

X-RAY ANALYSIS OF THE CRYSTAL STRUCTURES OF SOME MESOGENIC COMPOUNDS

Thesis submitted to the
UNIVERSITY OF MYSORE
for the Degree of
DOCTOR OF PHILOSOPHY

By

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August 1978

DECLARATION

I hereby declare that the thesis was composed by me independently and that it has not formed the basis for the award of any Degree, Diploma, Associateship, Fellowship or other similar title.

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CERTIFICATE

I certify that this thesis has been composed by Mrs. G.V. Vani based on investigations carried out by her at the Liquid Crystals Laboratory, Raman Research Institute, under my 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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ACKNOWLEDGEMENT

I thank **Professor S. Chandrasekhar** for his **constant** encouragement and **guidance** throughout the work reported in this thesis.

I am also greatly indebted to Dr. **Kalyani Vijayan**, without whose **stimulating guidance** and valuable cooperation **this** work would **not** have been possible. My most sincere thanks are due to her.

It is a **pleasure** to **acknowledge** all the help I **received** from my husband, **Ramesh Narayan**, during the **major** part of **this** thesis work. I **extend** my very **special** **thanks** to him.

I am grateful to Dr. **S. Ramaseshan** for allowing me to **use** the **facilities** available at the Materials **Science** Division, **National Aeronautical Laboratory**, Bangalore.

I would like to thank **all** my **colleagues** in the **Liquid** Crystals Laboratory for the help and cooperation **extended** to me during **various** **stages** of this work.

I am thankful to all my crystallographer **friends** at the Indian Institute of **Science**, Bangalore, for providing the **various** computer **programmes**.

My thanks are **also** due to Mr. **S. Raghavachar** for typing this **thesis** so neatly and efficiently.

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CHAPTER 1

INTRODUCTION

The work reported in this thesis deals mainly with the X-ray analysis of the crystal and molecular structures of some materials that form liquid crystals. The motivation for undertaking these studies was two-fold. In their pioneering investigations carried out in 1933, Bernal and Crowfoot [1] showed that there is a relationship between the molecular packing in the crystalline phase and the structures of liquid crystals. With the tremendous revival of interest in liquid crystals in recent years, it was felt that a more detailed study of this fundamental problem would be of significance. Secondly, a knowledge of the crystal structure of the material is in itself of considerable importance in the study of the physics of liquid crystals. For instance, in order to interpret properties like the birefringence or the diamagnetic anisotropy in the liquid crystalline phase, it is necessary to know the anisotropy of the polarizability or the susceptibility of a single molecule, and this can be determined from measurements in the solid state, but only if the crystal structure is known.

We shall begin this introductory chapter with a brief description of liquid crystals and their broad

structural characteristics. A more **detailed** account of their structures and physical **properties** may be **found** in several **reviews and monographs** available in the literature [2].

1.1 What are liquid crystals?

Liquid crystals **represent** states of matter intermediate between the crystalline solid and the **isotropic** liquid. Liquid **crystallinity** is also referred to as '**mesomorphism**' and liquid **crystalline** phases as '**mesophases**'. A compound which exhibits a mesophase is known as a '**mesogen**'. Depending on the various molecular **characteristics** (discussed in the next section) and also on the intermolecular **forces** of attraction, a crystal may pass through one or more **mesophases** before transforming into the **isotropic** liquid.

A liquid crystalline **system** could be either lyotropic or thermotropic. **The former** refers to a two or more **component** system in which the mesomorphic behaviour is brought **about** by the influence of solvents. **Thermotropic** liquid **crystals** are obtained by **purely thermal** processes, **i.e.**, by melting or partial melting of **solids**. **As this thesis** is concerned with the study of **thermotropic** systems **only**, all further **discussion** will be limited to this type of liquid crystal.

Thermotropic liquid crystals are conventionally classified into three broad **groups**: nematic, cholesteric and **smectic**.

(a) **Nematic liquid crystals**

The nematic **mesophase** is **characterised** by a high degree of long-range orientational order, but no long-range **translational** order. The molecules in this **meso**-phase are **spontaneously** oriented approximately **parallel** to **each** other. Fig. 1.1 shows a schematic representation of the molecular arrangement in the crystalline, nematic and isotropic phases.

