X-RAY ANALYSIS OF THE CRYSTAL AND MOLECULAR STRUCTURES OF SOME DISCOTIC COMPOUNDS

A *thesis submitted* to *the*
Bangalore University
for the degree of
Doctor of Philosophy
in *the* Faculty of Science

by

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December 1992

DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently in the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship, Fellowship or any other similar title.

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We certify that this thesis has been composed by Ms. K. Usha based on the investigations carried out by her at the Liquid Crystal Laboratory, Raman Research Institute, Bangalore, under our supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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Acknowledgements

I am deeply indebted to Prof. S. Chandrasekhar for his stimulating guidance and constant encouragement. I am also grateful to him for suggesting that I work on this problem and for all the useful discussions.

It has indeed been a great pleasure working with Dr. Kalyani Vijayan of the Materials Science Division, NAL. I gratefully acknowledge her untiring help throughout the course of this work. Without her valuable guidance, this work would not have been possible.

I thank Prof. B.K. Sadashiva for giving me all the complexes studied in this thesis.

I am very grateful to Prof. M. Vijayan for allowing me to use some of the facilities at the Molecular Biophysics Unit, IISc. His timely help will always be remembered.

I am indebted to Prof. K. Venkatesan of the Organic Chemistry Department, IISc, for his kind help and many useful suggestions. I also thank him for having allowed me to work in his laboratory as a short term research worker.

Prof. H. Manohar and Dr. M. Nethaji of the Inorganic and Physical Chemistry Department, Prof M.A. Vishwamitra, of the Physics Department and Dr. N.C. Shivaprakash of the Instrumentation and Services Unit, IISc, generously permitted me to make use of the diffractometers in their departments. I am thankful to them for their help.

I am also thankful to Dr. A.K. Singh for providing access to the facilities at NAL.

My thanks are due to Dr. Puttaraja for his kind help and encouragement.

I thank Prof. N.V. Madhusudana for his keen interest in the progress of my work.

Dr. V. Dhanaraj, Mr. J. Narasimha Murthy and Dr. V. A. Raghunathan have helped me a great deal during the course of this work. I express my sincere thanks to them. Thanks are also due to Ms. Priya for her help.

The pleasant company of Ads. Geetha G. Nair has made my stay at RRI enjoyable. I also thank her, Mr. G. Raju and Ms. Andal for their help in the final stages of the thesis. I also thank my friends Raji, Rajashree, Ganesh, Lakshmi, Tara and Ratnakar for their wonderful company.

The cordial assistance of Dr. A. Ratnakar, Mr. Hanumappa, Mr. Chowdappa and other staff of RRI library is gratefully acknowledged. I also thank everyone in the computer section for their help.

The cover of this thesis was designed by Mr. C. Ramachandra Rao. I thank him and Mr. Raju Verghese for their help in making all the photographs.

I am thankful to Mr. S. Raghavachar for his help.

It is only the affectionate support and encouragement of my uncle M. Veeraraj Urs, and my mother which enabled me to cope with the difficult times. Words cannot express my gratitude to them. I thank my uncles Mallaraj Urs, Channaraj Urs and my aunts, Jayalakshammanni and Lingajammanni for their unfailing support. I also thank Meenakshi mami for her encouragement.

I thank all my colleagues and friends at RRI who have helped me in many ways.

K. Usha

Contents

Chapter 1

Introduction

It is well known that crystals are characterized by a lattice structure corresponding to long-range *positional* order in three dimensions. Further, in the case of molecular crystals, the orientation of the molecules with respect to the lattice is also fixed. Thus there is long range *orientational* order as well in these systems. In most molecular crystals, both these types of long range order are destroyed at the temperature at which the crystal melts to the isotropic liquid. In general, however, this need not be the case. There are materials in which the long range orientational order vanishes first when the crystal is heated and then the long range positional order vanishes at a higher temperature. Consequently in these materials, there exists a phase between the crystalline and the isotropic phases that has no long range orientational order but only long range positional order. This phase is called a plastic crystal. On the other hand, in materials with molecules having geometric shape anisotropy (for example, rod-like or disc-like molecules), the disappearance of the long range positional order occurs first before the long range orientational order is destroyed at a higher temperature. Moreover, the positional order need not be lost in all three dimensions at the same temperature. Hence, in such cases we have a set of orientationally ordered intermediate phases with differing degrees of molecular ordering. These phases are called thermotropic liquid crystals. The term thermotropic signifies the fact that the transition to these phases is brought about by a change of temperature. All the materials studied in this thesis belong to this class.

There is also another class of liquid crystals called lyotropic, which is formed by amphiphilic molecules in solutions. These systems are often characterized by the ordering of aggregates of molecules and not of the molecules themselves. Liquid crystals may therefore be formally defined as partially ordered phases, with the degree of orientational and translational ordering (of molecules or of aggregates of molecules) intermediate between those in a crystal and in an isotropic liquid.

Liquid crystals of rod-like molecules can be broadly classified into three types, nematic, cholesteric and smectic [Chandrasekhar, 1992; Pershan, 1988; Leadbetter, 1987]. The nematic phase is characterized by only long range orientational order with no long range positional order (Figure 1.1(a)). The local mean direction of orientation of the molecules is denoted by a unit vector $\hat{n}$, called the director. If the constituent molecules are chiral, or if a chiral dopant is added to a nematic, it acquires a twisted structure with the twist axis normal to the preferred molecular direction. This chiral nematic phase is also known as cholesteric (Figure 1.1(b)).

