

Chapter 1

Introduction

chapter 1

1.1 Liquid crystals

Liquid crystals are states of matter in which the degrees of molecular order lie intermediate between the crystalline solid and the isotropic liquid. Liquid crystals are broadly divided into two classes, *viz.*, the lyotropic and the thermotropic liquid crystals. As already mentioned in the preface, this thesis deals only with thermotropic liquid crystals.

1.2 Thermotropic liquid crystals

Liquid crystals which are obtained by the action of heat on certain pure compounds (or their mixtures) are called thermotropic liquid crystals. The first observations of thermotropic liquid crystalline behaviour were made towards the end of the last century by Reinitzer¹ and Lehmann.² Several thousands of organic compounds are now known to form thermotropic liquid crystals.³ The majority of thermotropic liquid crystals are composed of rod-like molecules. Friedel classified thermotropic liquid crystals broadly into three types: nematic, cholesteric and smectic.

1.2.1 Nematic phase

In this phase the constituent molecules have a long-range orientational order but no long-range positional order. The arrangement of molecules in two dimensions in a nematic liquid crystal is represented schematically in figure 1.1.

1.2.2 Cholesteric phase

Strictly speaking, the cholesteric phase is a "twisted" form of the nematic phase. Certain compounds composed of optically active molecules exhibit this kind of phase.

As a consequence the structure acquires a spontaneous twist about an axis normal to the preferred molecular directions, as shown in figure 1.2.

1.2.3 Smectic phase

The molecules in the smectic phase possess an orientational as well as positional order. The smectic phase is further classified according to the positional ordering of molecules present within the layers. In smectic A phase, the molecules lie parallel to the layer normal as shown in figure 1.3. The smectic C phase is the tilted analogue of the smectic A phase. The molecular long axes are tilted with respect to the layer normal as shown in figure 1.4. In smectic A and smectic C phases the centres of mass of molecules are randomly distributed in each layer.

In recent years, increasing number of higher order smectic phases have been discovered. These are classified according to the positional ordering of molecules present within the layers. To make a clear distinction between a liquid crystal and a true (but disordered) crystal, Leadbetter⁵ has suggested the following nomenclature. "When a structure has long-range order of molecular positions in three dimensions it is a crystal, despite the presence of various other kinds of disorder, and structures having less than this degree of positional order, but retaining some aspects of order above that possessed by an isotropic liquid are properly called liquid crystals." The principal phase types which have been established so far are summarised in table 1.1 and the possible order in which mesophases can occur is shown in table 1.2.

1.3 Liquid crystals of disc-like molecules

The first liquid crystals of disc-shaped molecules were prepared and identified in 1977 in this laboratory.⁸ Mesophases exhibited by such compounds are generally

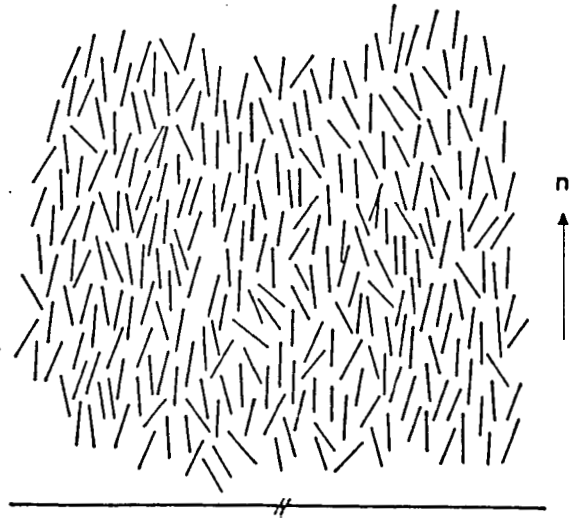


Figure 1.1: Schematic representation of the molecular arrangement in nematic phase (after Leadbetter⁵).

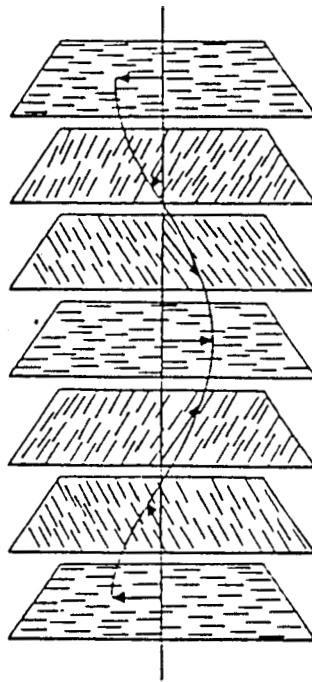


Figure 1.2: Schematic representation of the molecular arrangement in cholesteric phase (after Chandrasekhar⁶).

