SYNTHESIS AND CHARACTERIZATION OF ISOFLAVONE DERIVATIVES EXHIBITING LIQUID CRYSTALLINE PROPERTIES

by

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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: MATERIALS AND METHODS

CHAPTER 5: RESULTS AND DISCUSSION FOR SERIES 2:

7-*n* -ALKYLOXY-3-(4’-*n* -ALKYLOXYPHENYL)-4H-1-BENZOPYRAN-4-ONE

CHAPTER 6: RESULTS AND DISCUSSION FOR SERIES 3:

7-*n* -ACYLOXY-3-[4’-(3-METHYLBUTYLOXYPHENYL)]-4H-1-BENZOPYRAN-4-ONE

CHAPTER 7: RESULTS AND DISCUSSION FOR SERIES 4:

7-*n* -ALYLOXY-3-[4’-(3-METHYLBUTYLOXYPHENYL)]-4H-1-BENZOPYRAN-4-ONE

CHAPTER 8: RESULTS AND DISCUSSION FOR SERIES 5:

7-DECANOYLOXY-3-(4’-SUBSTITUTEDPHENYL)-4H-1-BENZOPYRAN-4-ONES

CHAPTER 9: RESULTS AND DISCUSSION FOR SERIES 6:

7-(4''-*n*-DECYLOXYBENZOYLOXY)-3-(4'-SUBSTITUTEDPHENYL)-4H-1-BENZOPYRAN-4-ONE

CHAPTER 10: CONCLUSION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

Fourier-Transform Infrared = FTIR

Nuclear Magnetic Resonance = NMR

ppm = part per million

TMS = trimethylsilane

s = singlet

d = doublet

dd = double doublet

t = triplet

m = multiplet

COSY = Correlated Spectroscopy

DEPT = Distortionless Enhancement by Polarization Transfer

HMQC = Heteronuclear Multiple Quantum Correlation

HMBC = Heteronuclear Multiple Band Correlation

Liquid Crystal = LC

Polarized optical microscope = POM

Differential scanning calorimetry = DSC

Cr, Cr_1 = crystal

N = nematic

Sm = smectic

SmA = smectic A

SmC = smectic C

I = isotropic

T_m = melting temperature

T_c = clearing temperature

? H = enthalpy change

a = critical exponent

? = molecular tilt angle

X-Ray Diffraction = XRD

LIST OF APPENDICES

SINTESIS DAN PENCIRIAN TERBITAN ISOFLAVON YANG MEMPAMERKAN CIRI-CIRI HABLUR CECAIR

ABSTRAK

Sintesis dan kerja pencirian telah dilaksanakan ke atas enam siri hablur cecair klasik kalamitik yang berbentuk rod. Komponen tengah bagi kesemua halur cecair tersebut mengandungi 3-fenil-4H-4-on-benzopiran atau lebih dikenali sebagai isoflavon. Sintesis sebatian-sebatian tersebut melibatkan tindak balas-tindak balas pengalkilan, pengasilan Friedel-Crafts, penutupan gelang aromatic dan pengesteran. Analisis mikro CHN serta teknik-teknik spektroskopi seperti FTIR, 1D- dan 2D NMR telah digunakan untuk menentukan struktur molekul bagi sebatian–sebatian tersebut. Suhu peralihan fasa dan nilai perubahan entalpi yang berkenaan telah ditentukan dengan menggunakan kalorimetri pembiasan pembezaan manakala mikroskop optik terkutub digunakan untuk kerja pemerhatian tekstur. Empat siri pertama, yang mana setiap satunya mengandungi lapan homolog, merangkumi isoflavon sebagai komponen tengah dengan satu atau dua rantai terminel asiloksi atau alkiloksi yang fleksibel. Rantai-rantai asiloksi atau alkiloksi tersebut mengandungi atom karbon yang bernombor ganjil atau genap. Sebatian-sebatian dalam keempat-empat siri tersebut mempamerkan fasa-fasa nematik (N), smektik A (SmA) dan smektik C (SmC). Sebatian-sebatian dalam siri kelima dan keenam pula merupakan terbitan isoflavon yang mengandungi rantai desiloksi di satu belah molekul dan pelbagai kumpulan penukar ganti, R, yang mana R = F, Cl, Br, CH_3, OCH_3 dan H di sebelah rantai yang lain. Sebatian-sebatian dengan R = F, Cl dan Br adalah smektogenik dan mempamerkan fasa SmA sahaja manakala sebatian dengan R = OCH_3 adalah nematogenik. Sebatian dengan R = CH_3 mempamerkan kedua-dua fasa N dan SmA. Sebatian dengan R = H dalam siri kelima bukan mesogenik tetapi sebatian yang serupa dalam siri keenam dengan R = H dan lebih panjang molekulnya adalah mesogenik dan menunjukkan fasa SmA. Untuk menyiasat susunan molekul yang berkaitan dengan daya tarikan intermolekul dan korelasi antara sifat termal molekul-molekul dengan ciri-ciri anisotopi dalam fasa-fasa nematik dan