The smectic phases are characterized by a layered structure. These are further classified on the basis of the ordering of the molecules within the layers. More than a dozen modifications have been identified, the simplest of these being smectics A and C (Figure 1.1(c) and (d)). In the smectic A phase, the arrangement within the layers is liquid-like with no long range positional ordering of the molecules. Further the long axes of the molecules are on an average, along the layer normal. Smectic C is similar to smectic A except that the molecules are tilted with respect to the layer normal, the degree of tilt being same in all the layers.

Another class of thermotropic liquid crystals composed of disc-like molecules

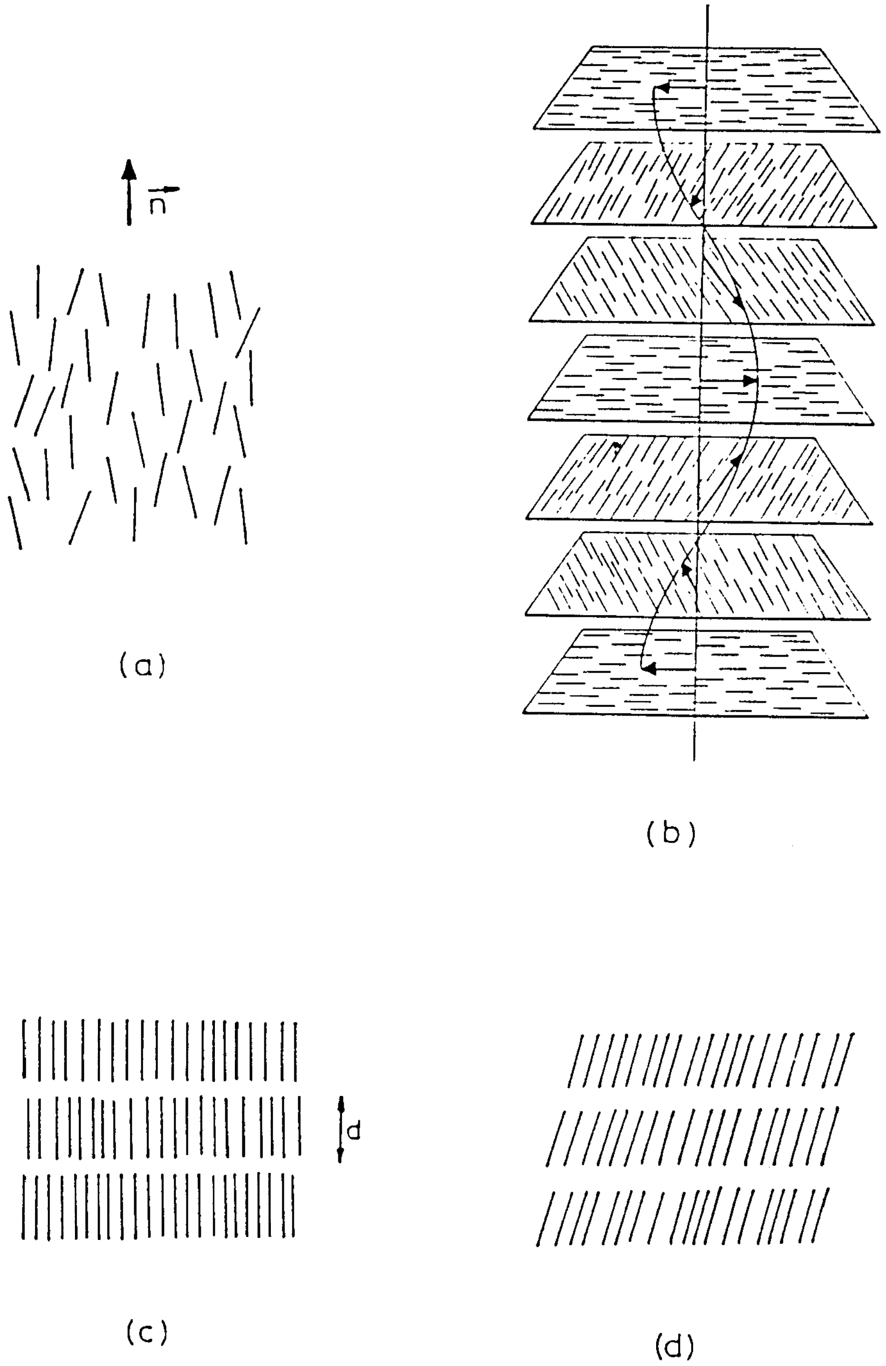


Figure 1.1: Schematic diagram showing the molecular arrangement in different types of mesophases exhibited by rod-like molecules. (a) nematic, (b) cholesteric, (c) smectic A and (d) smectic C.

was discovered more recently by Chandrasekhar et al [1977]. They studied the hexa substituted esters of benzene and showed that in the mesophase the discs form liquid-like columns, the columns themselves forming a two-dimensional lattice (Figure 1.2(a)). The later studies of Levelut [1979, 1983] confirmed this basic structure in other systems and also established the occurrence of rectangular and orthorhombic arrangements of columns (Figure 1.3). Subsequently, it was found that some disc-like molecules form nematic (N_D) (Figure 1.2(b)) and twisted nematic (N_D^*) (Figure 1.2(c)), the latter if the constituent molecules are chiral. In discotic liquid crystals, the preferred direction of orientation or the director is defined by the normal to the discs [Chandrasekhar, 1992]. Figure 1.2(d) shows the tilted columnar arrangement (D_t). Giroud-Godquin and Billard [1981] reported metal complexes with a lamellar arrangement in the mesophase. From X-ray studies, Ohta et *al* [1986] also proposed a lamellar structure (D_L) (Figure 1.2(e)) for the mesophase of some copper complexes. The structural formulae of some liquid crystalline molecules which exhibit discotic mesomorphism are given in Figure 1.4.

