CHAPTER ONE

INTRODUCTION to LIQUID CRYSTALS

1.1   Historical background

Liquid crystals display are well known today to a broad community, since these devices are widely used in electronic watches and calculators. However, the function of these displays or scientific background of the liquid crystalline state is less commonly known to the public, eventhough the liquid crystalline state was detected more than 100 years ago. The earliest recognition of liquid crystals is normally attributed to the Austrian botanist Reinitzer [1] who in 1888 observed colour changes when melts of cholesteryl acetate or benzoate were cooled. These phenomena were investigated by Lehmann [2] (whom at that time, was the leading crystalographer in Germany) with his polarzing microscope and he called these new phases " liquid crystals" because they appeared to be liquid with optical properties reminiscent of those of a crystal.

Over the next few year about 15 liquid crystalline compounds became known; in all these cases the detection of the liquid crystalline phases occured by chance since no connection between the molecular shape and the liquid crystalline state was known. Soon after 1900, Daniel Vorlander, who was professor of chemistry at the University of Halle, started his systematic synthetic work in order to find connections between the molecular structure of chemical compounds and the occurrence of the liquid crystalline state. Proved by many examples and counter examples, Vorlander, already in 1908, was able to establish his rule that liquid crystalline compounds must have a molecular shape

as linear as possible. Until Vorlander's retirement in 1935, in his laboratory about 1100 liquid crystalline substances were synthesized; they constituted about 90% of the liquid crystals known until 1960. He may be considered the "father of the liquid crystal chemistry".

In the first three decades of this century, especially French crystallographers were very active in liquid crystal research. The most outstanding contribution to thier work was by G. Friedel [3] (University of Strasbourg), who in 1922 proposed a classification and nomenclature of such phases which has since been widely adopted. He also introduced the term " mesophase " (meaning " middle phase") to replace the more ambiguous " liquid crystal" and substances forming mesophases were consequently called " mesogens".

Induced by the applications of liquid crystals in optoelectronic displays and for thermography in mid-1960s, liquid crystal research increased exponentially and spread from a few centers to many institutions in all developed industrial countries. Due to strong success in the practical as well as the theoretical investigation of the liquid crystalline state in the 1970s there seemed to be a certain stagnation in " spectacular " findings until 1977, when Chandrasekhar was able to show that not only rod -like molecules, but also compounds with disc like molecular shape are able to form liquid crystals of different phase structures. In recent years the gap between rod-like and disc-like molecules could be filled with lath-like molecules, which also are able to form liquid crystalline phases. In actual fact any derivation from spherical shape has the potential to form liquid crystals.

There was little commercial interest in liquid crystals untill the 1960's when the first electro-optic display were developed . Problems with phase stability were only overcome in the early 1970's with the introduction of the cyanobiphenyls by Gray [4,5]. There has since been considerable research into all aspects of liquid crystal behaviour for example the in recent years there has been particular interest in liquid crystal polymers which offer an impressive range of mechanical and optical properties with many potential applications[6].

1.2   The Position and Types of Liquid Crystals

Liquid crystals represent a number of different states of matter in which the degrees of molecular order are intermediate between the almost perfect long range positional and orientational order in crystalline solids and the long range disorder found in normal isotropic liquids. In general they possess long range orientational order with varying degrees of translational order. They have physical properties characteristic of both isotropic liquids and crystals; a liquid crystal flows like an ordinary liquid but some properties, such as birefringence, are more typical of the crystalline phase. Liquid crystals are also called crystalline liquids, mesophase or mesomorphic phases. Compounds with mesomorphic properties may be called "mesogenic". Liquid crystals can be divided into two main classes; lyotropics and thermotropics.

Lyotropics are formed by amphiphilic compounds (i.e. compounds that consist of molecules which contain both lipophilic and hydrophilic groups) and solvents,

commmonly water [7]. At concentrations intermediate between the pure amphiphile and the isotropic liquid, there exist structured phases consisting of amphiphile and solvent which exhibit anisotropic properties characteristic of liquid crystal phases. The mesophases are thus said to be "solvent induced". Common examples of lyotropics are those produced from soaps and other detergent systems and water.

Thermotropics are formed by heating the pure crystalline solid or cooling the isotropic liquid and so the mesophases are "temperature induced". Their constituent molecules tends to be elongated and rod-like, lath-like or disc-like [8], although more recently mesophases formed by bowl-like and banana-shape [9] molecules have also been reported. Often non-mesogenic components may be added to alter physical properties such as the melting point or other transition temperatures. Since in this thesis applications of liquid crystals have involved those of the thermotropic type, therefore we shall discuss these in more detail.