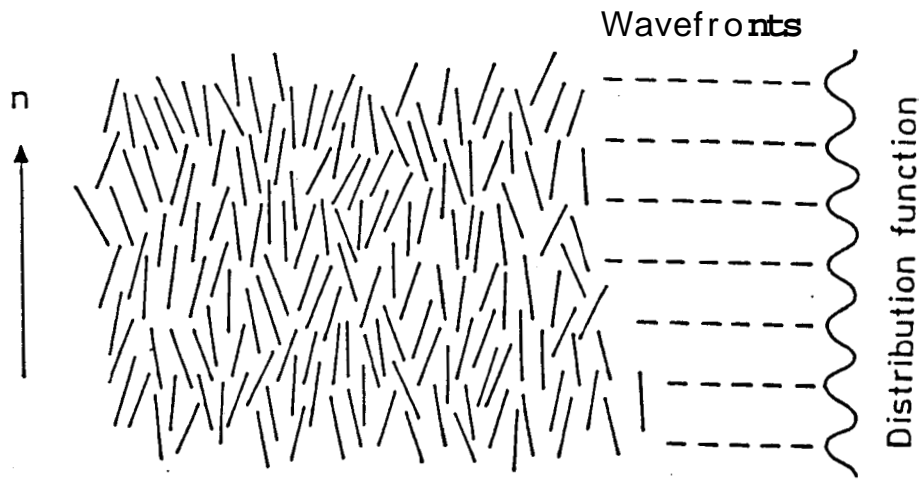


Figure 1.3: Schematic representation of the molecular arrangement in smectic A phase (after Leadbetter⁵).

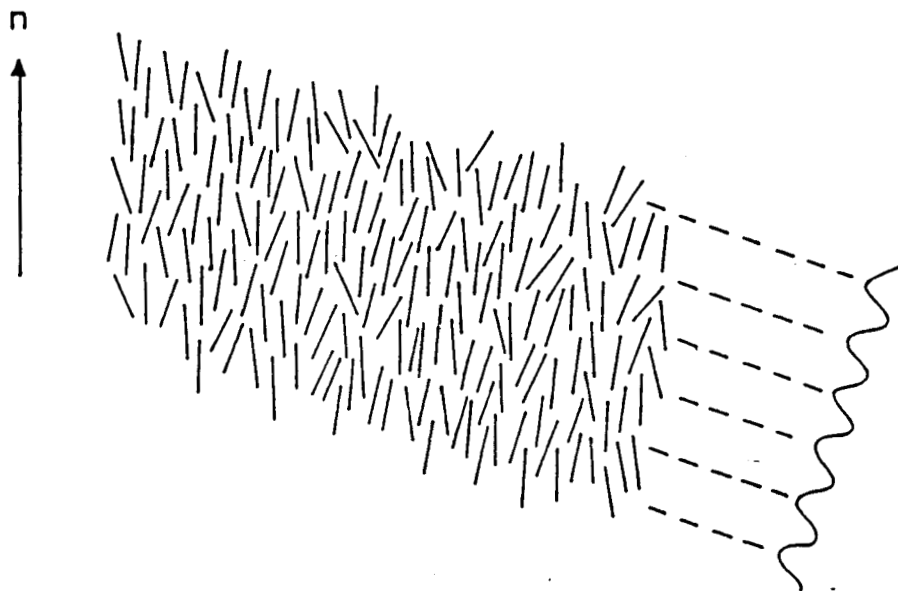


Figure 1.4: Schematic representation of the molecular arrangement in smectic C phase (after Leadbetter⁵).

Table 1.2
Polymorphic variants (after Sackmann⁷).

Monomorphic	Dimorphic	Trimorphic
N	S _A N	S _B S _A N
S _A	S _B N	S _C S _A N
S _B	S _C N	S _G S _A N
S _C	S _G N	S _E S _A N
S _E	S _B S _A	S _G S _B N
S _I	S _C S _A	S _I S _C N
	S _E S _A	S _E S _B S _A
	S _G S _C	S _B S _C S _A
	S _I S _C	S _E S _C S _A
	S _E S _B	S _I S _C S _A
	S _G S _I	S _G S _C S _A
	S _G S _F	S _G S _B S _A
		S _G S _F S _A
		S _F S _I S _C
		S _G S _I S _C
Tetramorphic	Pentamorphic	Hexamorphic
S _G S _B S _A N	S _G S _B S _C S _A N	S _G S _F S _B S _C S _A N
S _E S _B S _A N	S _H S _G S _C S _A N	S _G S _F S _I S _C S _A N
S _B S _C S _A N	S _G S _I S _C S _A N	S _K S _J S _I S _C S _A N
S _G S _C S _A N	S _G S _F S _C S _A N	S _H S _G S _F S _C S _A N
S _I S _C S _A N	S _K S _J S _I S _C N	
S _H S _G S _C N	S _G S _F S _I S _C S _A	
S _E S _B S _C S _A	S _H S _G S _F S _C S _A	
S _G S _B S _C S _A		
S _G S _F S _C S _A		
S _H S _G S _C S _A		
S _G S _I S _C S _A		
S _K S _I S _C N		
<div style="display: flex; justify-content: space-between; align-items: center;"> Temperature → </div>		

referred to as discotic liquid crystals. A large number of compounds made of disc-like molecules are now known to exhibit a variety of discotic mesophases.⁹ Structurally, most of them fall into two distinct categories; the columnar and the nematic. The principal discotic mesophase types are given in table 1.3.