smektik, kajian pembiasan X-ray telah dijalankan ke atas sebatian-sebatian tertentu seperti 7-*n*-heksiloksi-3-(4-*n*-heksiloksifenil)-4H-1-benzopiran-4-on, **ALAB-OC$_6$** dan 7-*n*-heksadesiloksi-3-(4-*n*-heksadesiloksifenil)-4H-1-benzopiran-4-on, **ALAB-OC$_{16}$** daripada siri kedua, 7-*n*-dekanoiloksi-3-[4'-(3-metilbutiloksifenil)]-4H-1-benzopiran-4-on, **MBPB-COOC$_9$** daripada siri ketiga, 7-*n*-dekanoiloksi-3-(4'-metilfenil)-4H-1-benzopiran-4-on, **10PB-CH$_3$** dan 7-(4''-*n*-desiloksibenzoiloksi)-3-(4'-florofenil)-4H-1-benzopiran-4-on, **10BB-F**, masing-masing daripada siri kelima dan keenam. Daripada data X-ray yang diperolehi, molekul-molekul **ALAB-OC$_6$** didapati menyusun secara lapisan dalam fasa SmA manakala sudut condong, ? dari garis normal kepada lapisan bagi molekul-molekul tersebut dalam fasa SmC ialah 15°. Nilai tersebut direkodkan pada 11°C di bawah suhu peralihan fasa. Walau bagaimanapun, nilai sudut condong bagi molekul-molekul **ALAB-OC$_{16}$** dan **MBPB-COOC$_9$** tidak dapat ditentukan kerana peralihan fasa dari kristal ke SmC bagi sebatian-sebatian tersebut adalah peralihan tertib pertama. Analisis pembiasan X-ray turut mendedahkan bahawa molekul-molekul **10PB-CH$_3$** menunjukkan interkalasi yang kuat dalam fasa SmA. Molekul-molekul **10BB-F** disusun secara dwilapisan dalam fasa hablur tetapi susunan dalam lapisan tunggal lebih dicenderungi dalam fasa SmA. Kajian pembiasan X-ray untuk hablur-hablur tunggal juga dijalankan ke atas sebatian-sebatian **ALAB-OC$_6$**, **MBPB-COOC$_9$**, 7-*n*-heksiloksi-3-[4'-(3-metilbutiloksifenil)]-4H-1-benzopiran-4-on, **MBPB-OC$_6$** dan **10PB-CH$_3$**, yang mana kesemuanya adalah triklinik. Struktur molekul bagi sebatian-sebatian tersebut telah dikenalpasti untuk kali pertama dengan menggunakan teknik pembiasan X-ray kristalografi dan didapati bersetuju dengan struktur molekul yang disimpulkan menerusi teknik-teknik FTIR dan NMR. Rantai terminel panjang bagi kristal-kristal tersebut didapati lurus dengan sepenuhnya, kecuali sebatian **ALAB-OC$_6$** yang mempunyai struktur molekul yang amat tidak teratur. Sebatian **10PB-CH$_3$** mempunyai sudut regangan yang paling rendah berbanding dengan terbitan-terbitan isoflavon yang pernah dilaporkan. Molekul-molekul bagi sebatian-sebatian tersebut didapati tersusun secara anti selari antara satu sama lain. Susunan tersebut distabilkan oleh daya lekatan kristal yang merupakan satu kesan daripada interaksi dipolar antara kumpulan eter atau ester yang disusun secara anti selari serta daya tarikan van der Waals antara molekul-molekul.

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ABSTRACT

Six series of classical rod-like, calamitic liquid crystals had been synthesized and characterized. These liquid crystals contained 3-phenyl-4H-4-one-benzopyran or generally known as isoflavone within the central moiety. The syntheses of these liquid crystalline compounds involved alkylation, Friedel-Crafts acylation, cyclization and esterification reactions. CHN microanalysis, FTIR, 1D and 2D-NMR spectroscopic methods were used to elucidate the structures of these compounds. The transition temperatures of the synthesized compounds and respective enthalpy values were determined by differential scanning calorimetry whilst a polarized optical microscope was used for texture observation. The first four series, each consisted of eight homologues, incorporated isoflavone within their central cores with either one or two flexible acyloxy or alkyloxy terminal chains in odd or even parity. The compounds thus obtained exhibited nematic (N), smectic A (SmA) and smectic C (SmC) phases. Compounds from the fifth and sixth series, on the other hand, were isoflavone derivatives bearing decyloxy chain on one end and different substutuents, R, on the other, of which R = F, Cl, Br, CH_3, OCH_3 and H. Compounds with substituents, R = F, Cl and Br are smectogenic displaying only SmA phase whilst compound with R = OCH_3 was nematogenic. Compound with R = CH_3 exhibited both N and SmA phases. Compound with R = H was non-mesogenic in the fifth series but the elongated derivative bearing the same substituent was mesogenic showing SmA phase in the sixth series. In order to investigate the molecular packing associated with the intermolecular attraction as well as the correlation between the thermal behaviour of these molecules with their anisotropy properties in N and smectic phases, the X-ray diffraction studies had been carried out on representative compounds 7-*n*-hexyloxy-3-(4-*n*-hexyloxyphenyl)-4H-1-benzopyran-4-one, **ALAB-OC$_6$** and 7-*n*-hexadecyloxy-3-(4-*n*-hexadecyloxyphenyl)-4H-1-benzopyran-4-one, **ALAB-OC$_{16}$** from the second series, 7-*n*-

decanoyloxy-3-[4’-(3-methylbutyloxyphenyl)]-4H-1-benzopyran-4-one, **MBPB-COOC$_9$** from the third, 7-*n*-decanoyloxy-3-(4’-methylphenyl)-4H-1-benzopyran-4-one, **10PB-CH$_3$** and 7-(4’’-*n*-decyloxybenzoyloxy)-3-(4’-fluorophenyl)-4H-1-benzopyran-4-one, **10BB-F** from fifth and sixth series, respectively. From the X-ray data, molecules of compounds **ALAB-OC$_6$** were arranged in layers in SmA phase whilst the molecular tilt angles, ? from the normal to layer within the SmC phase was approximately 15° as obtained at 11°C below the transition temperature. However**,** the molecular tilt angles, ? for compounds **ALAB-OC$_{16}$** and **MBPB-COOC$_9$** could not be determined due to a first order transition from crystal to SmC phases in these compounds. The X-ray diffraction analyses also revealed that the molecules in compound **10PB-CH$_3$** were intercalated in SmA phase. Molecules in compound **10BB-F** were arranged in bilayers in crystal phase but monolayers were favoured in SmA phase. Single crystal X-ray diffraction analyses had also been carried out on compounds **ALAB-OC$_6$, MBPB-COOC$_9$,** 7-*n*-hexyloxy-3-[4’-(3-methylbutyloxyphenyl)]-4H-1-benzopyran-4-one, **MBPB-OC$_6$** and **10PB-CH$_3$,** wherein all crystals were found to be triclinic. The molecular structures of the earlier mentioned compounds were confirmed for the first time by X-ray crystallography and found to conform to those as inferred from FTIR and NMR techniques. The long flexible terminal chains of these crystals were found to be fully stretched, except for compound **ALAB-OC$_6$** which had a highly disordered structure. Compound **10PB-CH$_3$** had the lowest torsion angle in any hitherto reported isoflavone derivatives. The packing of molecules of these compounds showed that they lay anti-parallel to one another and the crystal cohesion resulted from dipolar interactions between anti-parallel ether or ester groups as well as van der Waals interaction of neighbouring molecules stabilized the packing of the molecules.

CHAPTER 1

INTRODUCTION

1.1 History of Liquid Crystals

In 1888, Friedrich Reinitzer (1858-1927), an Austrian botanical physiologist, then working at the German University of Prague, was extracting cholesterol from carrots in order to determine its chemical formula. Reinitzer found out that cholesteryl benzoate (Figure 1.1), had two melting points. At 145.5°C, the crystal of this material melted into a cloudy liquid, and it melted again at 178.5°C and the cloudy liquid finally became clear. Later, Reinitzer had discovered and described three important features of cholesteric liquid crystals (this name was coined by Georges Friedel in 1922): the existence of two melting points, the reflection of circularly polarized light and the ability to rotate the polarization direction of light. Further investigations of those phenomena were carried out by Otto Lehmann, a German physicist (Collings and Hird, 1998).

