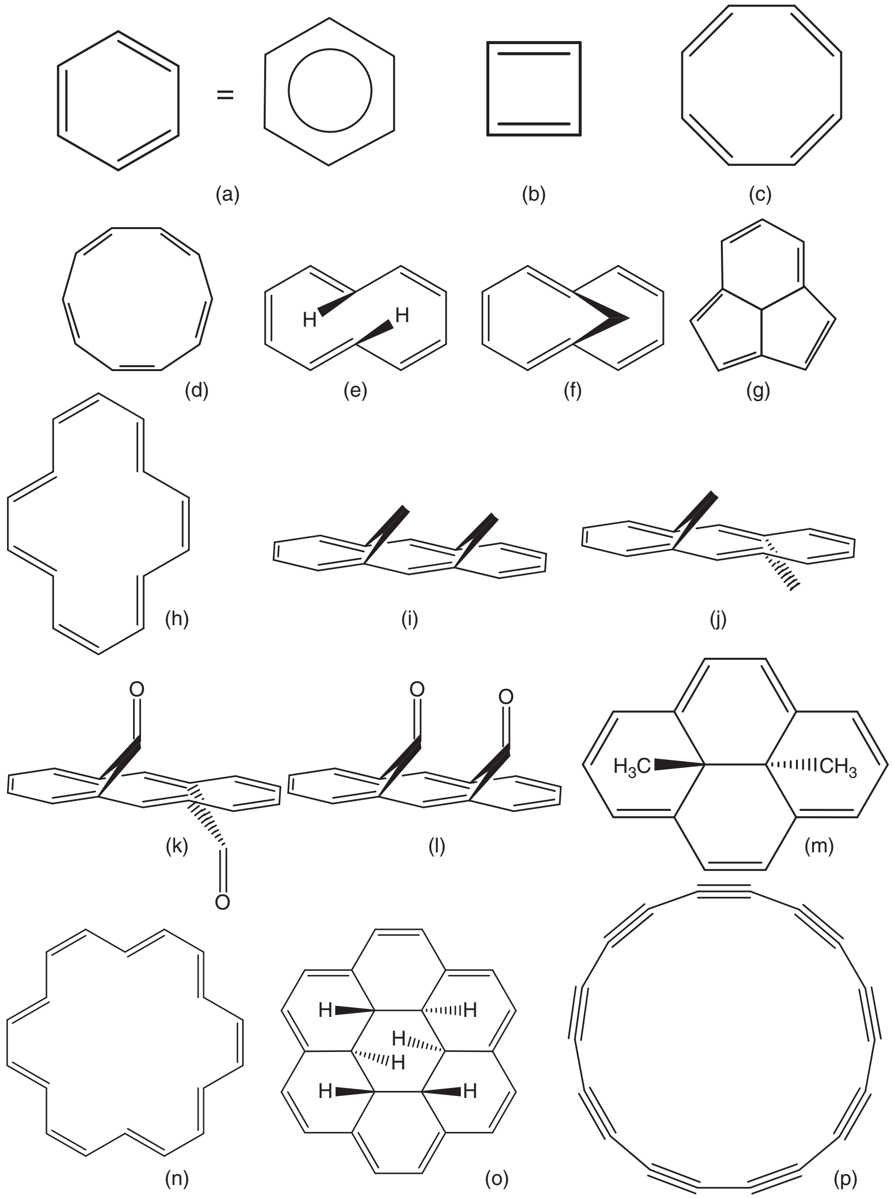


Figure 1.5 *Structures of the annulenes*

[12]annulene behaves similarly to cyclooctatetraene in that it is nonplanar and highly reactive. Reaction with lithium metal gives the dianion,[25] which does obey the $4n + 2$ rule and although nonplanar is much more stable than the parent compound, indicating some aromaticity. Very similar behaviour is observed for 16-annulene,[26] with the parent compound displaying polyene-type chemistry and the dianion being much more stable and almost planar.