In the columnar phase first described,⁸ the discs are stacked aperiodically atop one another to form liquid-like columns, the different columns constituting a two-dimensional lattice, as shown in figure 1.5. A number of variants of this structure have been identified; hexagonal, rectangular, tilted, etc. The discotic nematic phase has an orientationally ordered arrangement of the discs without any long-range translational order, as shown in figure 1.5. A discotic cholesteric phase has also been identified."

Giroud-Godquin and Billard¹¹ synthesised a metal complex consisting of disc-like molecules which exhibited a lamellar phase. Billard¹² suggested that this mesophase has "both columnar and layered structure" characteristics. Later Ohta *et al.*^{13,14} synthesised a number of similar compounds and also established the nature of the mesophase through X-ray studies. They designated this new phase as discotic lamellar or D_L phase, the structure of which is discussed in detail in chapter 2. Giroud-Godquin *et al.*¹⁵ have reported mesogenic copper β -diketonates, substituted with eight alkyloxy chains. These exhibited hexagonal columnar (D_h) mesophase.

1.4 Mesomorphism and chemical constitution

Compounds which exhibit thermotropic mesomorphism vary widely in their chemical constitution, but all possess the common feature of molecular geometrical anisotropy. That is to say, the shape of the molecules will be either rod-like or disc-like. The relationship between the molecular structure and mesomorphic properties of rod-

Table 1.3
Principal discotic mesophases (after Leadbetter⁵).

	Columnar structures	Nematic	
Ordered crystal	Based on columns of molecules stacked in ordered (o) or disordered (d) manner; columns form two-dimensional lattice	N_D	Isotropic liquid
	Hexagonal: D_{ho}, C_{6h} Rectangular: $D_{rd}; P2_1/a, P2/a, C2/m$ Oblique: D_{obd}		

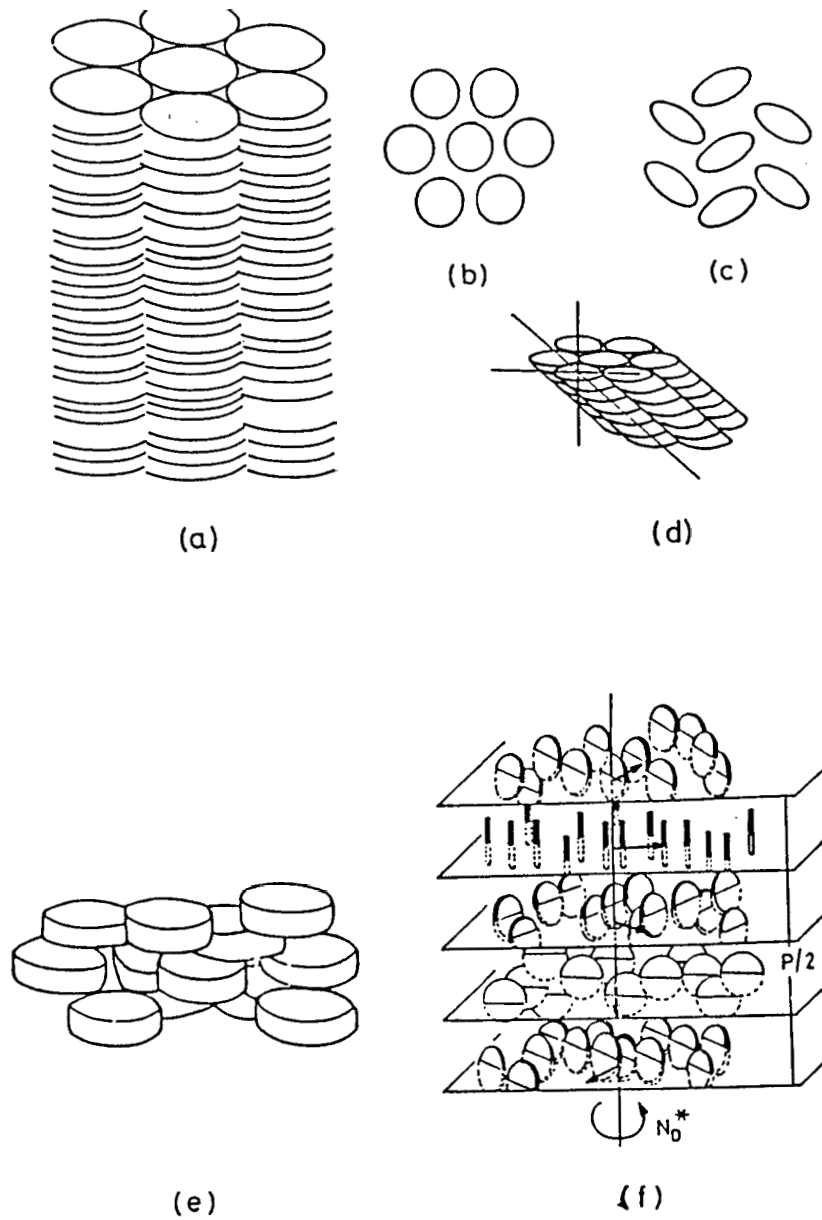


Figure 1.5: Schematic representation of the molecular arrangement in discotic liquid crystals. (a) Columnar phase, (b) hexagonal and (c) rectangular modifications of the columnar structure, (d) tilted columnar phase, (e) N_d phase, (f) twisted nematic (N_d^*).