It was proposed by Frank and Chandrasekhar [1980], that the mesophases of benzene-hexa-n-alkanoates should form a pseudo hexagonal lattice (*i.e.*, a rectangular lattice with the ratio of the sides b/a differing slightly from the ideal hexagonal value of $\sqrt{3}$). According to their model, only the molecular cores are tilted with respect to the column axis and the aliphatic chains are disordered (Figure 1.5). The high precision X-ray studies of Levelut [1983] and de Jeu [1983] supported this conclusion.

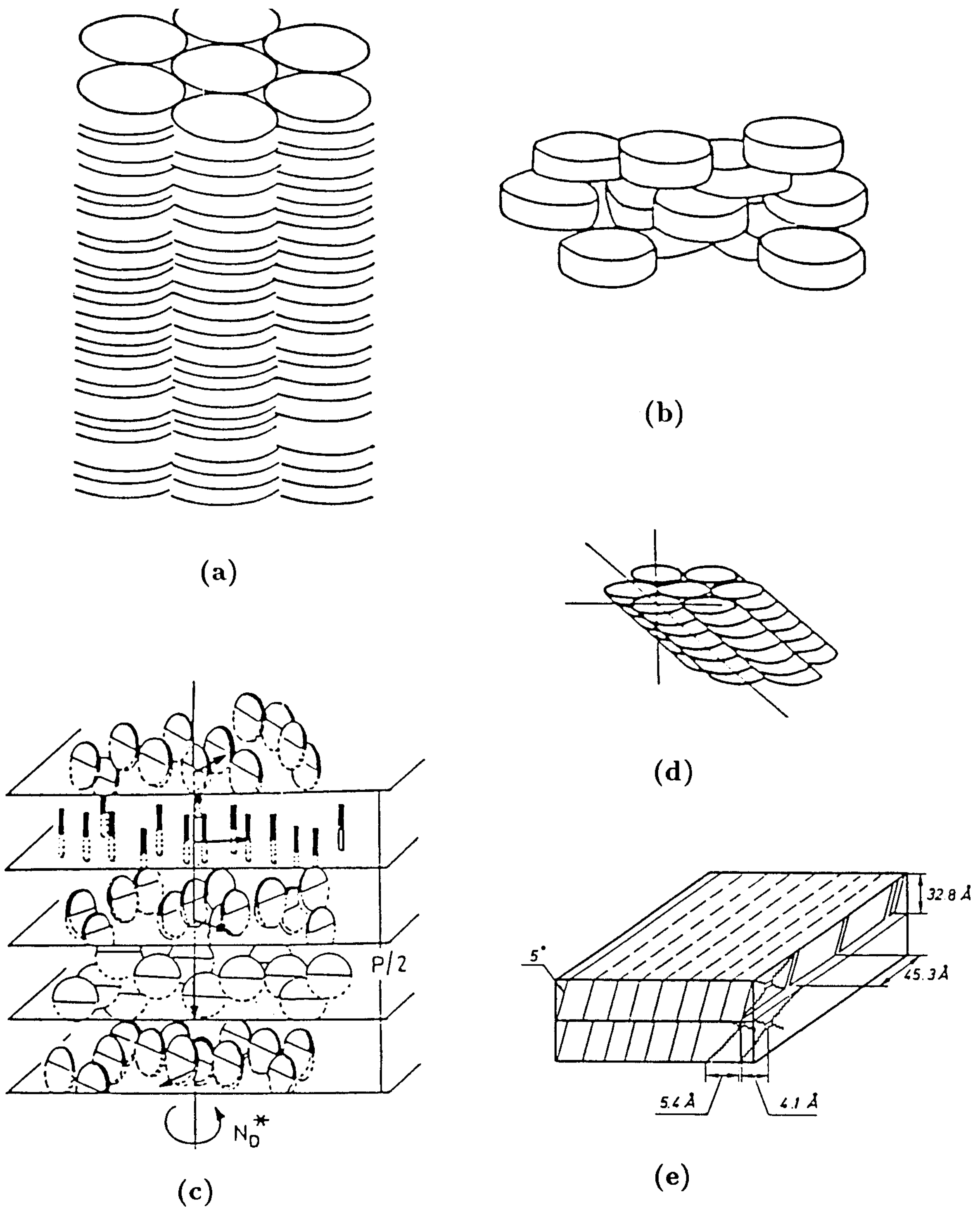


Figure 1.2: Schematic diagram showing the molecular arrangement in some discotic mesophases. (a) columnar phase, (b) nematic (N_D), (c) chiral nematic (N_D^*) (d) tilted columnar phase (D_t), and (e) discotic lamellar (D_L) [Sakashita *et al*, 1988].