1.3   Description of Thermotropic Liquid Crystals

Based on the molecular structure of constituting molecules, thermotropic liquid crystals can be classify into three types namely calamitic, discotic and sanidic. The *calamitic* liquid crystals which occur in rod-like molecule, may considered as the classical liquid crystals namedly nematic, cholestric and smectic (section 1.3.1). *Discotic* liquid crystals are formed by disc-like molecules, up to the present knowlegde, only the columnar and the nematic counter part of the discotic liquid crystals have been

observed (section 1.3.2) and lastly the *sanidic* liquid crystals occuring in lath - like (board -like) molecules which were first found in 1986 were discussed in section 1.3.3. A brief outline characteristic of each phases are presented in following section.

1.3.1   Calamitic Liquid Crystals

Nematic

In the nematic phase (N) the molecules are, on average, aligned with thier long axes parallel to some prefered direction. Around this direction there is rotational symmetry and so the phase is uniaxial. The local direction of alignment is described by a unit vector ñ, the director, which gives at each point in a sample the direction of the preferred axis. The sign of the director has no significance, that is n is indistinguishable from -ñ The director will vary continuously throughout a sample but a uniform director pattern can be obtained with relatively small external fields (e.g. a magnetic field of 0.02 T) or by using aligning substrates [10]. A schematic representation of the nematic phase is given in Figure 1.1 (a).

Cholesteric

As the name suggests cholesteric liquid crystals can be observed with cholesterol deriavatives, e.g. cholesteryl benzoate, but non-sterol compounds also form this phase, the only necessary condition being that the compounds are optically active. Alternatively, a cholesteric phase can be produced by dissolving optically active materials into a nematic. The phase is thus more appropriately called a chiral nematic (N*). The
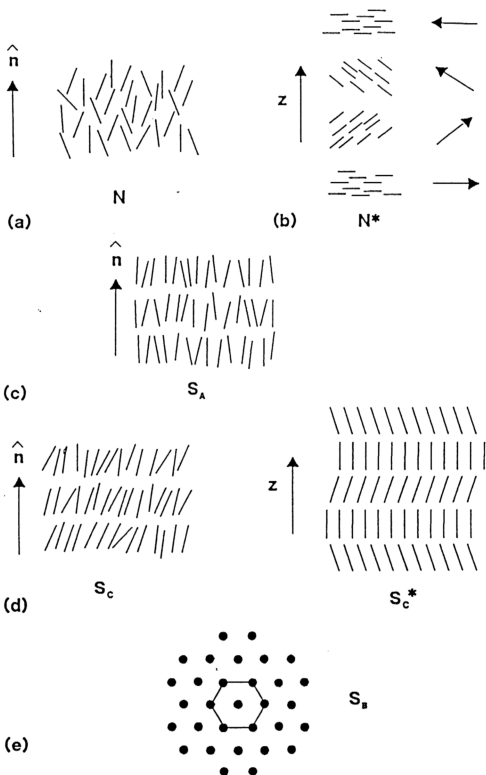
Figure 1.1   Schematic representations of mesophases: (a) nematic (N),
(b) cholesteric or chiral nematic (N*), (c) smectic A (S_A),
(d) smectic C (S_c) and chiral smectic C(S_c*), (e) arrangement
of centres of mass in a single layer of a smectic B.

local order is similar to that found in nematics but there is a spatial variation of the director leading to a helical structure (see Figure 1.1 (b)). The pitch of the helix can be strongly temperature dependent hence the optical properties are directly related to the pitch. Indeed, the cholesteric phases, over the past twenty years, there were many hundreds of patents and papers have been published describing a remarkable range of thermometric, thermographic and other application devices [11]. In biomedical, thermography [12] is an important diagnostic aid which is used to assist in the identification of a wide range of medical conditions. For example cholesteric liquid crystals have been used to produce visual thermal maps like breast cancer detection [13], placental location [14], vascular disorder [15], skin grafting [16] and etc.

Smectic

Smectic phases exhibit long range orientational order as in the nematic phase but, in addition , there is some positional order. The molecular centres of mass, on average, arranged in equidistant planes. Several types of smectic phase have been observed, the most common being the A,B and C phases. Schematic representations of these are shown in Figure 1.1 (c), (d) and (e).