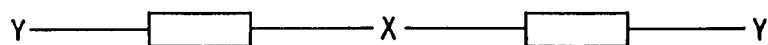
like molecules has been very rigorously studied by Gray.^{16,17} Amongst the main parameters which play an important role in the formation of a liquid crystal are intermolecular forces operating between the molecules. These can be divided into three classes.

(i) Dipole-dipole attractions: the direct interaction between permanent dipoles in the molecules.

(ii) Induced dipole attractions arising from the mutual polarisation of the molecules by their permanent dipole moments.

(iii) Dispersion forces: the attractions between instantaneous dipoles produced by spontaneous oscillations of the electron clouds of the molecules.

Therefore to constitute a potentially mesomorphic system, the long narrow molecules must contain groups of atoms with which are associated permanent dipole moments and the molecule itself must be highly polarisable. The thermal stabilities of the mesophases of liquid crystalline compounds are likely to be high if dipolar or polarisable groups occur terminally (Y) or centrally (X) in the rod-like molecule; but, it will be low if these occur laterally, as a result of significant increase in the molecular breadth.



This is a general statement and certain exceptions are known. Due to the rapidly increasing variety in the structures of mesogens¹⁸ and only a qualitative understanding of intermolecular interactions, no concrete generalisation seems to be possible.

Generally speaking, discotic phases are formed by compounds having flat or nearly flat cores surrounded by several flexible chains. Initially, it was believed that

only those compounds with at least six chains can form this type of mesophase. Later, it was shown that compounds with four chains can also form a discotic mesophase. However, copper n-alkanoates,¹⁹ forming a hexagonal discotic mesophase, bear only four alkyl chains (as dimers).

1.5 Effect of terminal and lateral substituents on mesomorphic behaviour

Replacement of a terminal hydrogen by a different substituent generally enhances the potentiality of the system to exhibit a mesophase and usually affects the thermal stability of the parent system. The terminal group efficiency order²⁰ which has been compiled for nematic and cholesteric phases in aromatic systems is,



Highly polarisable terminal substituents increase intermolecular forces of attraction and increase mesophase stability; $-\text{C}_6\text{H}_5$ and $-\text{NHCOCH}_3$ are effective in promoting both nematic and smectic phase stability. Smectic phase is favoured²¹ by increasing the length of terminal n-alkyl chains; terminal substituents such as ring- C_6H_5 , ring- NHCOCH_3 and ring- OCOCH_3 favour smectic more than nematic phase formation; terminal substituents such as ring- CN , ring- NO_2 and ring- OCH_3 strongly enhance thermal stability of the nematic phase and often decrease that of a smectic phase.

Lateral substituents that broaden a molecule diminish markedly the tendency of a compound to form mesophase²¹; substituents that are weakly dipolar, eg., methyl, or large and only moderately dipolar, eg., iodine, are more detrimental to smectic than to nematic phase thermal stability. Lateral substituents that do not broaden the molecule enhance mesophase thermal stability; the smectic phase thermal stability

is especially enhanced if the substituents are dipolar. However, in 1983, Weissflog and Demus²² have found a new molecular structure concept for thermotropic liquid crystals, by investigating compounds with lateral long-chain substituents. Later, they examined²³ this new concept by synthesising and studying a large number of mesogenic compounds containing lateral long-chain substituents. Mesogenic β -diketones containing lateral long-chains have been synthesised by the author and the results of these have been discussed in chapter 5.

1.6 Mesomorphic behaviour in a homologous series

In order to study the liquid crystalline behaviour systematically, the general practice has been to prepare a homologous series in which the length of terminal alkyl (C_nH_{2n+1}) or alkyloxy ($C_nH_{2n+1}O$) chain is increased successively. A large number of such homologous series of compounds comprising rod-like molecules have been reported in the literature and these have been reviewed by Gray.¹⁶ A common pattern of behaviour in various homologous series is that the lower homologues are nematic, the middle members exhibit nematic and smectic phases and the higher homologues containing long-chains are purely smectic.

By plotting the transition temperatures (mesophase \rightarrow mesophase or mesophase \rightarrow isotropic liquid) against the number of carbon atoms in the alkyl or alkyloxy chain for a homologous series, one of the several possible smooth curve relationships can be obtained.¹⁶

1.7 Metallomesogens

In recent years, there is growing interest in the synthesis of liquid crystals containing metal atoms. These have been termed as metallomesogens. Many thermotropic

metallomesogens have been prepared by incorporating different metals, including representatives of s-, p-, d- and even f- block elements. Both rod-like and disc-like metallomesogens are known and examples of all the main mesophase types have been observed.