[14]annulene (Figure 1.5h) obeys the 4n + 2 rule and is therefore aromatic. However, there is some steric interference from hydrogen atoms located within the ring, which leads to deviations from planarity. X-ray crystallographic studies[27] demonstrate this, but there is no single/double bond alternation and other studies such as the NMR spectra also confirm the aromatic structure.[21,22] Attempts have been made to reduce the ring strain by replacing the internal hydrogens with bridging groups such as methylene. For example, compounds have been synthesised with two methylene bridges (Figure 1.5i). When the bridges are on the same side of the ring, a stable compound with an aromatic structure results,[28] whereas when the bridges are opposite to each other (Figure 1.5j) a puckered polyene structure is observed[29] and the compound reacts readily with oxygen. Similar behaviour occurs when carbonyl bridging groups are used,[30,31] with the *syn* (Figure 1.5k) isomer being highly stable and displaying a flat aromatic system, whereas the *anti* (Figure 1.5l) isomer is unstable and shows no evidence of aromaticity. More complex bridging units have also been utilised, such as in the dihydrodimethylpyrene molecule shown in Figure 1.5m, which has an outer 14-carbon ring with alternating double bonds and is strongly aromatic. X-ray studies show a structure in which all the peripheral bonds are essentially the same length and in the same plane.[32] A large number of compounds of this nature have been synthesised and their aromaticity has been investigated in detail.[22]

Apart from benzene itself, [18]annulene (Figure 1.5n) is the most stable of the annulenes[22] and it has the correct number of atoms to allow bond angles of 120°, thereby eliminating ring strain. X-ray studies show that it has an approximately planar structure with C—C bond lengths varying from 0.138 to 0.142 nm throughout the structure,[33] although there are some minor deviations from planarity due to steric interactions and crystal packing. An interesting structure has been synthesised[34] in which bridging groups increase the rigidity of the ring, as shown in Figure 1.5o; this compound has been shown to have a higher ring current (88% of the predicted maximum), indicating more efficient conjugation than [18]annulene (56%).

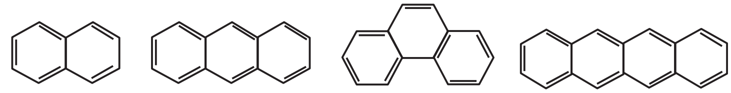
The higher annulenes, [20]annulene,[35] [22]annulene[36] and [24]annulene,[37] have all been successfully synthesised. NMR spectra indicate as expected that [22]annulene is aromatic (unfortunately as yet no X-ray structures have been obtained to confirm this), whereas [20] and [24]annulene are not. Syntheses of [30]annulene have been reported[38] but yields were too low to adequately characterise the material, the product was quite unstable and no evidence for aromaticity could be obtained. Theoretical studies on annulenes containing up to 66 carbons have been carried out;[39] these indicate that for annulenes containing 30 or more carbon atoms, conformational flexibility will lead to a drop in electron delocalisation and nonaromatic structures with alternating single/double bonds will predominate.

A range of dehydroannulenes with one or more triple bonds within the ring system have been synthesised, often as intermediates in the process of making various annulenes.[21,22] These usually tend to show less aromaticity and be less stable than the annulenes themselves. However, they are systems of interest and have been the subject of several reviews[21,22,38,40]. One of the simplest dehydroannulenes is benzyne or didehydrobenzene, C_6H_4, which is an extremely reactive species that can be trapped by, for example, a Diels–Alder reaction with such species as cyclopentadiene or anthracene, and can be stabilised by complexation with transition-metal atoms. A hexadehydrobenzene species with alternating single and triple bonds would be highly unlikely to exist due to the extremely high ring strain within such a molecule, but the larger C_{18} ring has been predicted to be relatively stable, possibly as a polycumulene with all the bonds being C═C double bonds rather than with the alternating single/triple bond structure, as shown in Figure 1.5p.[41] The C_{18} ring system and larger C_{24} and C_{30} rings have not been synthesised and characterised as yet but evidence of the C_{18} ring has been detected in mass spectra[42] and by trapping it as a reaction product in a low-temperature glass.[43] It has also been postulated to be a component of interstellar clouds and to exist in the hearts of dying stars.[22]

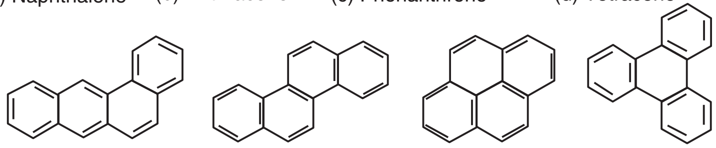
1.4 Multi-Ring Aromatic Structures

Hexagons are one of the shapes that can pack perfectly without any intervening space, as shown for example by the structure of a honeycomb. This is exemplified in aromatic chemistry by the large number of fused-aromatic-ring-system compounds that have been discovered in natural substances or synthesised over the years. Although aromatic, not all of these compounds obey the Huckel 4n + 2 rule, which appears not to be valid for many compounds containing more than three fused aromatic rings. Examples of some of these are shown in Figure 1.6.