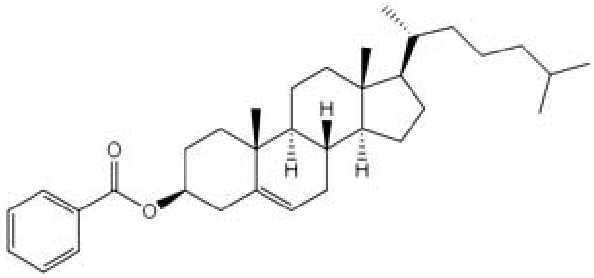


Figure 1.1: Structure of chlolesteryl benzoate.

Liquid crystals (LCs) were not popular among scientists in the early 20th century and the material remained a pure scientific curiosity for about 80 years. In 1969, Hans Kelker succeeded in synthesizing a substance that has a nematic phase at room temperature, MBBA (*p*-methoxybenzyliden-*p'*-n-butylaniline), the well known "fruit-fly" of liquid crystal research, as illustrated in Figure 1.2 (Kelker and Scheurle, 1969). The next step to commercialization of Liquid Crystal Displays (LCD) was the synthesis of further chemically stable substances, leading to the technologically and commercially important class of LCs, for example, cyanobiphenyl derivatives with low melting temperatures (Gray *et al.*, 1973). In 1991, when LCDs were already well established in our everyday life, Pierre-Gilles de Gennes (1932-2007) received the Nobel price in physics for discovering the methods developed for studying order phenomena in simple systems which can be generalized to more complex forms of matter, in particular to LCs and polymers.

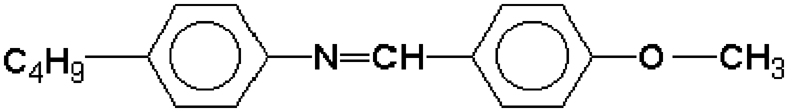


Figure 1.2: Structure of *p*-methoxybenzyliden-*p'*-n-butylaniline, (MBBA)

A detailed description of the applications and technologies of LCDs had been published in "Liquid Crystals for Display Applications" (Geelhaar, 1998). However, LCD technology still has a few drawbacks in comparison to some other display technologies. Hence, researchers and scientists working in this field are still striving to obtain the liquid crystalline materials which possess complex but superior properties to achieve improved device performances.

1.2 Definition of Liquid Crystals

LC phase is a phase of matter whose order is intermediate between that of a liquid and that of a crystal. They are composed of moderate sized organic molecules, about 25 angstroms in length or substances which tend to be elongated and shaped like a cigar or of a variety of other, highly exotic shapes that exhibit a phase of matter that has properties between those of a conventional liquid and those of a solid crystal. For instance, LCs may flow like liquids but due to their elongated shapes, under appropriate conditions the molecules can exhibit orientational order, such that all the axes line up in a particular direction. To specify quantitatively the amount of orientational order in a LC phase, the scalar parameter, S, is commonly used. In a perfectly ordered system (such as in a crystal), S =1 whilst an isotropic liquid has S = 0 with no orientational order (Singh, 2000). As a consequence, the bulk order has profound influences on the way light and electricity behaves in the material. For example, if the direction of the orientation varies in space, the orientation of the light (i.e., the polarization) can follow this variation. Under other conditions the molecules may form a stack of layers along one direction, but remain liquid like (in terms of the absence of translational order) within the layers. There are many different types of LC phases, which can be distinguished based on their different optical properties (such as birefringence). When viewed under a microscope using a polarized light source, different LC phases will appear to have a distinct texture. Each "patch" in the texture corresponds to a domain where the LC molecules are oriented in a different direction. Within a domain, however, the molecules are well ordered. Liquid crystalline materials may not always be in a LC phase (just as water is not always in the liquid phase) it may also be found in the solid or gas phase.

1.3 Types of Liquid Crystals

There are two most common types of LCs though many other different types of molecules are able to give liquid crystalline properties. They are:

i. Thermotropic LCs which exhibit a variety of phases as temperature is changed. Therefore, they are temperature dependent.

ii. Lyotropic LCs which consist of two or more components that exhibit liquid-crystalline properties in certain concentration range.

1.3.1 Thermotropic Liquid Crystals

Thermotropic LCs can be divided into two distinct classes, namely the calamitic LCs and discotic LCs. A thermotropic LC consists of a rigid central core, generally aromatic and a flexible peripheral moiety, most often long alkyl or alkoxy chains.

1.3.1.1 Calamitic Liquid Crystals

According to Collings and Hird (1998), calamitic LCs, also known as rod-like LCs, are mesogens or mesogenic compounds with elongated shape where the molecular length, L being significantly greater than the breath of the molecule, B. The difference in both parameters is responsible for the anisotropy of the mesogens. Figure 1.3 shows a typical shape of a calamitic LC.

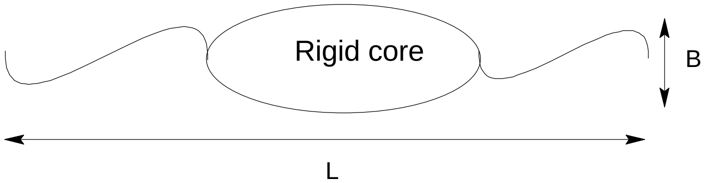


Figure 1.3: Typical shape of a calamitic liquid crystal.

1.3.1.2 Discotic Liquid Crystals

Discotic LCs show several types of mesophases with varying degrees of oganization. Disk-shaped mesogens can orient themselves in a layer-like fashion known as the discotic nematic phase. If the disks pack into stacks, the phase is called a discotic columnar. The columns themselves may be organized into rectangular or hexagonal arrays. Chiral discotic phases are also known.

Similar to calamitic LCs, discotic LCs possess a general structure comprising of a rigid planar (usually aromatic) central core surrounded by a flexible periphery chains as represented in Figure 1.4. A discotic LC has a molecule wherein the molecular diameter (D) which is much greater than the thickness (T). Figure 1.5 shows the first discotic LC reported by Chandrasekhar *et al*. (1997).

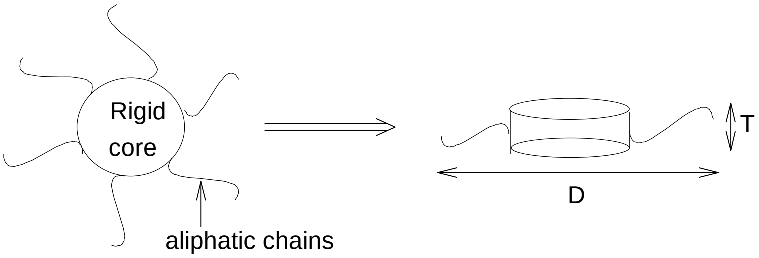


Figure 1.4: General shape of discotic LCs, where D>>T.