There are a few advantages in incorporating a metal atom into certain organic compounds which result in metallomesogens:

- (i) Molecular shape: as already mentioned, the molecular shape and intermolecular forces are the main features which influence the formation of liquid crystalline phases. By introducing a metal atom into certain compounds the molecular shape can be altered.
- (ii) It has been found that introduction of metal atoms into certain organic compounds induces or sometimes enhances the mesogenic properties of the resulting metal complexes.
- (iii) The metal atoms are very rich in electron density. As a result of this the physical properties (eg., high birefringence) of the compound will be enhanced and many interesting possibilities regarding optical, magnetic and electrical properties may result.

The first thermotropic liquid crystals containing a metal atom were reported by Vorlander²⁴ in 1910. They are the alkali-metal(M) carboxylates ($R(CH_2)_nCOOM$), showing classical lamellar phases. He also synthesised²⁵ the first mesogens containing a transition metal atom. The compounds investigated were the diarylmercurials, exhibiting smectic phases. However, for a considerably long period, very little work was carried out in this new area. It is only in the last decade or so that metal-containing liquid crystalline substances are being investigated in greater detail.

The smectic ferrocenyl Schiff's bases are the first well-characterised organotran-

sition metallomesogens, synthesised by Malthete and Billard²⁶ in 1976. In 1977, Giroud and Muller-Westerhoff reported²⁷ mesogenic nickel and platinum dithiolenes. These results as well as those reported by Ohta et *al.*²⁸ on non-mesogenic copper β -diketonates laid the foundation for the study of mesogens containing d-block elements and the actual practical beginnings of interest in the subject. Since then many research groups have entered the field and a variety of metallomesogens have been synthesised. Interestingly, different mesophases, *viz.*, nematic, smectic, columnar, discotic lamellar, etc. have been observed in different transition metal complexes.

The ligands from which these complexes are derived play an important role on the properties of the corresponding metallomesogens, because, mesophase formation depends on intermolecular forces and much of the space around the metal is occupied by the ligand. Thus, for example, long monodentate ligands will tend to give rod-like nematics and smectics, while flat, disc-like ligands (eg., macrocycles) will give discotics. However, there are certain exceptions. The metallomesogens may therefore be arranged by ligand types, starting with the simplest monodentate and progressing to more complex bidentate and polydentate types; carboxylates, β -diketones, dithiolenes and dithiocarboxylates, polyamines, salicylaldimines, etc.

Of the several different ligands that may be utilised to obtain metal complexes, the β -diketones and *ortho*-hydroxy substituted Schiff's bases have been employed widely.

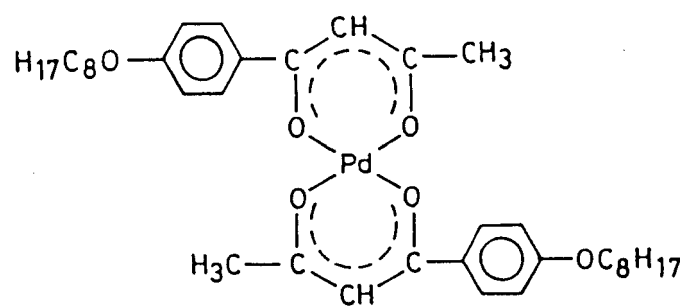
1.7.1 Mesogenic metal β -diketonates

β -Diketones are useful for obtaining mesomorphic derivatives and are easily synthesised.^{14,29,30} Furthermore, these compounds have a great ability to complex with various metal ions.³¹ Many examples of metal β -diketonates are known, forming

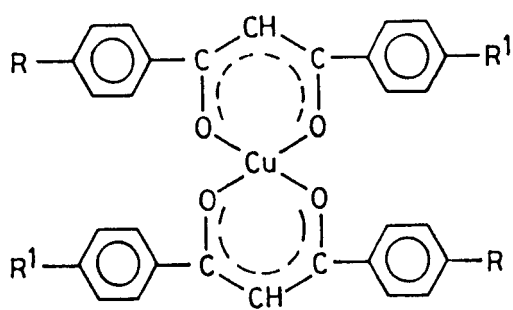
flat bis-ligand complexes. These include complexes of Ni, Pd, Cu, etc. which can take up square planar geometries. The first metal β -diketonate to be examined for mesogenic behaviour was the palladium(II) complex, 1.a. Bulkin *et al.*³² reported that the dsc data for this complex indicated potential mesomorphism, but were unable to confirm this optically because the complex darkened on heating.