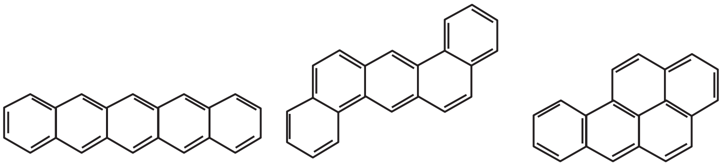
[TI]Naphthalene consists of two benzene rings fused together and is commercially extracted from coal tar. Its major uses include as a fumigant, for example in mothballs, and as an intermediate in the synthesis



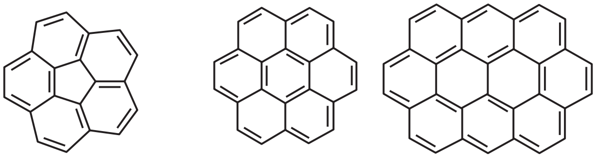
(a) Naphthalene (b) Anthracene (c) Phenanthrene (d) Tetracene



(e) Benzanthracene (f) Chrysene (g) Pyrene (h) Triphenylene



(i) Pentacene (j) Dibenzanthracene (k) Benzopyrene



(l) Corannulene (m) Coronene (n) Ovalene

(o) Kekulene (p) Hexahelicene

Figure 1.6 *Multi-ring aromatic compounds* of other industrial chemicals such as phthalic anhydride. The molecule is planar, with carbon–carbon bond lengths that are not all identical to each other but are close to those of benzene. Extended versions of naphthalene with three (anthracene), four (tetracene), five (pentacene) and more rings have been either isolated from products such as coal tar or synthesised in the laboratory.

Anthracene, with three fused benzene rings, is again commonly extracted from coal tar. Anthracene is planar and the central ring is much more reactive than the others. For example, the central positions are easily oxidised to give anthraquinone and the central rings participate readily in Diels–Alder type reactions with a variety of dienes. Irradiation with UV light causes anthracene to dimerise via a $4+4$ cycloaddition reaction of the central rings. Tetracene is a pale orange powder which can act as a molecular organic semiconductor. Again it is planar, prone to oxidation and readily participates in Diels–Alder reactions. Pentacene is a blue oxygen-sensitive compound and is being investigated for such purposes as use in organic thin film transistors[44] and photovoltaic devices.[45] Hexacene and heptacene cannot be isolated in bulk since they readily dimerise and are extremely oxygen-sensitive, although derivatives of these compounds have been isolated.

Other polycyclic aromatic hydrocarbons include the three-ring-system phenanthrene (Figure 1.6f), again with the central ring being the preferred site for a wide range of chemical reactions. Larger systems include pyrene, which is widely used as a fluorescent probe, and chrysene, which is similar in reactivity to phenanthrene. Many of these hydrocarbons have been found in tobacco smoke and some, such as benzopyrene, have been shown to be highly carcinogenic.[46]

Larger ring systems have also been studied, such as coronene, which occurs naturally in the mineral carpathite, and ovalene, which can be formed in deep-sea hydrothermal vents. One of the larger systems synthesised is kekulene, with its large inner cavity. X-ray experiments[47] have demonstrated that the structure of kekulene is that of a large flat ring, but not all of the bond lengths are equivalent and it appears it contains six discrete aromatic rings linked together, rather than being one large aromatic system. One of the largest systems synthesised contains 222 carbon atoms.[48] As these systems become larger, the compounds become less soluble and their properties approach those of graphite, which has a structure essentially of layers of infinite benzene rings, that is carbon atoms arranged in a hexagonal lattice with carbon–carbon distances of 0.142 nm, and planes separated by 0.335 nm. Single-graphite planes have been isolated; this material is known as graphene and is the subject of much current research due to its potential novel physical and electronic properties.[49]