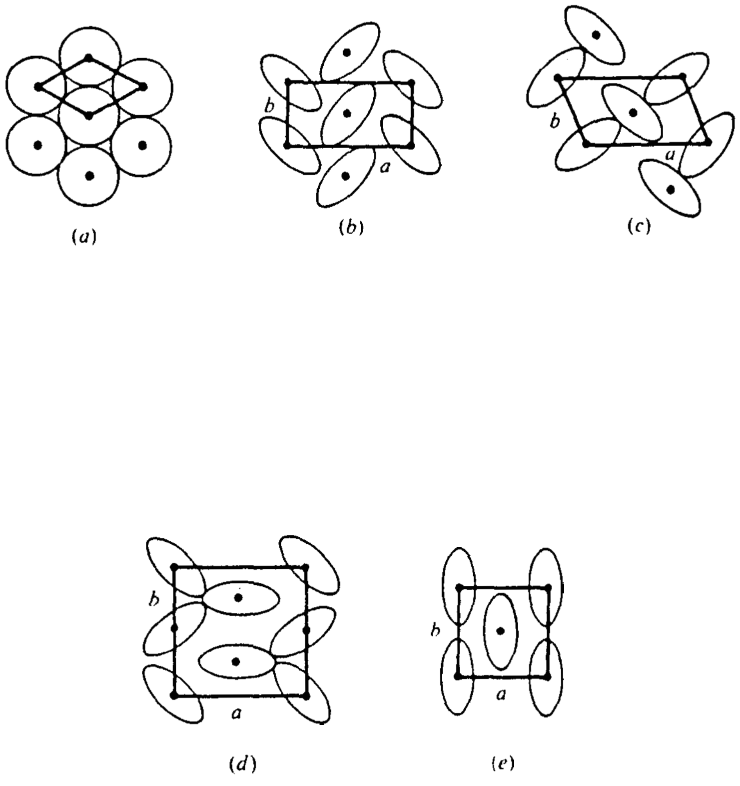
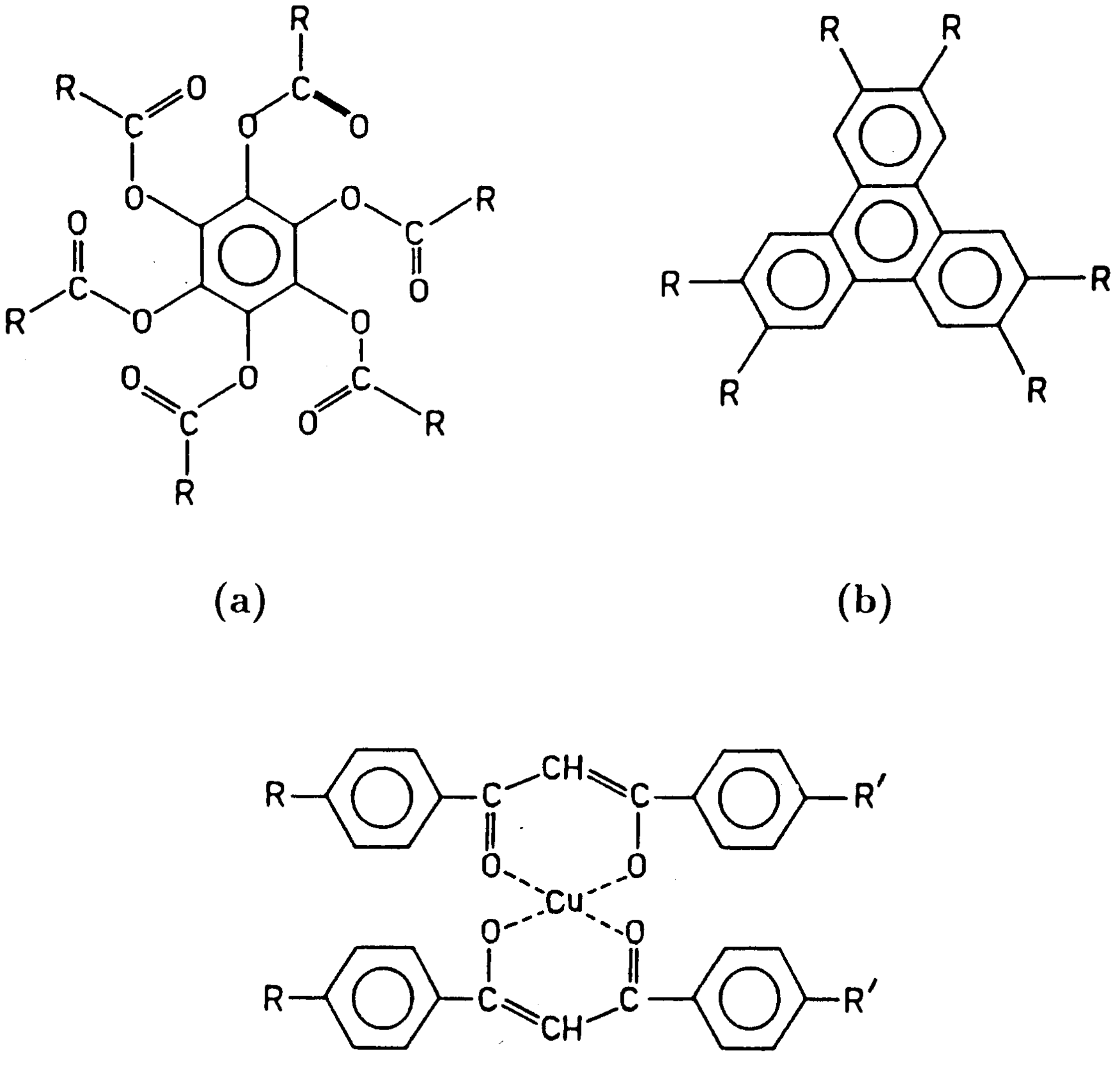