(b) **Cholesteric liquid crystals**

The **cholesteric** liquid crystal **could** be **considered** to be a nematic liquid crystal **except** that it is composed of optically active molecules. It **has** a nematic-like structure **with** a **screw axis** superposed normal to the **preferred** direction of the **molecules** (Fig. 1.2). The pitch of this helical arrangement **may range** from a **fraction** of a micron to several **microns** and is temperature **dependent**.

(c) **Smectic liquid crystals**

Smectic liquid crystals have layered **structures**. The molecular arrangement within the layer can be ^{of} **various** types. **Smectic A** is the most common type, in which the molecules within a layer are upright with their centres

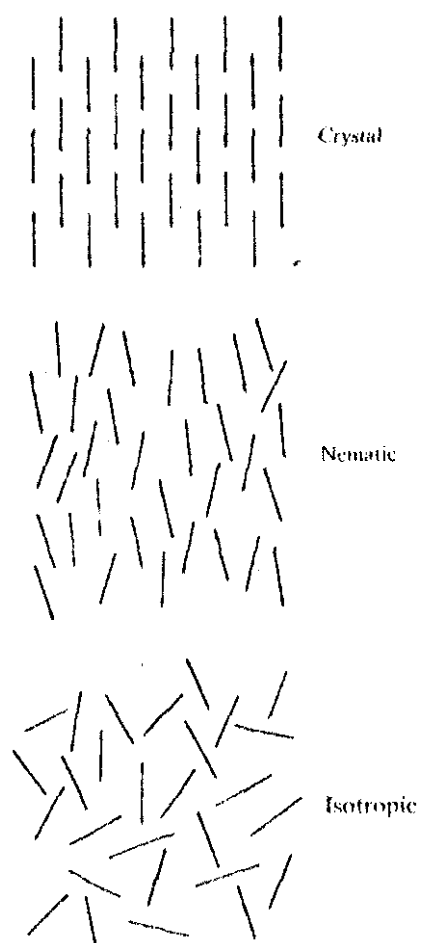


FIGURE 1.1

Schematic representation of the molecular arrangement in the crystalline, nematic and isotropic phases.

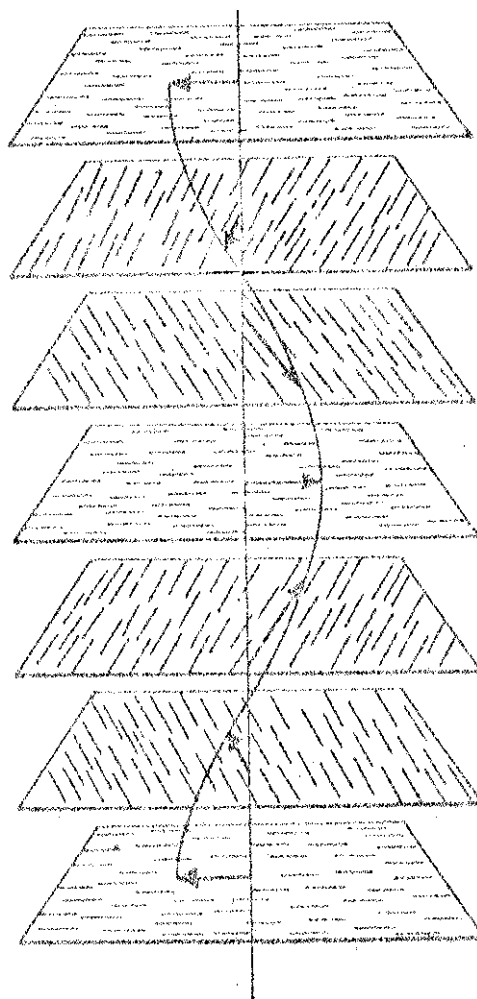


Figure 1.2

**Schematic representation of the molecular arrangement
in the cholesteric phase**

irregularly spaced (Fig. 1.3(a)). The layer thickness is generally of the order of the length of the molecule. In smectic B, the molecules are upright as in smectic A but their centres are hexagonal close-packed within a layer. The molecules in smectic C are inclined with respect to the layers and their centres are irregularly spaced as in smectic A [Fig. 1.3(b)]. Smectic D is reported to have a cubic structure. A few other smectic modifications have also been reported but as yet their detailed structures have not been established conclusively.

