SYNTHESIS AND CHARACTERIZATION OF SOME CALAMITIC LIQUID CRYSTALS CONSISTING OF CHOLESTEROL, ROD-LIKE IMINE AND BIPHENYL-4-CARBOXYLATE COMPONENTS

by

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LIST OF ABBREVIATIONS

Fourier-Transform Infrared = FTIR

Electron-Ionization Mass Spectrometry = EI-MS

Nuclear Magnetic Resonance = NMR

ppm = part per million

TMS = trimethylsilane

s = singlet

d = doublet

t = triplet

q = quartet

dd = double doublets

qt = quintet

st = sextet

m = multiplet

brd = broad

COSY = Correlated Spectroscopy

NOESY = Nuclear Overhauser Enhancement Spectroscopy

ROESY = Rotating-Frame Nuclear Overhauser Effect Spectroscopy

DEPT = Distortionless Enhancement by Polarization Transfer

HMQC = Heteronuclear Multiple Quantum Correlation

HMBC = Heteronuclear Multiple Bond Correlation

Liquid Crystal = LC

Polarized optical microscope = POM

Differential scanning calorimetry= DSC

Cr, Cr_1, Cr_2 or Cr_3 = crystal

N = nematic

N* = chiral nematic or cholesteric

Sm = smectic

SmA = smectic A

SmC = smectic C

SmC* = chiral smectic C

I = isotropic

T_m = melting temperature

T_c = clearing temperature

ΔH = associated enthalpy

ΔT = phase range

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SINTESIS DAN PENCIRIAN BEBERAPA HABLUR CECAIR KALAMITIK YANG MENGANDUNGI KOMPONEN KOLESTEROL, IMINA BERBENTUK ROD DAN BIFENIL-4-KARBOKSILAT

ABSTRAK

Sebanyak tujuh siri hablur cecair kalamitik berjaya disintesis dan dicirikan. Kesemua hablur cecair tersebut dibahagikan kepada tiga jenis yang berlainan berdasarkan struktur teras masing-masing, sama ada komponen kolesterol, imina aromatik berbentuk rod atau bifenil-4-karbosilat. Secara umum, sebatian-sebatian ini disintesiskan melalui tindak balas pengalkilan, pengesteran dan kondensasi. Struktur sebatian yang disintesis ditentukan dengan menggunakan mikroanalisis CHN serta beberapa teknik spektroskopi seperti FTIR, 1D- dan 2D-NMR. Peralihan fasa dan tekstur hablur cecair diperhatikan melalui mikroskop optik terkutub, sementara suhu peralihan dan entalpi yang berkaitan ditentukan melalui analisis DSC. Siri pertama dan kedua masing-masing terdiri daripada tujuh homolog kolesteril 4-*n*-alkoksibenzoat (**nOACh**) dan tujuh homolog kolesteril 4-*n*-alkoksifenil-4'-benzoat (**nOABCh**). Pelbagai kumpulan alkoksi yang mengandungi karbon bernombor genap daripada julat enam sehingga lapan belas digunakan dalam kajian ini. Pelbagai teknik spektroskopi NMR yang digunakan menunjukkan bahawa O=C-O yang menghubungkan kumpulan fenil dan fragmen kolesteril didapati bengkok dan menyebabkan fragmen kolesteril membengkok ke atas. Konformasi yang unik ini ditemui untuk kali pertama dalam kolesteril ester. Kedua-dua siri ini menunjukkan bahawa homolog dengan bilangan karbon yang rendah lebih cenderung untuk mempamerkan fasa nematik kiral (N*), manakala homolog dengan bilangan karbon yang tinggi lebih cenderung untuk mempamerkan fasa smektik A (SmA). Siri ketiga, keempat, kelima dan keenam terdiri daripada