The smectic A phase (S_A) consists of layers of molecules with the director parallel to the layer normal. There is no long range order within the layers and the layer spacing is about one molecular length. The S_A phase has point symmetry $D_{\infty h}$ and is optically uniaxial.

The smectic C phase (S_C) has a similar structure to that of the S_A phase but the

director is tilted away from the layer normal. The symmetry of the phase is now C_{2h} and is optically biaxial. If a chiral molecule forms a smectic phase or is incorporated into one then the resulting structure becomes chiral and contains a helical twist (see Figure 1.1 (d)). This does not occur in the a conventional smectic A although a chiral A phase has been reported where there is a helical distortion of the smectic layers [17]. Chiral smectic phases are of particular interest because of thier application in ferroelectric display devices which show extremely fast response speeds [18,19,20,21].

Cooling a smectic A or smectic C phase for some material or molecules may result in the formation of a phase known as a smectic B (S_B) which is characterised by the presence of the long range positional order within the layers. X-ray studies have shown that in fact the molecules are packed in an hexagonal array [22]. There is also true long range bond orientational order. In other words, even though the short range positional order extends over only one or two layers, the layers may not rotate relative to each other and so there is long range order of the local lattice vectors. The phase is necessarily optically uniaxial and has symmetry D_∞. Various other smectics include the S_F and the S_I phases which are tilted analogues of the S_B which possesses a herringbone type packing within the layers [23].

A single mesogenic compound can exhibit a considerable number of mesophases. Normally, in order of increasing temperature, they occur in the sequence   crystal (C) - S_B- S_C- S_A- N - Isotropic liquid (I). Some examples of mesogens and thier respective transition temperature are given in Table 1.1.

4,4´-dimethoxyazoxybenzene

CH_3O—⟨benzene⟩—N=N—⟨benzene⟩—OCH_3
|
O
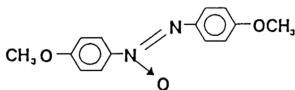
C 118°C N 135.5°C I

4-n-heptyl-4´-cyanobiphenyl (7CB)

C_7H_{15}—⟨biphenyl⟩—CN
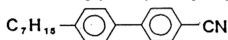
C 28.5°C N 42°C I

cholesteryl chloride

Cl
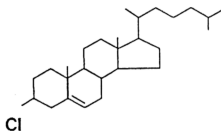
C 96°C I (64 N*)

4,4´-dinonylazobenzene

C_9H_{19}—⟨benzene⟩—N=N—⟨benzene⟩—C_9H_{19}
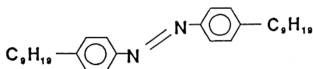
C 38°C S_B 41°C S_A 54°C I

4,4´-diheptyloxyazoxybenzene (HOAB)

$C_7H_{15}O$—⟨benzene⟩—N=N—⟨benzene⟩—OC_7H_{15}
|
O
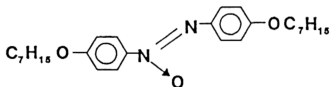
C 74.5°C S_C 95.5°C N 124°C I

Table 1.1   Examples of mesogens and their transition temperatures.
The () denotes a transition which is observed only on cooling
the isotropic liquid.   9

1.3.2 Discotic Liquid Crystals

Disc-shaped molecules or discotic can form a nematic phase characterized by the usual long-range orientational order, but having no positional order. The director now corresponds to the prefered direction of the disc normals (see Fig. 1.2). In most cases, the disc-shaped molecules can be packed one upon another to form columns. Within the columns the molecules can have a certain order. The columns itself are arranged in a two-dimensional network leading to columnar phases with hexagonal rectangular or oblique symmetry leading to tilted variants (see Fig. 1.3).

Discotic compounds consist of flat, rigid cores which are surrounded by flexible chains (alkyl,alkyloxy, alkanoyloxy). There are compounds with 3, 4, 6, 8, 9 or 12 flexible chains. The effect of the latter is to lower the melting temperatue and to isolate the columns one to another so that a structure with some mobility can be formed. Typical examples are complied in Table 1.2. Compound number 1 is the first observed discotic phase reported. Compound number 2 is without flexible chains form an exceptionally columnar structures, while compound number 7 should be considered with special interest since the core of this substance is not flat, but rather cone-shaped. The substance class derived from cores with that property is therefore called " bowlic" or " pyramidic".