1.2 Structural characteristics of mesogenic compounds

From chemical studies, it has been found that in order to be a mesogen a compound should satisfy the following structural characteristics:

(1) The molecules should be geometrically anisotropic, generally long, narrow and rod-like in shape with a high value for the length/breadth ratio. (However, mesomorphic behaviour in disc-like molecules has been discovered recently [3]). Geometrical anisotropy is a very essential characteristic of a mesogen and its importance will be evident from the following example. The compound p-n-decyloxybenzoic acid [Fig. 1.4(a)] exhibits both smectic and nematic mesophases. However, 3-bromo-4-n-decyloxybenzoic acid [Fig. 1.4(b)] is not a mesogen at



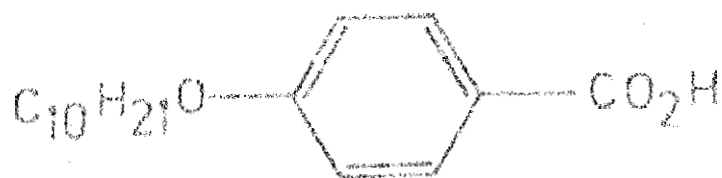
(a)



(b)

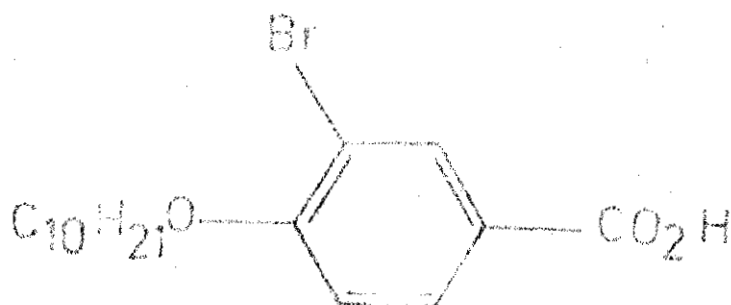
Figure 1.3

Schematic representation of the molecular arrangement in (a) smectic A phase, (b) smectic C phase.



(a)

p-n-Decyloxybenzoic acid



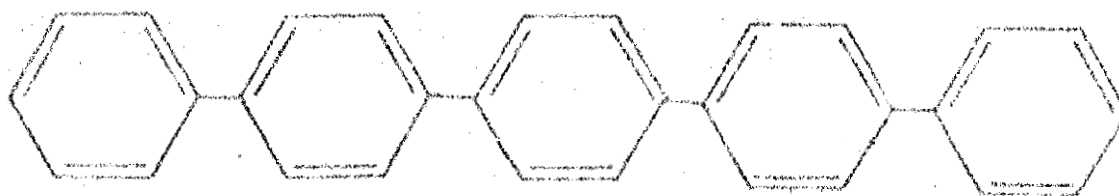
(b)

3-Bromo-4-n-decyloxybenzoic acid.



(c)

4'-n-Propyloxy biphenyl-4-carboxylic acid



(d)

p-Quinquephenyl

FIGURE 1.4

all. The presence of an extra, laterally substituted bromine atom in the latter molecule increases its width and thus inhibits the formation of mesophase.

(ii) The molecules should contain active polarisable groups like unsaturated bonds and aromatic rings. The presence of polarisable groups enhances the mesomorphic thermal stability of the molecules. This is illustrated in the following example. The compound p-n-decyloxybenzoic acid [Fig. 1.4(a)] has a lower nematic thermal stability compared to 4'-n-propyloxy biphenyl-4-carboxylic acid [Fig. 1.4(c)]. Both the acids form dimers. The reason for the higher nematic thermal stability of the latter compound could be traced to the greater polarisability arising from the presence of two extra aromatic rings in each of its dimers.