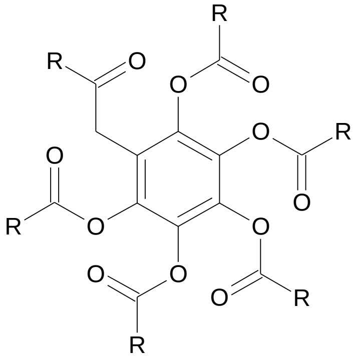


Figure 1.5: Structure of first discotic LCs discovered (Chandrasekhar *et al*., 1977).

1.3.2 Lyotropic Liquid Crystals

In the lyotropic phases, solvent molecules fill the space around the compounds to provide fluidity to the system. In contrast to thermotropic LCs, these lyotropic LCs have another degree of freedom of concentration that enables them to induce a variety of different phases. An example of which is phospholipids present in cell membranes as shown in Figure 1.6. Many amphiphilic molecules show lyotropic LC phase sequences depending on the volume balances between the hydrophilic tail and hydrophobic head (Bissell and Boden, 1995). These structures are formed through the micro-phase segregation of two incompatible components on a nanometer scale.

The content of water or other solvent molecules changes the self-assembled structures. At very low amphiphile concentration, the molecules will be dispersed randomly without any ordering. At slightly higher (but still low) concentration, amphiphilic molecules will spontaneously assemble into micelles or vesicles. This is done so as to 'hide' the hydrophobic tail of the amphiphile inside the micelle core, exposing a hydrophilic surface to aqueous solution. However, these spherical objects do not orderly arrange themselves in solution. At higher concentration, the assemblies will become ordered. At still higher concentration, a lamellar phase may form wherein extended sheets of amphiphiles are separated by thin layers of water.

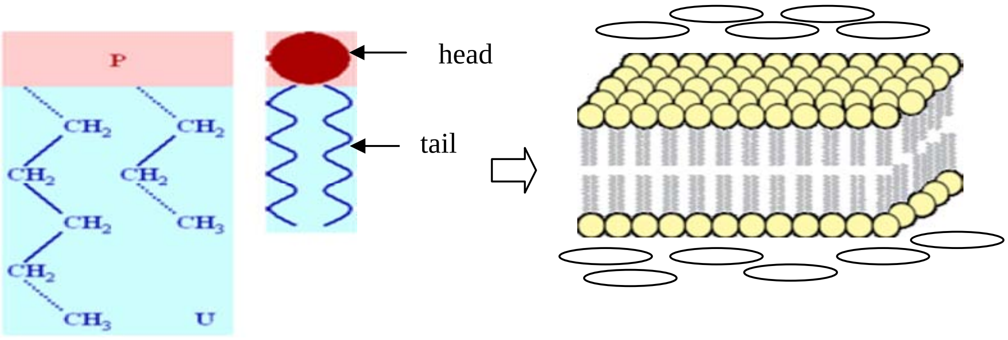


Figure 1.6: Illustration of phospholipids forming bilayers lyotropic liquid crystal, of which ⬭ represents water molecules.

1.4 Phase Structures of Achiral Calamitic Liquid Crystals

Various LC phases (called mesophases) can be characterized by the type of ordering that is present. One can distinguish positional order (whether molecules are arranged in any sort of ordered lattice) and orientational order (whether molecules are mostly pointing in the same direction). Moreover order can be either short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions). Two types of LC phases commonly exhibited by calamitic LCs are:

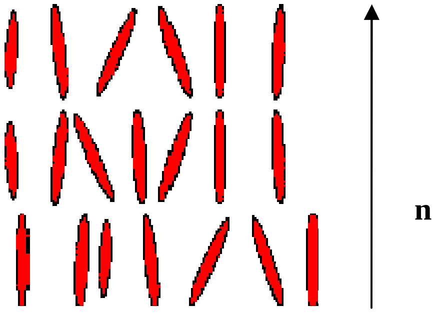
1.4.1 Nematic Phase

It is the most common phase which is characterized by the orientational order of the constituent molecules. The molecules have no positional order, but long-range orientational order. Thus, the molecules flow and their center of mass positions are randomly distributed as in a liquid, but they all point in the same direction referred to the *director,* **n** (Figure 1.7) (Singh, 2000). Nematic LCs are the most commonly used phase in LCDs, with many such devices using the twisted nematic geometry.

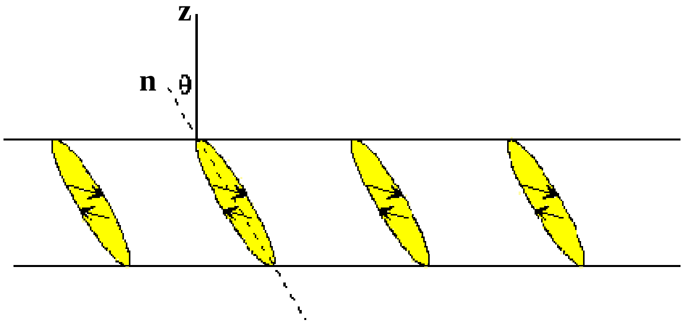
Figure 1.7: Illustration of molecular arrangement in N phase with arrow pointing towards the director, **n**.

1.4.2 Smectic Phase

There are different smectic phases, all characterized by different types and degrees of positional and orientational order. Generally, this phase occurs at temperatures lower than nematogens, form well-defined layers that can slide over one another like soaps. The smectics are thus positionally ordered along one direction. The least order orthogonal SmA phase has molecules oriented along the layer normal, also known as the director, **n,** as illustrated in Figure 1.8 (a) while in the SmC phase they are tilted away from the layer normal, **z** , shown in Figure 1.8 (b).



(a)



(b)

Figure 1.8: (a) Molecular alignment of orthogonal SmA phase where molecules are oriented along the director.

(b) Molecular allignment of SmC phase with a tilt angle, ?.

1.5 Phase Structures of Chiral Calamitic Liquid Crystals

The two common types of chiral mesophases are the chiral nematic and chiral smectic phases.

1.5.1 Chiral Nematic Phase

This is the simplest chiral LC phase which is denoted by N*. It is often called the cholesteric phase because it was first observed for cholesterol derivatives. The local molecular ordering is similar to that of the non-chiral nematic phase, except that it exhibits a twisting of the molecules perpendicular to the director, **n**, with the molecular axis parallel to the director, forming helical macrostructures. The finite twist angle between adjacent molecules is due to their asymmetric packing, which results in longer-range chiral order. According to Collings and Hird (1998), the helixity of the system depends on the absolute configuration of the molecules (enantiomers *R* or *S*). Figure 1.9 shows a helical structure of the cholesteric phase.