1.3.3 Sanidic Liquid Crystals

In the preceding sections rod -like and disc- like molecules have been discusses in view of their mesogenic properties. Both these molecular types form special cases of anisotropic molecules. These special cases are characterized by the rotational symmetry
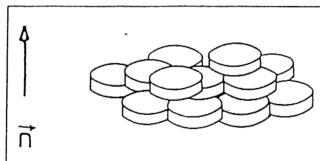
Fig. 1.2. Structure model of the discotic nematic phase (N_D) ($\vec{n}$: director).
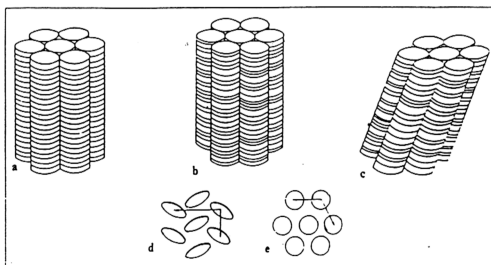
Fig. 1.3 Columnar phases of disc-shaped molecules a) ordered; b) disordered;
c) tilted d) rectangular (top view; ellipses denote discs that are tilted
with respect to the column axis e) hexagonal (top view))

Table 1. 2. Typical molecular structures of discotic liquid crystals.

1

— R = C₇H₁₅—COO—

cr 79.8 D 83.4 is

2

cr 288 D 293 is

3

R = C₇H₁₅—COO—

cr 107 (D₂ 95) D₁ 127 is

4

96 D 147 is

5

72.7 (N_D23.5) is

6

R = -CH₂OC_DH₂₅

78 D 264 is

7

R = C₆H_nCOO—

23.9 columnar 152.6 is

12
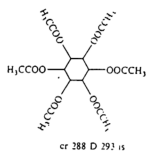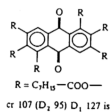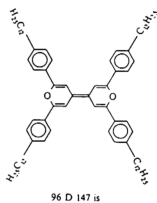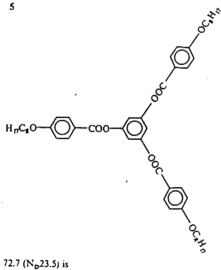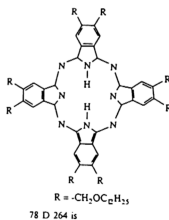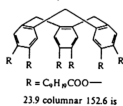
in the molecule, which means the anisotropy of the molecules can be described by two main axes. The more general case would be the consideration of the molecule with three main axes.

Molecules of this kind could be characterized by boards like-structure. Depending on the relative saiz of the main axes, these molecules can be derived from - like or disc - like molecules. Compounds of this kind can also exhibit mesomorphic properties. Derived from thr Greek word for board, these phases are called "sanidic". Sanidic phases were first was found in polymeric liquid crystals. According to the rule of Vorlander, the mesogenic compounds should have the utmost linear shape. The experimental results proved that lateral branches diminish the mesogenity; large branches in this sense should completely destroy the mesogenic properties. In recent years, however, a number of compounds has been found in which very long chains at the end of the molecules (No. 1 in Table 1.3) or attached in the center (No. 2 in Table 1.3) diminish the transition temperatures mesophase/ isotropic phase, but absolutely do not prevent liquis crystalline behaviour. The explanation for this behaviour is that the flexible alkyl chains adopts such a conformation that they are nearly parallel to the basic molecule. Despite the fact that they are not exacty rod - like , they exhibit the same types of mesomorphic phases as do the ordinary rod -like compounds. If the breath of molecules is even more enlarged, liquid crystalline properties may still exist, but the phase type is changed. The structure in Fig. 1.4 is characterized by three translational periods (in accordance with length, breath, and thickness of scattering maxima which cause three the molecular units by investigation with x -rays. From the model shown in

Table 1.3 . Non-conventional liquid crystals

$$H_{11}C_5OOC \atop H_{11}C_5OOC} C=CH-\!\!\!\!\bigcirc\!\!\!\!-O-OOC-\!\!\!\!\bigcirc\!\!\!\!-\!\!\!\!\bigcirc\!\!\!\!-COO-\!\!\!\!\bigcirc\!\!\!\!-O-CH=C {COOC_5H \atop COOC_5H}$$