komponen imina aromatik berbentuk rod. Siri ketiga boleh dibahagikan kepada tiga subsiri iaitu, 2-hidroksi-4-metoksibenzilidena-4'-*n*-alkanoiloksianilina (**nSBA**), 2-hidroksi-3-metoksibenzilidena-4'-*n*-alkanoiloksianilina (**nSBB**) dan 3-metoksi-4-*n*-alkanoiloksibenzilidena-4'-*n*-alkanoiloksianilina (**nSBC**). Setiap subsiri ini terdiri daripada empat ahli yang mempunyai panjang rantai alkanoiloksi yang berbeza. Homolog **nSBA** mempamerkan fasa enantiotropik nematik atau SmA, manakala homolog **nSBC** mempamerkan fasa monotropik smektik C (SmC). Namun demikian, homolog **nSBB** tidak mempamerkan sebarang mesofasa. Siri keempat, kelima dan keenam masing-masing terdiri daripada 2-hidroksi-4-*n*-heksadekanoiloksibenzilidena-4'-anilinatertukarganti (**16OHA-R**), *N*-[4-(4-*n*-heksadekanoiloksibenzoiloksi)benzilidena]-4-anilina-tertukarganti (**16AB-R**) dan *N*-[4-(4-*n*-heksadekanoiloksibenzoloiksi)-2-hidroksi-benzilidena]-4-anilinatertukarganti (**16OHAB-R**), dengan R ialah H, F, Cl, Br, OCH_3, CH_3, C_2H_5, CN, OH, SH atau NO_2. Sementara itu, sebatian **16OHA-R** dengan penukar ganti R = H, F, Cl, Br, OCH_3, CN, OH dan NO_2 mempamerkan fasa SmA, manakala sebatian dengan penukar ganti R = CH_3 dan C_2H_5 mempamerkan fasa monotropik SmC dan sebatian dengan R = SH mempamerkan fasa monotropik nematik. Sebatian **16AB-R** dan **16OHAB-R** (dengan R = H, OCH_3, CH_3, C_2H_5, OH dan NO_2) menunjukkan bukti fasa nematik, manakala sebatian **16AB-R** dan **16OHAB-R** (dengan R = F, Cl, Br dan CN) mempamerkan fasa SmA. Sebatian **16OHAB-SH** mempamerkan fasa nematik manakala sebatian **16AB-SH** tidak mempamerkan sebarang mesofasa. Molekul **16AB-R** dan **16OHAB-R** mempunyai kestabilan mesofasa yang lebih tinggi daripada molekul **16OHA-R** kerana molekul-molekul dalam siri **16AB-R** dan **16OHAB-R** adalah lebih panjang berbanding dengan molekul-

molekul dalam siri **16OHA-R**. Sifat mesomorfik sebatian-sebatian tersebut juga dipengaruhi oleh interaksi intramolekul dan intermolekul yang disebabkan kehadiran kumpulan *orto*-hidroksil. Siri ketujuh yang berteraskan bifenil-4-karbosilat terdiri daripada empat homolog (*S*)-2-metilbutil 4'-(4"-*n*-alkanoiloksi-benzoiloksi)bifenil-4-karbosilat (**S-MB-OOCn**). Kesemua homolog **S-MB-OOCn** mempamerkan fasa SmA dan smektik C kiral (SmC*).

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ABSTRACT

Seven series of calamitic liquid crystals were successfully synthesized and characterized. These liquid crystals are categorized into three different types according to their core structure; either a cholesterol, rod-like aromatic imine or biphenyl-4-carboxylate component. The synthesis of these compounds basically involved alkylation, esterification and condensation reactions. The structures of the synthesized compounds were established by CHN microanalysis along with several spectroscopic techniques such as FTIR, 1D- and 2D-NMR. Whilst the phase transitions and liquid crystal textures were observed by using polarized optical microscope, the respective transition temperatures and associated enthalpies were determined by using DSC analysis. The first and second series which consist of seven homologues each, include cholesteryl 4-*n*-alkoxybenzoates (**nOACh**) and cholesteryl 4-(4-*n*-alkoxyphenyl)benzoates (**nOABCh**). Various alkoxy groups consisting of even numbered carbons ranging from six to eighteen have been adopted throughout this study. The various NMR techniques which were employed revealed that the O=C-O bridging the phenyl group and the cholesteryl fragment was bent and led to the cholesteryl fragment to fold up. This unique conformation has been observed for the first time in cholesteryl esters. Both of the series showed that the lower members have a higher tendency to exhibit chiral nematic (N*) phase whereas the higher members showed a greater tendency to display the smectic A (SmA) phase. The third, fourth, fifth and sixth series each consists of a rod-like aromatic imine component. The third series is further divided into