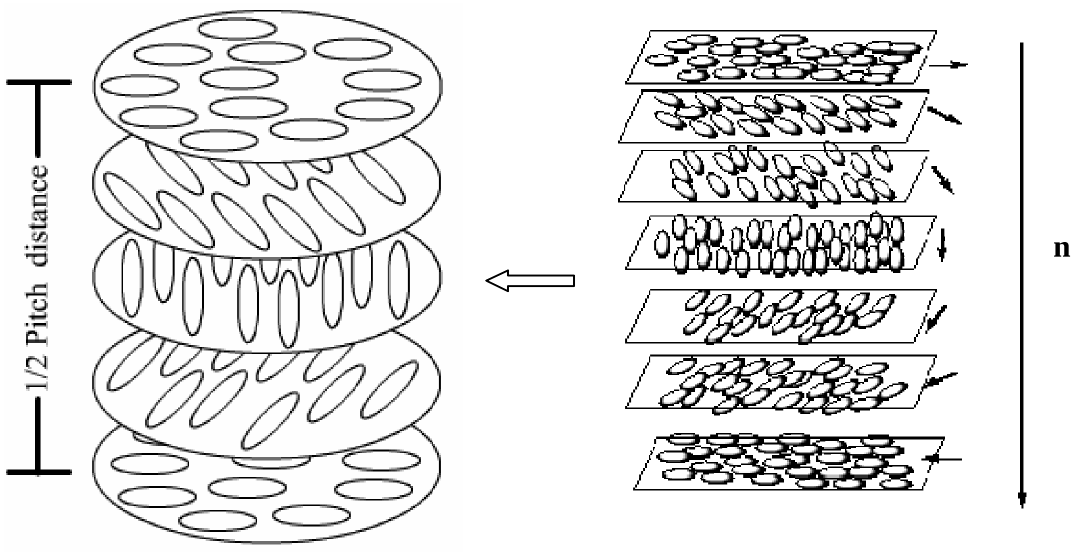


Figure 1.9: Helical structure of cholesteric phase.

1.5.2 Chiral Smectic Phase

In a chiral smectic phase, for example smectic C* phase, the molecules have positional ordering in a layered structure (as in the other smectic phases), with the molecules tilted by a finite angle with respect to the layer normal. The chirality induces a finite azimuthal twist from one layer to the next, producing a spiral twisting of the molecular axis along the layer normal. Hence, the layers are polarized due to their inherent asymmetry (Collings and Hird, 1998). However, the overall polarization is averaged to zero in the bulk.

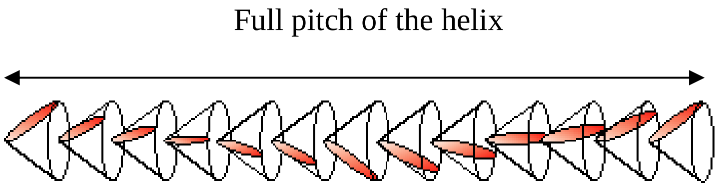


Figure 1.10: A chiral smectic C material, denoted by smectic C*. The tilted director rotates from layer to layer forming a helical structure.

The chiral pitch refers to the distance over which the mesogens undergo a full 360° twist (but note that the structure of the chiral nematic phase repeats itself every half-pitch, since in this phase directors at +180° and -180° are equivalent). The pitch typically changes when the temperature is altered or when other molecules are added to the LC host (an achiral LC host material will form a chiral phase if doped with a chiral material), allowing the pitch of a given material to be tuned accordingly. In some liquid crystal systems, the pitch is of the same order as the wavelength of visible light. This causes these systems to exhibit unique optical properties, such as selective reflection, and these properties are exploited in a number of optical applications.

1.6 Structure of Calamitic Liquid Crystals

A large number of different molecules have been shown to display various calamitic LC phases. All of these share a geometrical anisotropy in shape. Figure 1.11 shows a general template that can be used to describe the structure of calamitic LCs.

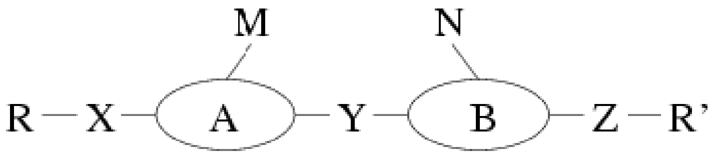


Figure 1.11**:** General structural template for calamitic LCs

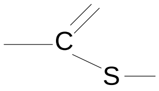
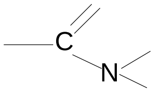
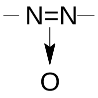
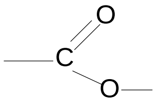
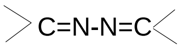
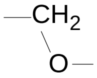
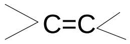
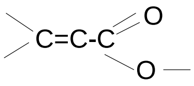
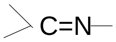
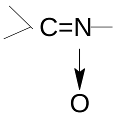
The constituent units within this general structure and their combinations determine the type of LC phase and the physical properties exhibited by a compound (Collings and Hird, 1998). Certain rigidity is required to provide the anisotropic molecular structure. This is achieved by linearly and directly linked ring systems (**A** and **B**) or joined by a connecting group (**Y**) which maintains the linearity of the central core. In order to generate a LC phase, terminal substituents (**R** and **R'**), which are usually alkyl or alkoxy chains are joined directly to the central core or linked via groups **X** and **Z** to provide a certain degree of flexibility. This is to ensure low melting points and to help stabilise the molecular alignment within the LC phase structure. However, one terminal unit may be a small polar substituent. The lateral substituents (**M** and **N**), whilst generally detrimental to the formation of LC phases, are used to modify the mesophase morphology and the physical properties of LCs to generate enhanced properties for applications.

The effects exerted by the connecting groups, **X, Y,** and **Z,** terminal substituents, **R** and **R’** as well as lateral substituents, **M** and **N** are discussed in the following sections.

1.6.1 Connecting group(s) X, Y and Z

Connecting groups, also known as spacer or bridging groups, must produce a linear molecule in order to generate or facilitate LC phases generation. Generally, a fairly rigid connecting group gives the best mesogens. Numerous functional groups have been used. Table 1.1 shows some of the more common examples (Neubert, 2001).

Table 1.1: Connecting groups and their common names (Neubert, 2001).