1   4,4′ bis-(di-n-pentyl 4-carbonyloxybenzylidene malonate)-biphenyl
     cr 95 (S_C 61) N 151 is

$$C_8H_{17}O-\!\!\!\!\bigcirc\!\!\!\!-COO-\!\!\!\!\bigcirc\!\!\!\!-OOC-\!\!\!\!\bigcirc\!\!\!\!-OC_8H_{17}$$
$$C_{12}H_{25}$$

2   1,4-bis-(4-n-octyloxy-benzoyloxy)-2-n-dodecyl-benzene
     cr 56.2 N 69.2 is
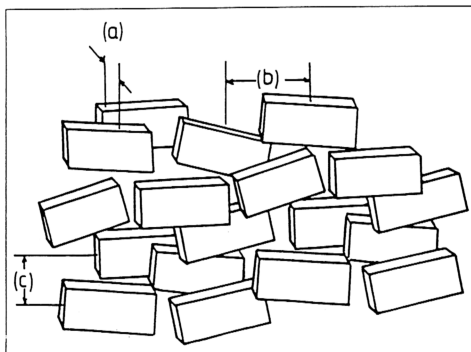
Fig. 1.4 . Structure model of the sanidic nematic phase; a. b. c are the lattice parameters according to x-ray data

14

Fig 1.4 phase biaxiallty could be expected. But up to now an unambiguous experimental proof is still lacking.

1.4   General Structural Features of Mesogens

A thermortropic compound generally has a rigid core or a mesogenic group with two wing groups. A mesogenic group consists of rings and bridges (which is a chain between two rings), whereas a wing group is composed of links (which is a chain between a ring and a terminal group) and terminal groups as indicated below,
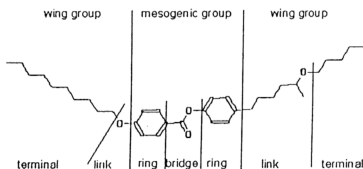
Rings:	Phenyl, Cyclohexane, Pyrimidine ;
Bridges:	$-CH_2-CH_2-$, $-CH_2 -O-$, $-COO-$, $-CH=N-$, $-N=N-$, $-N=N(O)$,$-(CH=CH)_2$
Links:	$-O-$, $-COO-$, $-OOC-$;
Terminals:	Cn (Alkylchain), CH2-CMe-Cn , COOH , Cholest-5ene;

The greater the extend of the core the higher the liquid crystal -isotropic transition. The

terminal groups varies widely in chemical nature.

Some examples for the rod-like mesogenic compounds are presented in Table 1.4. Compound No. 1 is an acyclic while compound No. 2 is a purely aromatic compound with a rigid exact linear molecule. In many cases the mesogenics are longitudinally or/and substituted by flexible chains, e.g., compound No. 3. Moieties suitable for these flexible chains are shown in Table 1.5. Beside aromatic ring, other ring systems such as cyclohexane are also suitable for mesogenic group, for example compound No. 4. There are also many examples (No. 5) of compounds consisting of a middle group which links two terminally substituted ring systems. Other possibilities for middle groups are collected in Table 1.6. One of the most effective bridging groups is the azomethine group, e.g., compound No. 6, which gives rise to a very high degree of polymorphism. The ring systems can have more than six atoms (compound No. 7; for other possiblities see Table 1.8) or less than six atoms (compound No. 8; for further possibilities see Table 1.9). In the last two decades many heterocyclic ring systems have been introduced into liquid crystal chemistry, an example is given in compound No. 9 and different heterocyclic rings are collected in Tables 1.7, 1.8, and 1.9. There are relatively few compounds with metal atoms in the center, e.g. compound No. 10 while compound No.11 is an interesting example of a liquid crystals compound formed via dimerization bonding due to hydrogen bonds (like all carboxylic acids). The last compound, No. 12, is one of the cholesteryl esters in which the liquid crystaline state was detected in 1888. By combination of the moieties complied in Tables 1.5 - 1.9, thousands of liquid crystaline compounds can be obtained.