(iii) The presence of permanent dipole moments in the molecule is conducive to the formation of mesophase. However, this is not an absolutely essential requirement, as can be seen in the case of p-quinquephenyl [Fig. 1.4(d)]. If there is a strong dipole moment along the long molecular axis, the nearest neighbours will tend to be antiparallel [4].

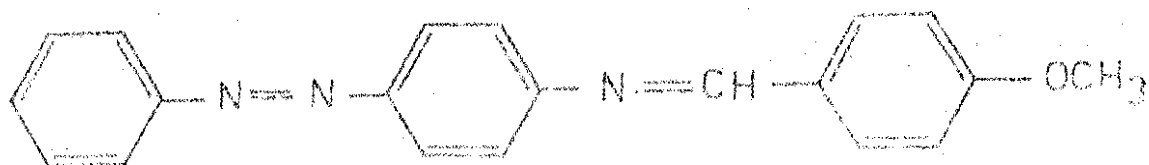
The presence and relative positioning of the polarisable groups governs the intermolecular forces which lead to specific molecular packing in the mesogenic

crystals. A detailed **discussion** on this aspect is given in chapter 5 of this thesis.

1.3 Outline of the thesis

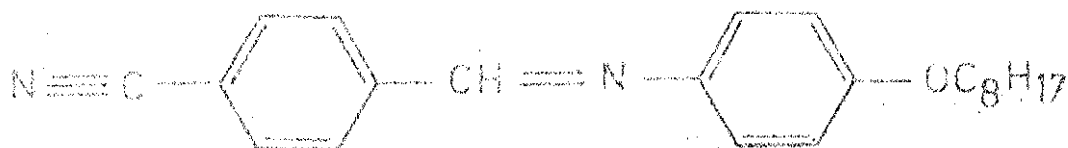
After the classic work of **Bernal** and **Crowfoot** [1], reported in **1933**, no attempt was made to determine the crystal **structures** of mesogens, until quite recently. When the author undertook the work described in this thesis, only a few mesogenic crystal structures had been analysed in detail, viz., those of anisaldehyde **azine** [5], 4-4'-**azodiphenetole** [6], **benzylideneaniline p-carboxylic acid** [7] and **p-asoxyanieole** [8], all of which are **nemato-genic** and ethyl **p-aaoxybenzoate** [9] which is **smectogenic**. In the present study, we report the analyses of the crystal structures of four compounds: a **nematogen**, a **smectogen**, and two isomorphous **cholesterogens**.

Chapter 2 deals with the crystal and molecular **structure** of the nematogenic compound, **n-p-methoxy-benaylidene p-phenyl azoaniline (MBPAA)** [Fig. 1.5(a)]. This **compound** crystallizes in the space group **P2₁/c** with eight molecules in the unit cell. The **crystal structure analysis** was rendered difficult due to the paucity of reflections data and the presence of 48 non-hydrogen **atoms** in the **asymmetric** part of the unit cell. A combination of **direct** methods and packing considerations: was



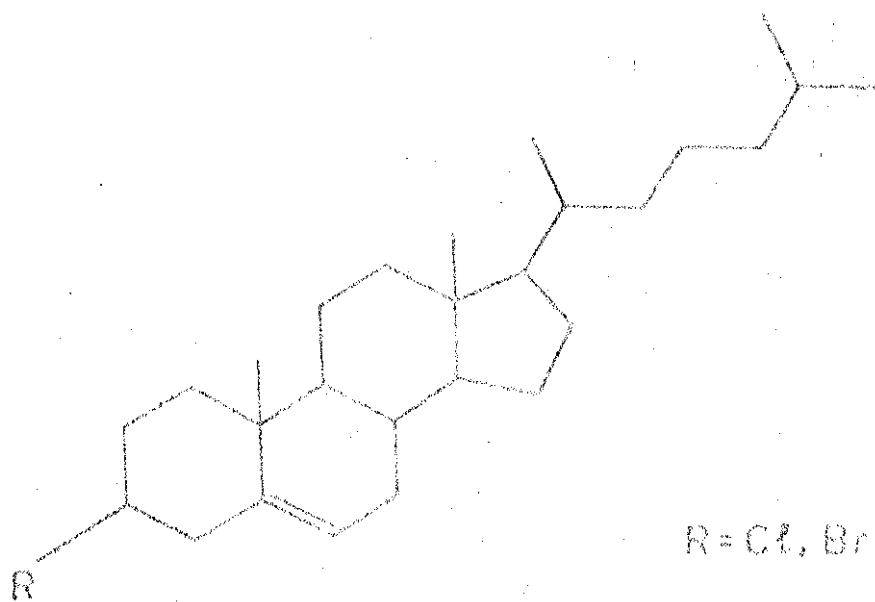
n-p-Methoxybenzylidene p-phenyl azoaniline (MBPAA)