The aromatic systems mentioned so far have been in the main planar or near-planar structures. Not all aromatic systems follow this rule. Hexahelicene (Figure 1.6p) consists of six aromatic rings and would be expected to have a planar structure. However, this would mean that the atoms at the extreme ends of the cyclic structure would have to occupy the same space. This is impossible, so the molecule is actually twisted into a spiral shape, meaning that it is chiral. Both of the isomers have been isolated[50] and display high optical rotation (3640°). Corannulene (Figure 1.6l) is not flat like the similar coronene structure, but is in fact bowl-shaped. The 'central' ring is five-rather than six-membered, which results in the loss of planarity. The ultimate example of the effect of five-membered rings on aromatic compounds is in buckminsterfullerene, where the presence of 12 five-membered rings along with 20 six-membered rings causes the C_{60} molecule to assume the shape of a sphere.

1.5 Porpyrins and Phthalocanines

Most of the ring systems described earlier in this chapter are simple hydrocarbons. However, there are a huge number of aromatic systems that include heteroatoms. These range from simple molecules such as pyridine, pyrrole, furan and thiophene through to much larger compounds. One very important class of compounds is the porphyrins.

The basic structure of the porphyrin unit is shown in Figure 1.7a; it consists of a large flat aromatic ring with four pyrrole units bound together by methane carbons. The parent macrocycle contains 22 electrons, thereby obeying the $4n + 2$ rule. Porphyrins are usually very highly coloured compounds due to the presence of this large aromatic system. There are many methods of synthesising porphyrins but the simplest involves cyclisation of pyrrole with substituted aldehydes, as shown in Figure 1.7b. Four aldehydes condense with four pyrrole units under acidic conditions to form a cyclic tetramer[51,52] (the initial tetramer formed is not actually aromatic but under the conditions of the reaction is readily oxidised to the porphyrin).