The copper(II) complexes can be easily prepared by the reaction of a β -diketone with a copper salt.³³ The mesogenic copper(II) β -diketonates 1.b, first described by Giroud-Godquin and Billard¹¹ in 1981, have a square-planar geometry about the metal³⁴ and a d^9 configuration (one unpaired electron).³³ Both the symmetrically^{30,35} and the unsymmetrically³⁶ substituted complexes 1.b, exhibit very organised discotic mesophases. Later, Giroud-Godquin *et al.*¹⁵ reported mesogenic copper β -diketonates, substituted with eight alkyloxy chains. These exhibited hexagonal columnar mesophase (D_h). However, the corresponding nickel complexes did not show any liquid crystalline property. Mesogenic properties of similar discotic mesogens have been discussed in detail in chapter 2.

A very interesting discovery, by Chandrasekhar *et al.*^{37,38} is that the mesophases of the copper(II) complexes of the alkyl or alkyloxy-substituted β -diketones 1.c, are monotropic nematic and are miscible with a nematic organic compound, 4''-n-pentyl-4-cyano-p-terphenyl (5-CT). These complexes incorporate features of both rod-like and disc-like molecules, and one of the derivatives has shown evidence of a biaxial nematic phase.³⁹ Detailed investigations of different metallo β -diketonates have been discussed in chapters 3, 4 and 5.



1.a



1.b

$R, R^1 = C_nH_{2n+1}$

$R, R^1 = OC_nH_{2n+1}$

$R = C_nH_{2n+1};$

$R^1 = OC_nH_{2n+1}$

chapter 1

1.7.2 Salicylaldimine complexes

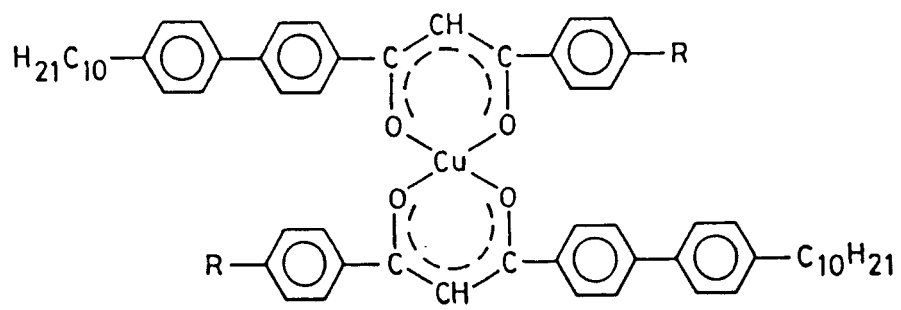
Schiff's bases obtained by condensing a 4-n-alkyloxy-2-hydroxybenzaldehyde with a 4-substituted aniline or any other suitable primary amine, are very useful ligands for getting mesomorphic metal complexes. Many of these ligands are themselves mesogenic. Most of the paramagnetic salicylaldimine copper(II) complexes 1.d, first reported by Ovchinnikov et al.⁴⁰ in 1984, showed smectic mesophases. Later on, many different kinds of mesogenic salicylaldimine metal complexes, incorporating various metals (*viz.*, Cu, Pd, Ni, V, etc.) have been reported. A detailed survey of these have been undertaken in chapter 6.

Apart from the above discussed metal complexes, there are many other mesogenic metal complexes^{41,42} derived from different kinds of ligands and a variety of metal atoms. For example, nitrile complexes of platinum and palladium, dithiolene complexes of nickel, palladium and platinum, phthalocyanine complexes of copper, manganese, cobalt, nickel, zinc, silicon, tin, lead, etc.

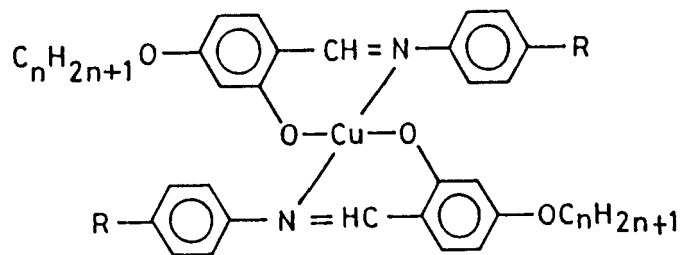
1.7.3 Structure-property relationships in metallomesogens

Many metallomesogens are coloured and this together with their somewhat high melting temperatures can make optical phase identification difficult. Compared with the usual organic compounds, coordination compounds produce stronger intermolecular interactions by means of intermolecular contacts (whenever a coordination site is accessible) and strong dipolar interactions (associated with the high polarisability of transition metal atoms), which are responsible for their high melting points.

The basic requirements for a metal complex to show mesomorphism are very similar to those for many simple organic compounds. Many metallomesogens are



1.c



1.d

composed of ligands which are riot mesomorphic. If the free ligarids are themselves mesomorphic, the derived metallomesogens show similar phase behaviour when incorporation of the metal changes the molecular shape only to a small extent: for eg., in the case of phthalocyanines. In other cases, considerable difference is seen in the structure of metal complex and quite different mesomorphic behaviour is observed: for eg., in the case of copper β -diketonates. These generalisations depend on the assumption that, the molecular packing in the crystal is closely related to that in the mesophase, but this may not always be valid.