Compounds	Common names	Compounds	Common names
	thioester		amide
$-N{=}N-$	azo	-CONH-NH-	hydrazine
 $-\underset{\overset{\downarrow}{O}}{N}{=}N-$	azoxy		ester
	azine		ether
	trans isomer of alkene or olefin		trans isomer of cinnamate
	anils or Schiff bases	$-C\equiv C-$	alkyne, acetylene or tolane
	nitrone	$(CH_2)_n$	alkane

In order to facilitate the generation of LC phases, a connecting group serves to increase the polarizability and length of the core of a mesogen besides maintaining its linearity (Collings and Hird, 1998). For example, connecting groups with odd numbers of atoms, such as –O- and –CH_2- do not generate mesophases but the more flexible ones like –OCH_2- and -CH_2CH_2- do show mesomorphic properties (Neubert, 2001). For the same reason, an alkene where (**X**=**Y**=**Z**= C=C), where *cis* and *trans* isomers can exist, only the latter is mesogenic. Nevertheless, the *trans* isomer can be converted to the *cis* isomer under certain conditions such as heat or exposure to UV light.

1.6.2 Terminal Substituents, R and R'

Terminal substituents are used to fine-tune mesomorphic properties. For example, straight or branched alkyloxy chains are used to raise or lower transition temperatures, CN or F substituents are introduced to create dipoles along or across axis in a molecule, alkyloxy or alkyl chains with chirality centres tend to produce chiral mesogens. Terminal substituents also enhance the preference of a specific LC phase, for instance, short alkyl chains favour the generation of N phase.

1.6.2.1 Straight Alkyl/Alkoxy Chains

Alkyl and alkoxy chains are two of the common terminal substituents. Extensive studies have been done on the effects of alkyl and alkoxy chains, along with their length, on mesomorphic properties. This has been accomplished by determining the mesomorphic properties for a wide variety of homologous series of mesogens where the homologues differ only in the number of methylene (CH_2) groups in an aliphatic chain. As the length of the alkyl chain increases, so does the lateral attraction whilst the terminal attraction remains unchanged or becomes relatively weaker. Figure 1.12 illustrates both the lateral and terminal attractions.

Hence, N phase generally occurs at short to mid-chain length then decreases at longer chain length. A reverse trend is usually observed for the smectic LC phases (Neubert, 2001).

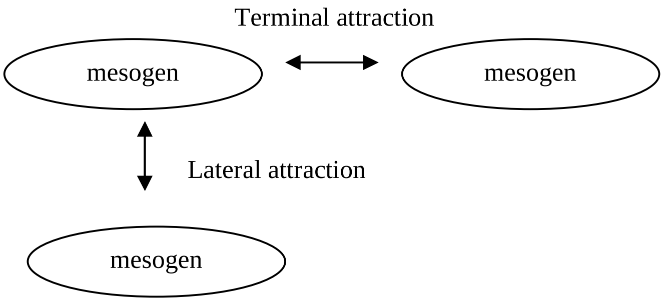
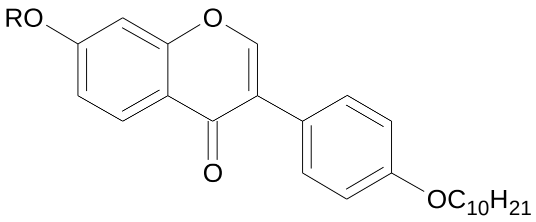


Figure 1.12: Illustration of terminal and lateral attractions between mesogens

The effect of varying the chain length for various compounds has been investigated. These studies have shown that the observed LC phases are strongly dependent upon terminal chain length. For example, 7-alkyldecyloxy-3-(4-decyloxyphenyl)-4H-1-benzopyran-4-one (Figure 1.13).



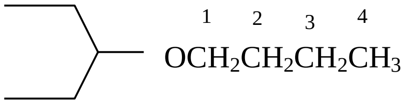
where R = C_nH_{2n+1}; n = 3-9

Figure 1.13: Structure of 7-*n*-alkyloxy-3-(4-decyloxyphenyl)-4H-1-benzopyran-4-one (Belmar *et al*., 1999).

1.6.2.2 Branched Alkyl/Alkoxy Chains

Modifications can be made to the terminal chains, such as the introduction of a double bond or chain branching. The former modification reduces the flexibility of the alkyl chain. If the double bond is positioned such that molecule remains in an approximately linear conformation, then the transition temperatures may be reduced.

Branching of the alkyl chain, along with introducing chirality into the molecule, causes a disruption in the molecular packing which may also reduce transition temperatures. D. Vorlander and Apel (1932) found that the introduction of a branched alkyl group strongly depressed the clearing temperatures as compared to the analogous *n*-alkyl isomers. This is attributed to the broadening of the molecules of mesogens. A branching substituent can be located in any of the carbon atoms in one or both terminal chain(s) as shown in Figure 1.14. Studies of the effect of the location of a branching group in esters on the mesomorphic properties indicated that a methyl group attached to a carbon atom directly to a benzene ring tends to form LC phases only when the other terminal chain is long. However, it is only monotropic smectic A phase. A methyl group on either the 2- or 3- position tends to give the best ferroelectric liquid crystalline (FLC) properties.



$\mathrm{O\overset{1}{CH_2}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_3}}$

Figure 1.14: Possible location of a branching group (Neubert, 2001).

The position of a branching group affects (i) the type of LC phases observed and (ii) the transition temperatures. These temperatures are generally higher when the branching group is positioned further from the core along the terminal chain(s). However, mesogens with nonbranched terminal chain(s) will possess relatively higher clearing temperatures as compared to those with branching groups at the end of the chain(s).

If two chiral carbon atoms are incorporated into the terminal chains, be it in the same or different chains, the chirality of each branch must be such that a racemic material is not formed.

1.6.2.3 Polar Groups

LCs must consist of a terminal polar group (Kelker and Hatz, 1980). However, compounds with terminal groups such as OH and NH_2 do not always form LC phases.

Schroeder and Schroeder (1974) suggested that phenolic compounds must have three benzene rings in order to exhibit liquid crystalline properties. Another criterion is the ability of those molecules to form intramolecular hydrogen bonding. For example, they reported that *p*-phenylene di-*p*-hydroxybenzoate were mesogenic. The structure of the compound is illustrated in Figure 1.15.

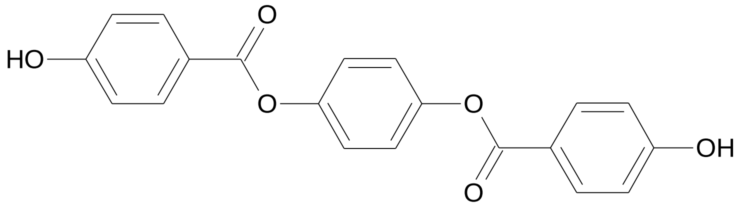
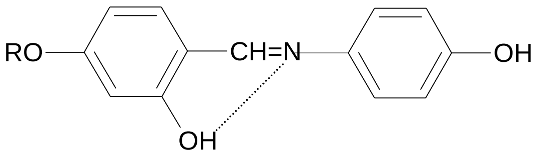


Figure 1.15: The structure of *p*-phenylene di-*p*-hydroxybenzoate (Schroeder and Schroeder, 1974)

On top of the criteria suggested by Schroeder and Schroeder (1974), Sakagami and Takase (1995) also claimed that phenolic compounds with two benzene rings could also be mesogenic (Figure 1.16). Furthermore, in order for compounds bearing OH group to generate mesomorphic properties, the OH group must be present at the *ortho* position, thus forming zwitterions via intramolecular hydrogen bonding.