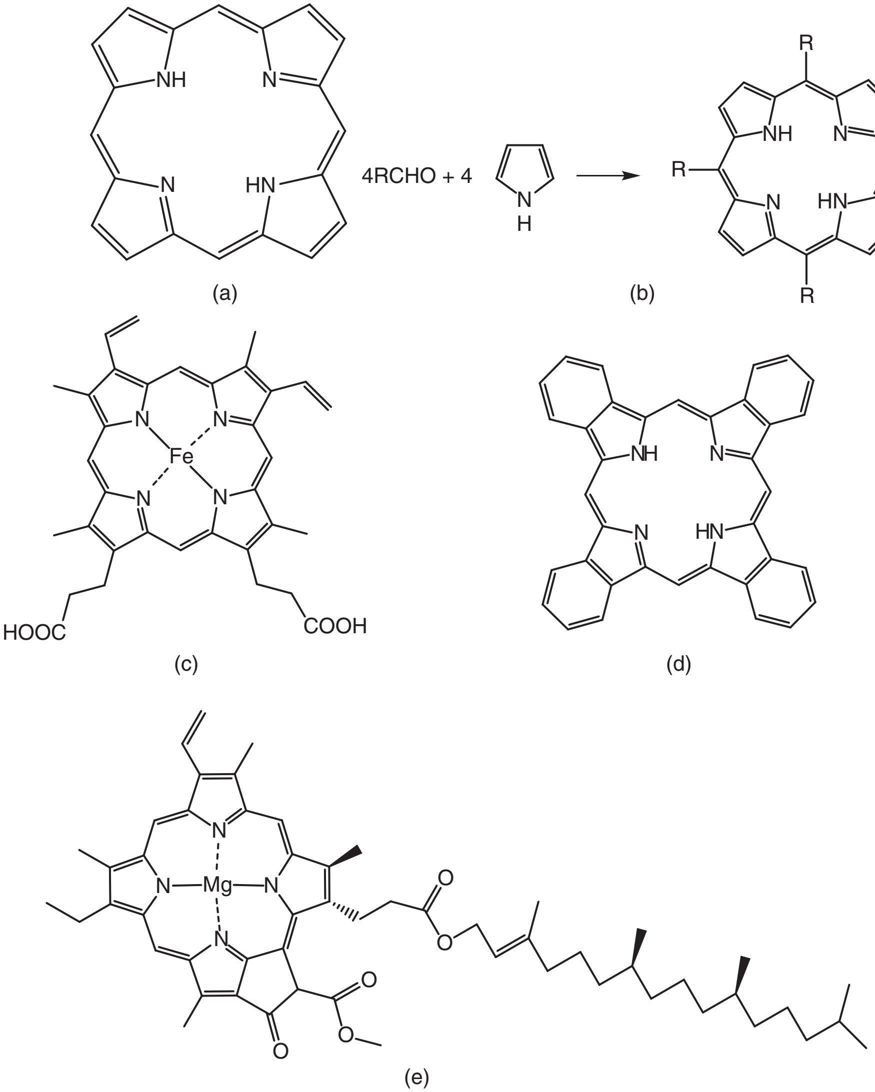


Figure 1.7 *Structures of some porphyrins*

The presence of the nitrogen atoms within the ring facilitates the binding of metal atoms to form metalloporphyrins. In the parent porphyrin structure (known as a free-base porphyrin), two of the nitrogen atoms have hydrogen atoms bound to them. Upon binding of metals these hydrogen atoms are lost and the metal is bound within the central N_4 cavity. One example of this metal binding can be found in the heme porphyrins such as heme B (Figure 1.7.c). These types of porphyrin reversibly form complexes with oxygen and are found within haemoglobin, the oxygen-carrying protein that makes up much of our red blood cells.

Many variations on the porphyrin theme are known. The aromatic system can be extended as in the tetrabenzoporphyrins (Figure 1.7d). Alternatively, more reduced forms or variations where one of the methane units is missing and replaced by a direct pyrrole–pyrrole connection are known. These systems generally do not obey the $4n + 2$ rule. These related porphyrin analogues include corrins (containing a direct pyrrole–pyrrole link and found in such natural products as vitamin B12), along with the reduced forms known as chlorins, bacteriochlorophylls and corphins. Bacteriochlorophylls and corphins are used as subunits in enzymes found in certain bacteria. Chlorins, which can be thought of as dihydroporphyrins, are widely found in nature. A magnesium chlorin (Figure 1.7e) is a typical example, known as chlorophyll A; this unit is vital to the process of photosynthesis and without this group of materials, green plants and therefore ultimately most other forms of life would not exist.

Phthalocyanines are synthetic analogues of tetrabenzoporphyrins, in which the methine bridges are replaced by nitrogen atoms. These are flat aromatic systems similar to porphyrins and can complex metal atoms in a similar manner, as shown for copper phthalocyanine in Figure 1.8. The phthalocyanines are highly coloured systems due to their large aromatic ring systems and tend towards the blues and greens. This, combined with their stability, has led to extensive use of substituted phthalocyanines within the dye industry (for instance, copper phthalocyanine is known as phthalocyanine blue BN). There are a wide variety of methods for the synthesis of phthalocyanines, mostly based on similar cyclisation reactions to those used for the porphyrins. An example is given in Figure 1.8b, which shows the condensation of four phthalonitrile units to form phthalocyanine.

The simplicity of the phthalocyanine synthesis and the wide variety of structural variations available have made these compounds the subject of widespread interest. Possible applications abound due to the novel physical, electronic and optical properties of these materials, along with their thermal and chemical stability. A review of this is outside the scope of this work, but we will mention that phthalocyanines and their derivatives have been investigated for use as optical switches, liquid crystals, sensors, organic photoelectric cells, nonlinear optical materials, electrochromic materials and optical information-recording media.[53]

The wide synthetic flexibility of these materials has led to a plethora of variations on the basic phthalocyanine unit. For example, the benzo units can be replaced with naphthalene or anthracene units to give extended phthalocyanines. Polymeric materials based on phthalocyanines have been made by linking the phthalocyanines edge to edge, or via a substituent group or via atoms complexed in the centre of the phthalocyanine cavity.[53,54] In addition to this, the presence of an N_8 unit (rather than N_4 for porphyrins) has allowed the binding of larger metal atoms such as the lanthanides. Due to the presence of the d-orbitals on these metals, they can bind to more substituent atoms. This has enabled the development of compounds such as the bis-phthalocyanines:[55] for example lutetium bisphthalocyanine, whose optical spectra change dramatically on exposure to various vapours, giving rise to potential sensor applications. Trisphthalocyanines are also available; in this context workers have for example sandwiched a lutetium atom between two phthalocyanine rings and then added a europium atom and a third phthalocyanine ring (Figure 1.8d) to make a triple-decker sandwich compound.[56] It has also been possible to make polymeric phthalocyanines via a central atom, with examples including polyphthalocyanines linked by a central Si—O chain (Figure 1.8e), which have been synthesised and deposited as ultrathin films[57] and shown to display novel liquid-crystalline properties.[58]