1.8 Applications

Liquid crystals are beautiful and extremely useful. The main application of liquid crystals is in electronic displays. Netnatic liquid crystals are widely used for these purposes. The current applications for liquid crystal displays are summarised in table 1.4 . Cholesteric liquid crystals are used as temperature sensors in disposable thermometers, aerodynamic testing,⁴⁴ etc. Another important use of cholesteric liquid crystals is in the medical field.⁴⁵ They have also been used to produce panels that exhibit an optical memory effect.⁴⁶

Chromatography is of great importance in modern chemical analysis and physico-chemical investigations. Liquid crystals are among the materials used in chromatography. The use of liquid crystals as stationary phases in gas chromatography was described for the first time in 1963 by Kelker⁴⁷ and later by Dewar and Schroeder.⁴⁸ Ever since, liquid crystal stationary phases have been applied successfully for separation of composite mixtures, chiefly isomers, including those of polycyclic hydrocarbons.

Liquid crystals are used to control or alter the chemical reactivity of dissolved

Table 1.4

Current applications for liquid crystal displays (after Castellano⁴⁸).

Analytical Instruments	Jewelry, Assorted
Auto Dashboards	Marine Engine Indicators
Auto Radios & Clocks	Marine Speedometers
Battlefield Computers	Marine Depth Finders
Blood Pressure Indicators	Overhead Projector Plates
Calculators	Pens
Cameras	pH Meters
Cash Registers	Photocopy Machines
Clock Radios	Point-of-Purchase Displays
Digital Pyrometers	Point-of-Sale Terminals
Digital Multimeters	Portable Radios
Digital Thermometers	Portable Computers
Electric Shavers	Portable Word Processors
Electronic Billboards	Portable Oscilloscopes
Exercise Equipment	Telephones
Gasoline Pump Indicators	Toys & Games
Hand-Held TV	TV Channel Indicators
Hand-Held Terminals	Typewriters, Editing
Hand-Held Data Collection	Vacuum Cleaners
Heart Monitoring Devices	VCR Channel Indicators
Highway Signs	Windometers
Household Appliances	Wrist Watches

solutes.^{49,50} Liquid crystals do alter reactivity as a result of their ability to control solute diffusion, orient reactants and discriminate between stable solutes and **transition** states according to their sizes and shapes. This ability depends on the degree of order present in the liquid crystal and the structure of the reactant in relation to that of the mesogen.

Possible device applications for metallomesogens, which may presently be anticipated are as new thermal or nonlinear optical materials, in electrochemistry and as sensors. Copper laurate has been melt spun into fibers in its mesophase, by the Grenoble **group**.⁵¹ Electron microscopy and X-ray diffraction measurements indicate that, the fibers have high degrees of orientation both in the crystalline and the columnar phases.

References

- [1] F. Reinitzer, *Monatsch chem.*, 9, 421 (1888).
- [2] O. Lehmann, *Z. Phys. chem.*, 4, 462 (1889).
- [3] D. Demus, H. Demus and H. Zashke, *Flussige Krystalle in Tabellen*, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig (1974); D. Demus and H. Zashke, *Flussige Krystalle in Tabellen, Vol.II*, VEB Deutscher Verlag fur Grundstoffindustrie, Leipzig (1984).
- [4] G. Friedel, *Ann. Physique*, 18, 273 (1922).
- [5] A.J. Leadbetter, in *Thermotropic Liquid Crystals, critical reports on Applied Chemistry*, Ed. G.W. Gray (John Wiley and sons, Chichester, 1987).
- [6] S. Chandrasekhar, "*Liquid Crystals*" (Cambridge University press, Cambridge, 1977).
- [7] H. Sackmann, *Liq. Cryst.*, 5, 43 (1989).
- [8] S. Chandrasekhar, B.K. Sadashiva and K.A. Suresh, *Pramana*, 9, 471 (1977).
- [9] S. Chandrasekhar, *Advances in liquid crystals, Vol.5* (ed. G.H.Brown), p.47, Academic press, New York (1982).
- [10] C. Destrade, N.H. Tinh, J. Malthete and J. Jacques, *Phys. Lett.*, 79A, 189 (1980).
- [11] A.M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, 66, 147 (1'381).
- [12] J. Billard, *C.R. Acad. Sc. Paris*, 299, 905 (1984).