R = C_nH_{2n+1}, n = 1 to 18

Figure 1.16: Intramolecular hydrogen bonding in 2-hydroxy-4-*n*-alkyloxybenzylidene-4'-hydroxyanilines (Sakagami and Takase, 1995).

Compounds containing certain polar groups show tendency to form dimers, for example biphenyl analogous compounds with CN as the terminal substituent (Figure 1.16). The length to breath ratio controls the clearing temperatures of a mesogen (Collings and Hird, 1998). The correlation between the molecular length to breath ratio and the clearing temperatures can be observed in biphenyl analogous compounds with CN as the terminal substituent. The possible associates in polar biphenyl analogues are illustrated in Figure 1.17.

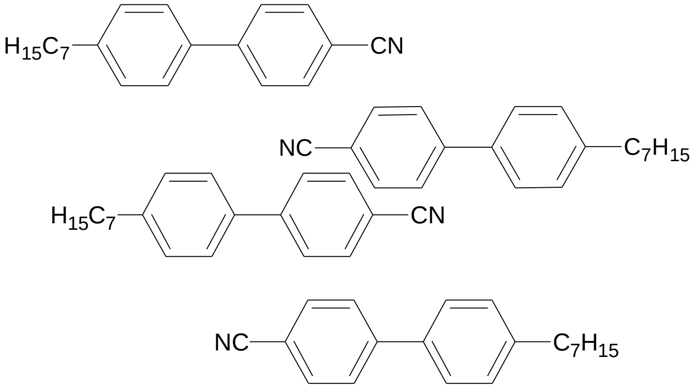


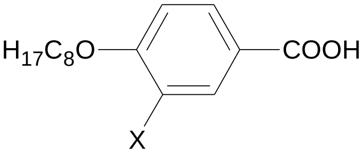
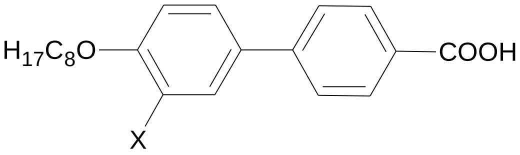
Figure 1.17: Possible dimerization in polar biphenyl analogous compounds.

1.6.3 Lateral Substituents M and N

The inclusion of a polar ester linkage is believed to aid lamellar packing, and, when in conjunction with sufficiently long alkoxy chains can generate a variety of LC phases. Finally, the structure may be modified by lateral substituents. Molecular breadth is considered an important feature in the investigations of the correlation between thermal stability and chemical constitution of LC phases (Neubert, 2001). The increase in molecular breadth due to substitution on the aromatic cores A and B would normally reduce the anisotropy of molecular shape, thus, depressing the stability of the nematic and smectic phases**.**

Twisting in biphenyl structures points out that twisting often accompanies substitution in these and other molecules. This often increases the molecular diameter and thus, lowers the clearing temperatures. The following examples as shown in Table 1.2 give the clearing temperature of some nematogens:

Table 1.2: Examples of nematogens with different lateral substituents and their respective clearing temperatures (Neubert, 2001).

Compound	Substituent, X	Clearing Temperatures/°C
	H	147.0
	F	120.5
	H	287.0
	Cl	248.5
	Br	239.0
	NO_2	224.0

Lateral substituents are introduced in a molecule to facilitate the generation of certain types of mesophases. For example, lateral fluoro substitution has been widely used to generate materials that exhibit the SmC phase. Whilst the inclusion of lateral substituents destabilises the smectic phases, the use of fluorine provides a strong lateral dipole moment which is thought to aid the tilting process (Collings and Hird, 1997). An example of a fluoro containing compound exhibiting SmC phase is shown in Figure 1.18.

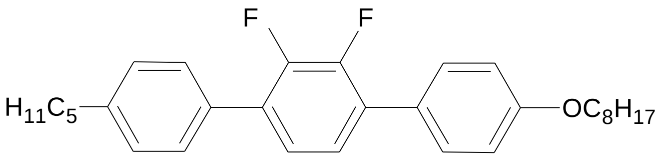


Figure 1.18: The formation of SmC phase by introducing a lateral fluorine atom at 95.0°C (Collings and Hird, 1997).

CHAPTER 2

LITERATURE REVIEW

2.1 Liquid Crystals Incorporating Isoflavone Within The Central Moiety

It has hitherto been documented that the understanding of liquid crystalline compounds is very important towards the continual development especially in the field of molecular engineering. The effort in modifying the existing molecules particularly on the natural products has well been considered as a viable approach to lead to some products showing liquid crystalline properties (Hirose *et al.*, 1989). Isoflavone made up the largest group of natural isoflavoids (Aldercreutz *et al.*, 1986). The pharmaceutical properties of isoflavones have been reported (Boland and Donelly, 1998). Similar to many natural products possessing heterocycles in their structures including flavone and coumarin derivatives, isoflavone-based compounds in biological systems show remarkable liquid crystalline properties (Hirose *et al.*, 1989). Figure 2.1 depicts a general structure of isoflavone.

Chudgar *et al.* were the first researchers who synthesized and characterized liquid crystals derived from isoflavone (1991). In recent years, the mesogenicity of several isoflavone derivatives with classical calamitic structure containing one or two terminal chains have been documented (Chudgar *et al.*, 1991; Belmar *et al.*, 1999). The introduction of heterocycle within the central moiety and the linking groups (ether or ester linkage) between the central moiety and terminal chains have been proven to influence the mesomorphic behaviour of classical calamitic mesogens and determine the variety of mesomorphism displayed due to the dipolar moment associated with the heterocyclic ring as well as these linking groups.