Figure **1.3:** Different columnar phases exhibited by disc-like molecules (Ellipses denote the discs that are tilted with respect to the column axis). (a) hexagonal (PG 2/m 2/m), (b) rectangular (P2_1/a), (c) oblique (P1), (d) rectangular (**P2/a**) (D$_C$) and (e) rectangular face centred (C2/m).



(a) (b)

(c)

Figure 1.4: Structural formulae of some molecules exhibiting discotic mesomorphism. (a) hexa-n-alkanoates of benzene, ($R=C_nH_{2n+1}$) (b) hexa-n-alkanoates of triphenylene (see Table 1.2 for the various substituents, R) and (c) copper(II) β-diketonates, ($R=C_mH_{2m+1}$; $R'=C_nH_{2n+1}$).

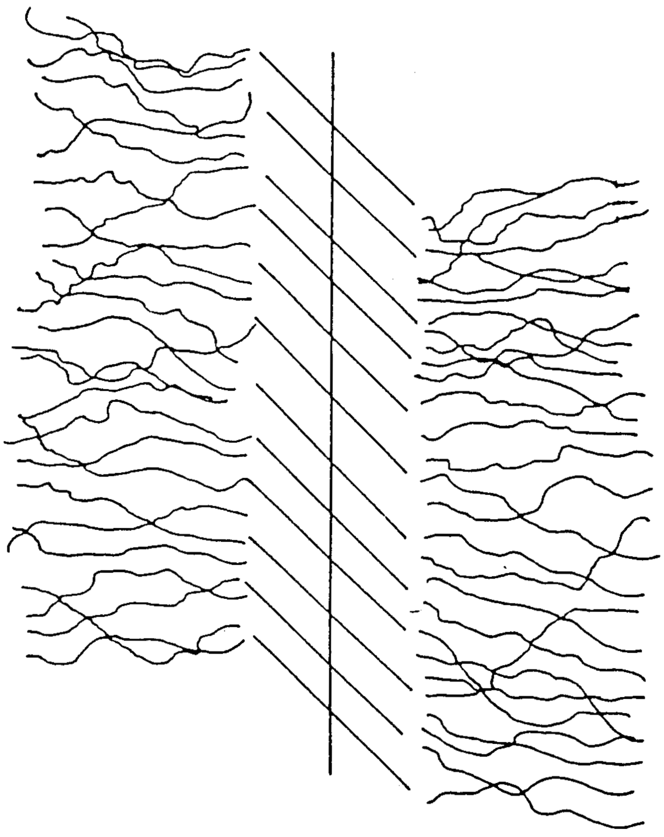


Figure 1.5: Column with only the core of the molecule tilted and the chains in a disordered state [Frank and Chandrasekhar, 1980].

Figure 1.3 shows the different types of columnar structures. The details of the nomenclature are given in Table 1.1. The ellipses denote discs that are tilted with respect to the column axis. Depending on whether the molecules within each column are stacked periodically or not, we get ordered and disordered arrangements within a column.

Polymorphism in columnar phases was also observed. In the higher homologue of hexa-n-alkanoates of triphenylene [Destrade et *al*, 1979] a transition from D_h to D_r was observed. From high resolution synchrotron X-ray studies carried out on freely suspended discotic strands in triphenylene hexa-n-dodecanoate, it was concluded that the molecular cores are tilted even in the D_h phase but the different columns form an orientationally disordered hexagonal structure [Safinya et al, 1984]. It was reported that hexa-hexyl thio triphenylene exhibited a transition from D_{ho} to D_{hd}. From X-ray studies, it was also established that in the ordered phase, D_{ho}, the stacking of the cores in each column is helical with the helical spacing incommensurate with the intermolecular spacing [Fontes et *al*, 1988]. In addition, a three column superlattice develops as a result of the frustration caused by interdigitation in triangular symmetry. The space groups of some derivatives of triphenylene which form columnar structures are listed in Table 1.2. Ruffigallol-hexa-n-octanoate shows two mesophases *viz.*, D_{rd} and D_C [Queguiner *et al*, 1979]. The D_C phase also has a rectangular lattice, but with three columns per unit cell (Figure 1.3(d)).

Discotic metal-containing liquid crystals were first reported by Giroud-Godquin and Billard [1981]. Since then, there has been an upsurge of interest in the field

Table 1.1: Symbols used for designating the discotic phases

D_{hd}	Columnar, hexagonal disordered
D_{rd}	Columnar, rectangular disordered
D_{ho}	Columnar, hexagonal ordered
D_{t}	Columnar, tilted
N_{D}	Nematic discotic
N_{D}^{*}	Twisted nematic discotic

Table 1.2: Columnar structures formed by some derivatives of triphenylene (Figure 1.4(b)).