Table 1.4. Rod-like mesogenic compounds.
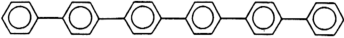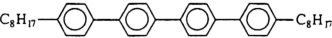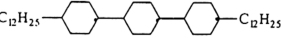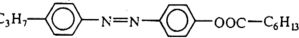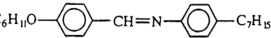
1. $CF_3 (CF_2)_9-(CH_2)_9-CH_3$

   (perfluorodecyl)-decane

   cr 38 S_B 61 is

2.

   p-sexiphenyl

   cr 435 S 465 N 565 is

3. C_8H_{17} C_8H_{17}

   4,4″-bis-(n-octyl)-p-terphenyl

   cr 176 S 191 is

4. $C_{12}H_{25}$ $C_{12}H_{25}$

   4,4″-bis-(n-dodecyl)-p-tercyclohexan

   cr 67 S 185 is

5. C_3H_7 $N=N$ $OOC-C_6H_{13}$

   4-n-propyl-4'-n-heptanoyloxy-azobenzene

   cr 42 N 71 is

6. $C_6H_{11}O$ $CH=N$ C_7H_{15}

   4-n-heptyl-N-(4-n-pentyloxy-benzylidene)-aniline

   cr 29.5 S_G 33.9 S_B 51.0 S_C 53.1 S_A 62.8 N 78.0 is

Table 1.4. contd.

7.
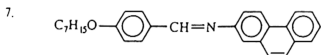
2-(4-n-heptyloxy-benzylideneamino)-phenanthrene
cr 116.5 S 129.5 N 187

8.
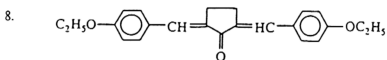
2,5-bis-(ethoxy-benzylidene)-cyclopentanone
cr 194 N 202 is

9.
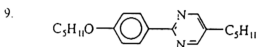
5-n-pentyl-2-(4-n-pentyloxy-phenyl)-pyrimidine
cr 37 N 55.5 is

10.
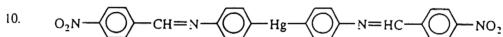
bis-(4-nitro-benzylideneamino)-phenyl-mercury
cr 236 N 241 is

11.
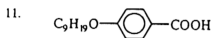
4-n-nonyloxy-benzoic acid
cr 94 S_C 117 N 143 is

12.
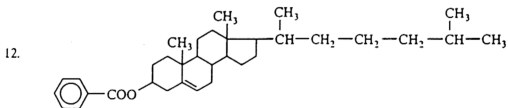
3-β-benzoyloxy-cholesten-(5)
(cholesteryl benzoate)
cr 150.5 N* 182.6 is

Table 1.5. Terminal groups.

alkyl	$-C_nH_{2n+1}$
alkyloxy	$-OC_rH_{2n+1}$
alkylmercapto	$-S-C_nH_{2n+1}$
acyl	$-\overset{\displaystyle \underset{O}{\|}}{C}-C_nH_{2n+1}$
acyloxy	$-O-\overset{\displaystyle \underset{O}{\|}}{C}-C_nH_{2n+1}$
alkylester	$-\overset{\displaystyle \underset{O}{\|}}{C}-O-C_nH_{2n+1}$
alkylcarbonates	$-O-\overset{\displaystyle \underset{O}{\|}}{C}-O-C_nH_{2n+1}$
halogeno	$-F,-Cl,-Br,-I$
cyano	$-CN$
nitro	$-NO_2$
alkylamino	$-NH-C_nH_{2n+1}$
cyanoalkyl	$-(CH_2)_a-CN$
cyanoethenyl	$-CH=CH-CN$
dicyanoethenyl	$-CH=C(CN)_2$

Table 1.6. Bridging groups.

azomethine	—CH=N—
ester	—COO—
thioester	—COS—
ethyl	—CH₂—CH₂—
butyl	—CH₂—CH₂—CH₂—CH₂—
stilbene	—C=C—
tolanes	—C≡C—
azo	—N=N—
azoxy	—N=N—↓O
oximbenzoate	—C=N—OOC—
dicarboxylate	—OOC—(CH₂)ₙ—COO—
azine	—CH=N—N=HC—
mercury	—Hg—

Table 1.7. Ring systems with 6 atoms.

phenyl	
cyclohexane	
cyclohexanone	
piperidine	
pyridine	
piperazine	
dioxane	
dithiane	
oxathiane	
pyridazine	
pyrimidine	
pyrazine	
triazine	
tetrazine	

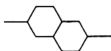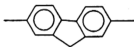**Table 1.8.** Ring systems with more than 6 atoms.

biphenyl
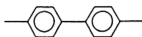
naphthalene
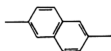
decaline

fluorene

perhydrophenanthrene

dioxanaphthalene

bicyclooctane

bicyclotrioxane

cubane

Table 1.9. Ring systems with 5 atoms.

cyclopentanone

pyrrole

furane

thiophene

thiazole

thiadiazole