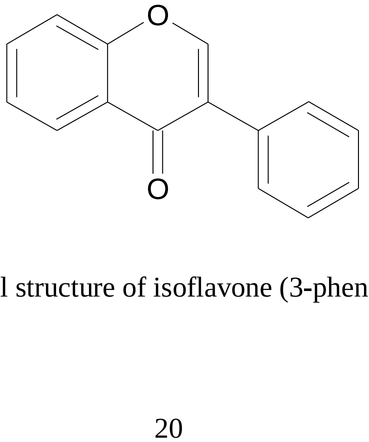


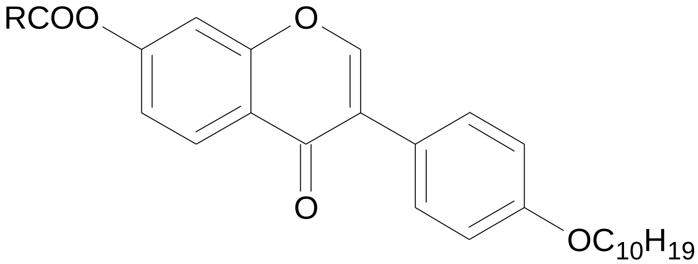
Figure 2.1: General structure of isoflavone (3-phenyl-4H-1-benzopyran-4-one).

In this project, six series of liquid crystalline compounds with classical calamitic structure containing one or two terminal chains incorporating isoflavone within the central core have been synthesized and characterized.

The introduction of heterocycles within the central moiety of isoflavone derivatives strongly influence their mesomorphic behaviour (Belmar *et al*., 1999). The molecular structure of these compounds can be carefully modified in order to generate types of mesophase which are sustainable and useful in the application of liquid crystals since the current application of liquid crystals on display devices rely on N, SmA and SmC materials (Sage, 1987).

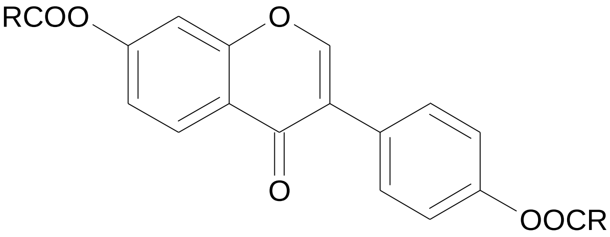
2.1.1 Series 1: 7-*n*-Acyloxy-3-(4'-*n*-acyloxyphenyl)-4H-1-benzopyran-4-one

In recent years, the mesogenicity of several classical calamitic isoflavone derivatives containing one or two terminal chains had been documented (Chudgar *et al*., 1991, 1995; Belmar *et al*., 1999). Chudgar *et al.* synthesized and characterized two series of mesogens derived from isoflavone with only one terminal chain in the years 1991 and 1995, respectively. Later, in the year 1999, mesogens bearing isoflavone within the central core with two terminal chains were synthesized and studied by Belmar *et al.* Both the present series and the earlier reported 7-acyloxy-3-(4'-decylphenyl)-4H-1-benzopyran-4-one (Belmar *et al*., 1999) share similar core structures. Whilst the latter possess an acyloxy and alkyloxy linkages in the terminal alkyl chains, compounds in the present series consist of acyloxy linkages in both terminal chains. Infrared and nuclear magnetic resonance spectroscopy as well as elemental analysis are employed to characterize these mesogens. Chudgar *et al*., and Belmar *et al*., also reported the liquid crystalline properties of these mesogens based on differential scanning calorimetry (DSC) data as well as liquid crystal textures observed under a polarizing optical microscope (POM). In current work, a series of mesogens incorporating isoflavone within the central moiety and two terminal chains have been synthesized and characterized using similar methods. Figure 2.2 shows the structure of mesogens derived from isoflavone synthesized by Belmar *et al*., in 1999. The structure of mesogens of Series 1 is illustrated in Figure 2.3.



where R = C_nH_{2n+1}; n = 3, 4, 5, 6, 7, 8, or 9

Figure 2.2: Structure of 7-*n*-acyloxy-3-(4’-decyloxyphenyl)-4H-1-benzopyran-4-one (Belmar *et al*, 1999).



Compound	R
ACAB-COOC$_3$	C_3H_7
ACAB-COOC$_5$	C_5H_{11}
ACAB-COOC$_7$	C_7H_{15}
ACAB-COOC$_9$	C_9H_{19}
ACAB-COOC$_{11}$	$C_{11}H_{23}$
ACAB-COOC$_{13}$	$C_{13}H_{27}$
ACAB-COOC$_{15}$	$C_{15}H_{31}$
ACAB-COOC$_{17}$	$C_{17}H_{35}$

Figure 2.3: Structure of 7-*n*-acyloxy-3-(4’-*n*-acyloxyphenyl)-4H-1-benzopyran-4-one.

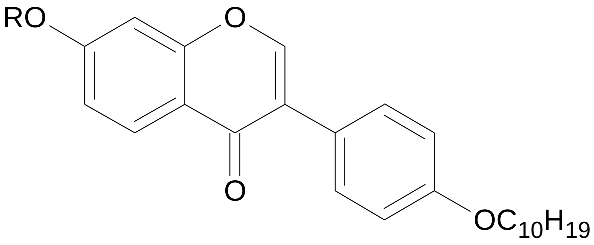
2.1.1.1 Objectives of Series 1

The objectives of Series 1 are:

1. To synthesize a novel series of mesogens derived from isoflavone with ester linking groups and terminal chains of varying number of carbon atoms, 7-*n*-acyloxy-3-(4’-*n*-acyloxyphenyl)-4H-1-benzopyran-4-one.
2. To characterize the liquid crystalline properties of the titled compounds using DSC and POM techniques.
3. To elucidate the structures of the titled compounds using CHN microanalysis, FTIR and NMR techniques.
4. To study the influence of structural changes on the liquid crystalline properties of the titled compounds.

2.1.2 Series 2: 7-*n*-Alkyloxy-3-(4’-*n*-acyloxyphenyl)-4H-1-benzopyran-4-one

A series of novel mesogens containing isoflavone core and two terminal chains have been synthesized and characterized using various methods which include CHN microanalysis, FTIR and NMR spectroscopy. DSC and POM techniques are employed in order to study the liquid crystalline properties of the titled compounds. In this series, the effects of connecting groups as well as the influence of the length of terminal chains on mesomorphic properties are investigated. Belmar *et al.* reported in the year 1999 a series of mesogens incorporating isoflavone within the central core with two terminal chains (Figure 2.4). The influence of the connecting groups and length of one of the terminal chains on the mesomorphic properties are studied. In the present series, the lengths of both terminal chains are changed. X-ray crystal structure elucidation of titled compounds is carried out in order to study their conformation in solid state. Furthermore, the layer spacing of titled compounds during transitions of several mesophases over a range of temperatures are also measured by XRD. Figure 2.5 illustrates the structure of compounds in the present series.



where R = where R = C_nH_{2n+1}; n = 3, 4, 5, 6, 7, 8, or 9

Figure 2.4: Structure of 7-*n*-alkyloxy-3-(4’-decyloxyphenyl)-4H-1-benzopyran-4-one (Belmar *et al*., 1999).