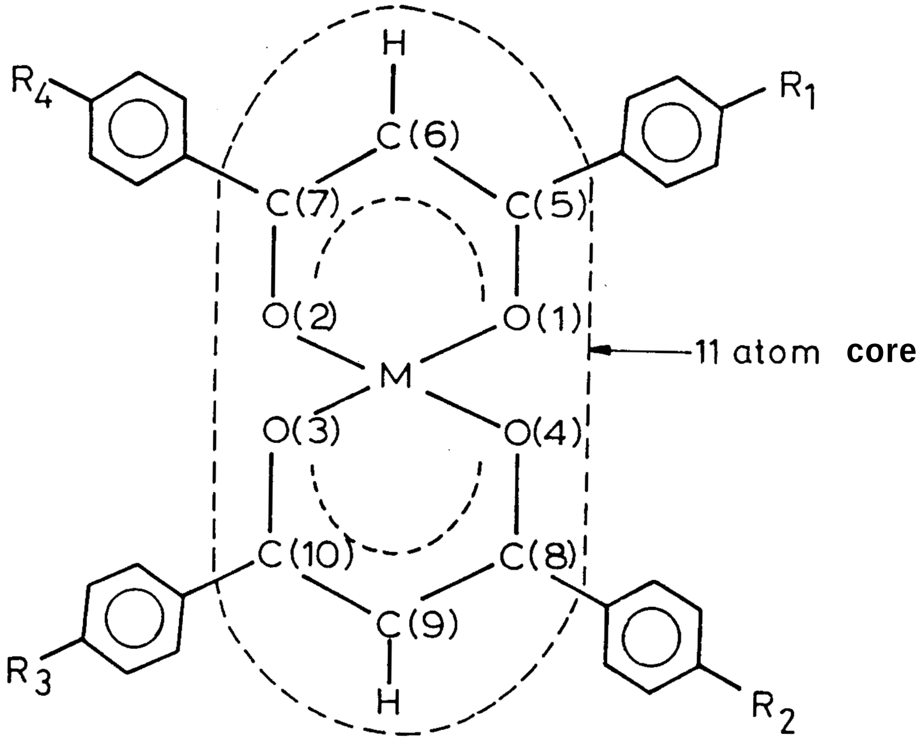
R	Space group	Lattice parameters (Å)
$C_5H_{11}O$	P6 2/m 2/m	a=18.95
$C_7H_{15}O$	PG 2/m 2/m	a=22.2
$C_8H_{17}O$	PG 2/m 2/m	a=23.3
$C_{11}H_{23}COO$	P2_1/a PG 2/m 2/m	a=44.9, b=26.4 a=26.3
$C_7H_{15}COO$	P2_1/a	a=37.8, b=22.2
$C_{11}H_{23}$-O-C_6H_4-COO	P2_1/a	a=51.8, b=32.6
C_6H_{13}-O-C_6H_4-COO	C2/m	a=30.7, b=28.4

of metallomesogens. A variety of metal complexes exhibiting discotic phases have been synthesized [Giroud-Godquin and Maitlis, 1990]. The molecules of substituted metallo phthalocyanines [Piecliocki et al, 1982] are stacked to form columns with an intermolecular separation of 3.7Å. The columns are arranged in a hexagonal lattice with an intercolumn distance of 34Å. ESR studies indicate a good mobility of charge carriers inside each column. Thus, these metallomesogens can be expected to form one dimensional electrical conductors.

After the pioneering work of Bernal and Crowfoot [1933], it is now well recognized that the molecular arrangement in the crystalline phase is most often related to the arrangement in the mesophase. A knowledge of the molecular arrangement in the crystalline phase is therefore important. Later, Krigbaum *et al* [1970], Vani and Kalyani Vijayan [1977a, 1977b], have shown that in the rod-like molecules, the mesophase structure is related to the crystal structure. When the work described in this thesis was initiated, X-ray data on the mesophase of some discogens were available, but the crystal structure of no discogen was accurately determined by crystallographic methods. Cotrait et *al* [1979] have determined the crystal structure of a substituted triphenylene. However, they could only locate the core of the molecule and not the chains. The reported R-factor is also high (0.38). In fact, the first detailed X-ray analysis of the crystal and molecular structure of a discogen was carried out by the present author. Miililburger and Haase [1989] have determined the crystal structure of two copper complexes of which, one is a discogen. Crystal structures of mesogenic metal complexes, where the molecules are flat, have been reported. But they exhibit only the classical smectic mesophases characteristic of rod-like molecules; none of them form discotic liquid crystals [Roviello *et al*, 1988; Hoshino *et al*, 1990; Iannelli *et* al, 1989; Polishchuk *et* al, 1986].

This thesis is concerned with X-ray investigations on single crystals of some metallo-organic discogens containing copper, palladium and nickel atoms with square planar coordination geometry. All the complexes studied were synthesized and made available to me by Prof. B.K. Sadashiva of Liquid Crystal Laboratory of this Institute. Figure 1.6 shows the structural formula of these discogens. The molecule could be considered to be comprised of two parts, *viz.*, a core and a fringe. The former includes the metal atom which is at the geometric centre of the molecule and the atoms O(1) to O(4) and C(5) to C(10) of the diketone moieties. Figure 1.6 shows that the 11-atom core could be planar and rigid. The fringe is composed of phenyl rings substituted at para positions by long aliphatic chains and hence conformationally flexible. Details of the crystal structure analysis of the six complexes shown in Figure 1.6 are described in the ensuing five chapters of the thesis.