- [13] K. Ohta, H. Muroki, A. Takagi, K.I. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 140, 131 (1986).
- [14] K. Ohta, H. Muroki, A. Takagi, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 135, 247 (1986).
- [15] A.M. Giroud-Godquin, M.M. Gauthier, G. Sigaud, F. Hardouin and M.F. Achard, *Mol. Cryst. Liq. Cryst.*, 132, 35 (1986).
- [16] G.W. Gray, "*Molecular structure and properties of liquid crystals*" (Academic press, London and New York, 1962).
- [17] G.W. Gray, in "*Advances in liquid crystals*" Vol.2, Ed. G.H. Brown (Academic press, New York, 1976).
- [18] D. Demus, *Liq. Cryst.*, 5, 75 (1989).
- [19] A.M. Giroud-Godquin, J.C. Marchon, D. Guillon, A. Skoulios, *J. Phys. Lett. Orsay, Fr.*, 45, L681 (1984).
- [20] G.W. Gray, in "*Liquid crystals and Plastic crystals*", Vol.1, Eds. G.W. Gray and P.A. Winsor (Ellis Horwood, Chichester, England, 1974).
- [21] G.W. Gray, in "*Liquid crystals and Plastic crystals*", Vol.1, Eds. G.W. Gray and P.A. Winsor (Halstead, New York, 1974).
- [22] W. Weissflog and D. Demus, *Cryst. Res. and Technol.*, 18, K21 (1983).
- [23] W. Weissflog and D. Demus, *Cryst. Res. and Technol.*, 19, 55 (1984).
- [24] D. Vorlander, *Ber. Dtsch. Chem. Ges.*, **43**, 3120 (1910).
- [25] D. Vorlander, *Z. Phy. Chem. Stoechiom. Verwandtschaftsl.*, 105, 211 (1923).

chapter 1

- [26] J. Malthete and J. Billard, *Mol. Cryst. Liq. Cryst.*, 34, 117 (1976).
- [27] A.M. Giroud and U.T. Muller-Westerhoff, *Mol. Cryst. Liq. Cryst. Lett.*, 41, 11 (1977).
- [28] K. Ohta, M. Yokoyama, S. Kusabayashi and H. Mikawa, *J. Chem. Soc. Chem. Commun.*, 392 (1980).
- [29] R. Eidenschink and L. Pohl, 8th Int. Liq. Cryst. Conf., (Kyoto), (1980). Abstract No. E-10.
- [30] K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *J. Chem. Soc. Chem. Commun.*, 1099 (1984); K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 116, 299 (1985); B.K. Sadashiva, P. Rani Rao and B.S. Srikanta, *Mol. Cryst. Liq. Cryst.*, 168, 103 (1989).
- [31] J.P. Fackler, Jr., *Progress in Inorganic Chemistry*, 7, 361 (1986).
- [32] B.J. Bulkin, R.K. Rose and A. Santoro, *Mol. Cryst. Liq. Cryst.*, 43, 53 (1977).
- [33] R.C. Mehrotra, R. Bohra, D.P. Gaur, *Metal β -Diketonates and Allied Derivatives*, Academic press, London, 1978.
- [34] K. Usha and Kalyani Vijayan, *Mol. Cryst. Liq. Cryst.*, 174, 39 (1989).
- [35] A.M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, 97, 287 (1983).
- [36] Veena Prasad and B.K. Sadashiva, *Mol. Cryst. Liq. Cryst.*, 195, 161 (1991).
- [37] S. Chandrasekhar, B.K. Sadashiva, S. Ramesha and B.S. Srikanta, *Pramana*, 27, L713 (1986).

- [38] S. Chandrasekhar, B.K. Sadashiva and B.S. Srikanta, *Mol. Cryst. Liq. Cryst.*, 151, 93 (1987).
- [39] S. Chandrasekhar, B.R. Ratna, B.K. Sadashiva, V.N. Raja, *Mol. Cryst. Liq. Cryst.*, 165, 123 (1988).
- [40] I.V. Ovchinnikov, Yu.G. Galyametdinov, G.I. Ivanova, L.M. Yagfarova, *Dokl. Akad. Nauk. SSR*, 276, 126 (1984).
- [41] A.M. Giroud-Godquin and P.M. Maitlis, *Angew. Chem. Int. Ed. Engl.*, 30, 375 (1991).
- [42] P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano and E. Sola, *Coordination Chemistry Reviews*, 117, 215 (1992).
- [43] J.A. Castellano, *Mol. Cryst. Liq. Cryst.*, 165, 389 (1988).
- [44] G.H. Brown, Ed., *Liquid Crystals 2, Part I*, Gordon and Breach, New York, (1969).
- [45] *Liquid Crystal Devices*, Ed. Thomas Kallard (Optosonic press, New York, 1973).
- [46] G.H. Heilmeyer and J.E. Goldnacher, *Proc.IEEE*, 57, 34 (1973).
- [47] H. Kelker, *Z. Anal. Chem.*, 198, 254 (1963).
- [48] M.J. Dewar and J.P. Schroeder, *J. Amer. Chem. Soc.*, 86, 5235 (1964).
- [49] R.G. Weiss, *Tetrahedron*, 44, 3413 (1988).
- [50] H. Kelker and R. Hatz, *Handbook of Liquid Crystals*, Verlag chemie: Weinheim, (1980).

- [51] A.M. Giroud-Godquin, P. Maldivi, J.C. Marchon, P. Aldebert, A. Peguy, D. Guillon and A. Skoulios, *J. Phys.*, (Orsay, Fr.) **50**, 513 (1989).