(a)



n-p-Cyanobenzylidene-p-n-octyloxyaniline (CBOOA)

(b)



R = Cl, Br

Cholesteryl chloride/bromide

(c)

FIGURE 1.5

employed to solve the crystal structure. One of the independent molecules in the asymmetric part of the unit cell is found to have a partial positional disorder about its azo bond.

The crystal and molecular structure of the smectogen, *n-p*-cyanobenzylidene-*p-n*-octyloxyaniline (CBOOA) [Fig. 1.5(b)] is described in Chapter 3. CBOOA crystallises in the space group $P2_1/c$ with 4 molecules in the unit cell. The crystal structure was determined by direct methods.

Chapter 4 describes the crystal structure analysis of two cholesterics, viz., cholesteryl chloride and isomorphous cholesteryl bromide [Fig. 1.5(c)]. These compounds crystallise in the space group $P2_1$, with two molecules per unit cell. The crystal structure was analysed by employing the heavy atom method.

While the work reported in these chapters was in progress, several other mesogenic crystal structures were reported in the literature [10-17]. In Chapter 5, a summary of the common and prominent structural characteristics which have emerged out of these crystal structure analyses is given, with special emphasis on the mode of packing in the crystalline phase and its relationship to the formation of mesophase.

As mentioned above, in the course of the refinement of the crystal structure of MBPAA (chapter 2), partial positional disorder about the azo-bond was detected in one of the independent molecules in the asymmetric part of the unit cell. A similar type of disorder about the asoxy bond had, in fact, been analysed by Krigbaum and Taga [13] in the high temperature polymorph of the smectogen ethyl p-aeoxybenzoate. Prior to this, Krigbaum et al [8b] had mentioned the possibility of a partial positional disorder about the azoxy bond in the crystal structure of PAA, though they did not present any quantitative analysis of the disorder. Disorder about the azo-bond had been found by Brown in two non-mesogenic compounds, viz., p-azotoluene [18] and trans-azobenzene [19]. In the present work, least-squares refinement has been carried out to investigate the partial disorder occurring about the -N=N- bonds of these compounds. The details and results of these investigations are given in chapter 6.

Some of the results presented in this thesis have already been reported. The references are given below:

- 1 Crystal structure of n-p-methoxybenzylidene-p-phenylazoaniline. (with Kalyani Vijayan) - Pramana, Suppl. No.1 (1975), 75.
- 2 The crystal structure of n-p-cyanobenzylidene-p-n-octyloxyaniline. (with Kalyani Vijayan) - Current Science (1976), 24, 857.

- 3 The crystal and molecular structure of the **nematogenic** compound **n-p-methoxybenzylidene-p-phenyl azoaniline (MBPAA)**. (with Kalyani Vijayan) - **Acta Cryst.** (1977), **B33**, 2236.
- 4 Crystal and molecular structure of **n-p-cyano-benzylidene-p-n-octyloxyaniline (CBOOA)**. (with Kalyani Vijayan) - **Mol. Cryst. Liq. Cryst.** (1977), **42**, 249.
- 5 Crystal and moleoular structure of **cholesteryl chloride** and **isomorphous cholesteryl bromide**. (with Kalyani Vijayan) - Presented at the VII International Liquid Crystals Conference, Bordeaux (1978) - **Mol. Cryst. Liq. Cryst.** (submitted).
- 6 **Studies** on partial positional disorder in some **azo** and **azoxy** compounds. (with Kalyani Vijayan) - **Aota Cryst.** (submitted).

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