Chapter 2 describes the first detailed X-ray crystal structure analysis of a discogen, *viz.*, bis[1,3-di(*p*-*n*- octyloxyphenyl) propane-1,3-dionato] copper(II), ((i) in Figure 1.6). The crystallization of this complex (as with the other complexes discussed in the subsequent chapters) was a difficult task. However, after much effort suitable single crystals were obtained. The crystal belongs to the triclinic space group $P\bar{1}$ with two molecules in the unit cell. A CAD4 single crystal diffractometer was used to collect the three dimensional intensity data for this crystal (and for all the other crystal structures discussed in this thesis). The



(i) M = Cu $R_1 = R_2 = R_3 = R_4 = OC_8H_{17}$

(ii) M = Cu $R_1 = R_2 = OC_7H_{15}; R_3 = R_4 = C_7H_{15}$

(iii) M = Cu $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

(iv) M = Pd $R_1 = R_2 = R_3 = R_4 = C_{10}H_{21}$

(v) M = Pd $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

(vi) M = Ni $R_1 = R_2 = R_3 = R_4 = C_8H_{17}$

Figure 1.6: Structural formula of the complexes studied in this thesis. The 11-atom core is shown encased.

structure was solved by direct methods and refined using block diagonal least squares procedure. The copper atom is surrounded by four oxygen atoms in a square-planar arrangement. The crystal structure has both layer like and tilted columnar characteristics. The columnar arrangement arises from the periodic stacking of layers along the a-axis. The repeating unit along the column is a molecular pair related by a centre of inversion. In each pair, the cores of the molecules are slightly staggered and exhibit substantial overlap. Although the two halves of the molecule are chemically identical, they are not related crystallographically by symmetry elements.

The crystal and molecular structure of bis [(1-*p*-*n*-heptylphenyl, 3-p-n-heptyl oxyphenyl) propane-1,3-dionato] copper(II), ((ii) in Figure 1.G) with dissimilarly substituted ligand is described in chapter 3. This crystal belongs to the triclinic space group P$\bar{1}$ with two molecules in the unit cell. The structure was solved by direct methods and refined using full matrix least squares procedure. Since there are two heptyl and two heptyloxy chains, the molecule could have either a cis or a *trans* conformation. It was conclusively established that the molecule in the crystalline phase has a cis conformation. The copper atom occupies a general position and is significantly displaced from the plane of the coordinating oxygen atoms. Although there is no overlap of the cores, the centrosymmetrically related molecules in the unit cell tend to pair. The molecular arrangement is essentially layer like.

The crystal and molecular structures of the dimorphs of the discogen bis[1,3-di(*p*-*n*-octylphenyl) propane-1,3-dionato] copper(II) ((iii) in Figure 1.6) are described in chapter 4. Both the needle-like and prismatic forms were crystallized from the same solvent,, *viz.*, acetone. The needle like crystals were found to be more abundant than the prismatic ones. With the view to finding out whether both the crystal forms correspond to the same molecular conformation and arrangement, crystal structures of both the forms were determined. It was also of interest to find out whether any disorder or lack of stability of the crystal structure led to the lower abundance of the prismatic form. Both the forms belong to the triclinic space group $P\bar{1}$. Since there is only one molecule in the unit cell, the copper atom was placed at (0,0,0) and a difference electron density map was computed for both the crystal forms. All the nonhydrogen atoms could be located from this map. The structures were refined using full matrix least squares procedure. Despite some similarities like the space group being the same, copper atoms occupying special positions, etc., significant differences have been observed in the molecular conformation as well as in the molecular arrangements in the two crystalline modifications. The molecules in the prismatic form are more planar than those in the needle-like form, the largest displacement of the atom from a least squares mean plane fitted to the core being 0.314(9)Å for the former and as large 2.016(8)Å for the latter. Although the atoms in the prismatic crystal are characterized by significantly higher thermal parameters, there is no evidence for any structural disorder. In both these crystals, the copper atom lies on an inversion centre and hence the molecular symmetry is retained in the crystal. They are both characterized by tilted columnar arrangements, the tilts being 122° and 111° for the needle like and prismatic crystals, respectively. The molecules in these two structures do not have any oxygen atoms in the chain. Our results suggest the possibility of a correlation existing between the presence or absense of oxygen atoms in the chains and the molecular symmetry. The structures discussed in chapters 2 and 3 contain oxygen atoms in the side chains and have no molecular symmetry, whereas in the two structures described in this chapter, the molecules do possess inversion symmetry. It was therefore of interest to investigate the crystal structure of other metal complexes with only alkyl side chains to see whether those molecules also possess inversion symmetry.

The crystal structure of a palladium complex bis [1,3-di(*p*-*n*-decylphenyl) propane-1,3-dionato] palladium(II) ((iv) in Figure 1.6) is described in chapter 5. It belongs to the triclinic space group $P\bar{1}$ with one molecule in the unit cell. The structure was solved using direct methods and refined using full matrix least squares procedure. The palladium atom lies on an inversion centre and the molecule has a centre of symmetry. The coordination geometry is square planar. The largest atomic displacement from the mean plane fitted to the core is only 0.35(1)Å, which is close to the corresponding value of 0.314(9)Å observed in the prismatic form of the copper complex (iii) described in chapter 4.