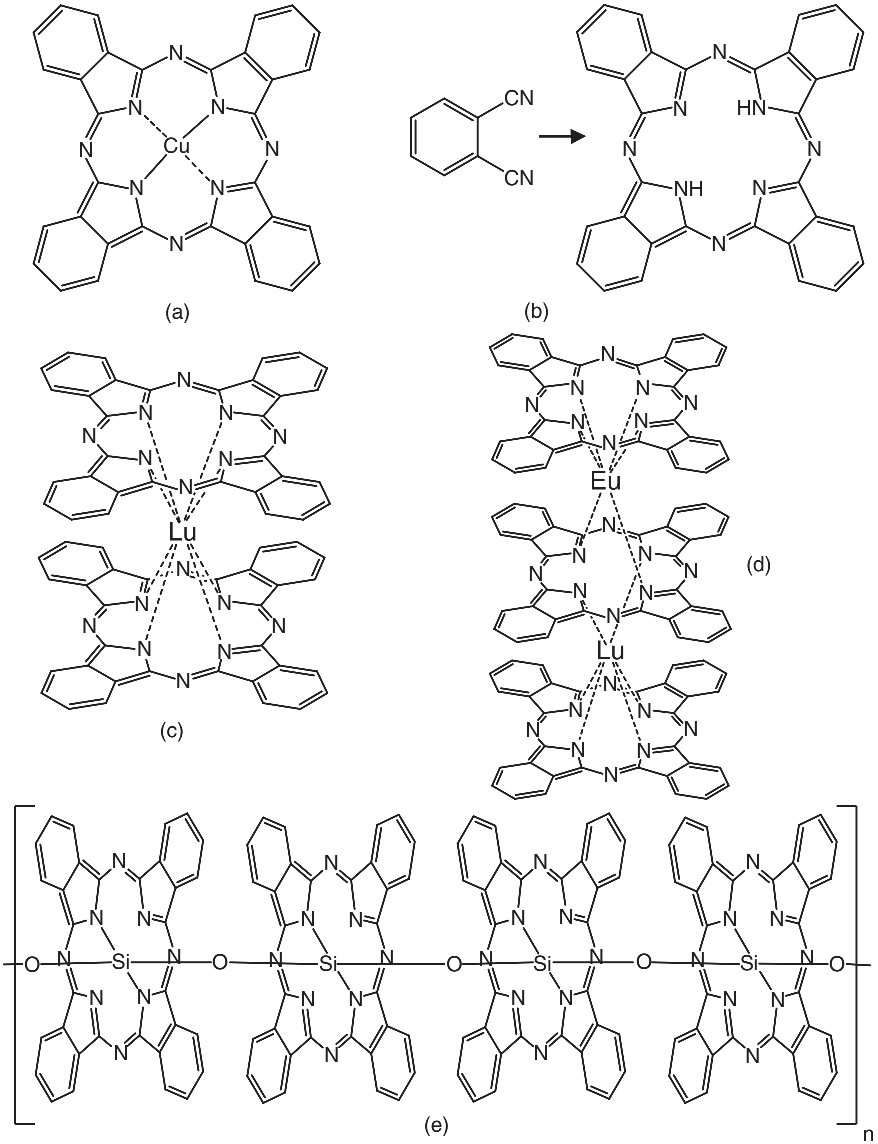


Figure 1.8 Structures of mono, bis, tris and poly phthalocyanines

1.6 Conclusions

This chapter has served to introduce some of the simpler ring systems, both aliphatic and aromatic in nature. The aromatic systems tend to have planar or distorted planar structures, which can limit their ability to form complexes (but not prevent it, as the examples of porphyrins and phthalocyanines prove). Further chapters will address the many ring systems that are nonplanar, which thus possess three-dimensional structures that allow for a richness and diversity of chemistry and complex formation.

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