In chapter 6 the crystal structures of a palladium complex, bis[1,3-di(*p*-*n*-octylphenyl) propane-1,3-dionato] palladium(II) ((v) in Figure 1.6) and a nickel complex, bis[1,3-di(*p*-*n*- octylphenyl) propane-1,3-dionato] nickel(II), ((vi) in Figure 1.6) are discussed. Both the crystals were found to belong to the triclinic space group $P\bar{1}$. In both the crystals, the respective unit cells contain only one molecule. All the nonhydrogen atoms of the palladium complex could be located from a difference electron density map computed after placing the palladium atom at (0,0,0). Refinement of the structure of the palladium complex was carried out using full matrix least squares procedure. The structure of the nickel complex was then refined by full matrix least squares procedure using the coordinates from the structure of the palladium complex. Both the structures were found to be isomorphous with that of the less abundant prismatic form of complex (iii). The metal atoms lie on an inversion centre and molecular symmetry is retained in the crystal. Although the three metal complexes are isomorphous, only the nickel complex is nonmesogenic.

Chapter 7 provides a resumé of the structural features of seven crystals. In complex (i), (Chapter 2), with four octyloxy chains, these are four oxygen atoms around the core. The complex (ii) (Chapter **3)**, is asymmetrically substituted with two heptyloxy and two heptyl chains and therefore has two oxygen atoms and complexes (iii) (Chapter 4), (iv) (Chapter 5), (v) and (vi) (Chapter 6) have only alkyl chains and hence no oxygen atoms around the core. The metal atoms chosen were Cu/Pd/Ni. Determination of the crystal and molecular structures of these discogens have led to the identification of the following similarities: (1) All the six discogens crystallize in the triclinic space group $P\bar{1}$. The recurrence of the space group may be correlated with the structural requirements for efficient packing of the molecules in the crystal lattice. (2) The coordination around the metal atom is square planar. **(3)** The 11-atom core is only nearly planar. (4) The phenyl rings and the chains are tilted with respect to the core. (5) The molecular conformation in the crystal confers a nearly rectangular shape to these discogens. (6) The chains are fully extended in an all-*trans* conformation. (7)

The molecular arrangement is tilted columnar except for the crystal structure of complex (ii) (chapter 3).

In addition to these similarities, distinct differences in the crystal structural characteristics have also been observed. For example, when oxygen atoms are present in the fringe, the molecules have no crystallographic symmetry and they tend to pair. In the crystal structure of complex (i) where the repeat unit along the column is a molecular pair, the metal atoms are distributed in a *zig-zag* fashion. In the other crystals with columnar arrangement, the metal atoms are stacked one over another. The complex (ii) has a layer like molecular arrangement in the crystalline phase.

In addition to these seven chapters, the thesis also includes an appendix which lists the observed (F,) and calculated (F,) structure factors for all the seven crystal structures.

In Chapters 2 to 6 of the thesis several colour photographs have been included. These are computer plots obtained using the program INSIGHT II. The colour code adopted was as follows:

carbon : green

oxygen : red

copper : blue

nickel : magenta

palladium : yellow

Some of the results presented in this thesis have been reported in the following publications:

1. X-ray investigations on the conformation and molecular arrangement of
   discotic bis[1,3-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato]copper(II)
   K.Usha, Kalyani Vijayan and B.K.Sadashiva
   Mol. Cryst. Liq. *Cryst. Lett.*,**5**, 67 (1987).

2. Crystal and molecular structure of the discogen bis[1,3-di (p-n-octyloxyphenyl)pr
   1,3-dionato]copper(II)
   K.Usha and Kalyani Vijayan
   Mol. Cryst. Liq. *Cryst.*, 174, 39 (1989).

3. Crystal and molecular structure of the discogen bis[1,3-di (*p*-*n*-decylphenyl)propa
   1,3-dionato]palladium(II)
   K.Usha, Kalyani Vijayan, B.K.Sadashiva and P.R.Rao
   Mol. Cryst. Liq. *Cryst.*, 185, 1 (1990).

4. Crystal and molecular structure of the discogen bis[1,3-di (*p*-*n*-octylphenyl)propa
   1,3-dionato]copper(II)
   K.Usha, Kalyani Vijayan and B.K.Sadashiva
   Mol. Cryst. Liq. *Cryst.*, **201,** 13 (1991).

5. Crystal and molecular structure of a discogen bis[(1-p- n-heptylphenyl,3-
   p-*n*-heptyloxyphenyl)propane-1,3-dionato] copper(II)
   K.Usha and Kalyani Vijayan
   Liq. *Cryst.*, 12, 137, 1992.

6. Crystal and molecular structure of a discogen bis [1,3-di (*p*-*n*-octylphenyl)propane 1,3-dionato]copper(II) - a second crystalline modification
   K.Usha and Kalyani Vijayan
   Mol. *Cryst. Liq. Cryst.*, **220,** 77, 1992.

7. Structural characteristics of some metallo-organic discogens
   K. Usha, Kalyani Vijayan and S. Chandrasekhar
   Liq. Cryst., (submitted)

These seven publications correspond to the crystal structures of the complexes (i) to (iv) in Figure 1.6 and also the resumé presented in Chapter 7. The paper describing the structural characteristics of the palladium and nickel complexes discussed in Chapter 6 is under preparation.