three sub-series; 2-hydroxy-4-methoxybenzylidene-4'-*n*-alkanoyloxyanilines (**nSBA**), 2-hydroxy-3-methoxybenzylidene-4'-*n*-alkanoy-loxyanilines (**nSBB**) and 3-methoxy-4-*n*-alkanoyloxybenzylidene-4'-*n*-alkanoy-loxyanilines (**nSBC**). Each of them comprised four members which differed in the alkanoyloxy chain length. Whilst the **nSBA** homologues exhibited the enantiotropic nematic or SmA phase, the **nSBC** homologues displayed the monotropic smectic C (SmC) phase. However, the **nSBB** homologues did not exhibit any mesophase. The fourth, fifth and sixth series encompassed 2-hydroxy-4-*n*-hexadecanoyloxybenzylidene-4'-substituted-anilines (**16OHA-R**), *N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)benzylidene]-4-substituted-anilines (**16AB-R**) and *N*-[4-(4-*n*-hexadecanoyloxybenzoyloxy)-2-hydroxybenzylidene]-4-substituted-anilines (**16OHAB-R**), in which R is H, F, Cl, Br, OCH_3, CH_3, C_2H_5, CN, OH, SH or NO_2. While compounds **16OHA-R** with the substituents R = H, F, Cl, Br, OCH_3, CN, OH and NO_2 exhibited SmA phase, those with the substituents R = CH_3 and C_2H_5 showed monotropic SmC phase and finally the compound with R = SH displayed monotropic nematic phase. Compounds **16AB-R** and **16OHAB-R** (where R = H, OCH_3, CH_3, C_2H_5, OH and NO_2) showed evidence of nematic phase while compounds **16AB-R** and **16OHAB-R** (where R = F, Cl, Br and CN) exhibited SmA phase. Compound **16OHAB-SH** exhibited nematic phase whereas compound **16AB-SH** did not show any mesophase. The **16AB-R** and **16OHAB-R** molecules have a higher mesophase stability compared to the **16OHA-R** molecules owing to their higher molecular length. The mesomorphic properties of these compounds were also influenced by the intermolecular and intramolecular interactions owing to the presence of the *ortho*-hydroxyl group. The seventh series with a biphenyl-4-carboxylate core consists of four *(S)*-2-

methylbutyl 4’-(4”-*n*-alkanoyloxybenzoyloxy)biphenyl-4-carboxylate (**S-MB-OOCn**) homologues. All the **S-MB-OOCn** homologues exhibited the chiral smectic C (SmC*) and SmA phases.

CHAPTER ONE

INTRODUCTION

1.1 Introduction To Liquid Crystals

The liquid crystal (LC) phase is a well-known state of matter, which lies between the solid and isotropic liquid phases. By definition, the LC state (mesomorphic or mesogenic state) is characterized by having a long-range orientational order and possible partial positional order. To specify quantitatively the amount of orientational order in the LC phase, the scalar order parameter S is commonly used ($0 < S < 1$). In a perfectly oriented system, $S = 1$ but in an isotropic liquid state where there is no orientational order, $S = 0$ (Singh, 2000).

In the crystal phase, the molecules have a high degree of order occupying fixed positions in the lattice, which is characterized by translation of the unit cell. Therefore, the molecules are positioned in fixed orientations with no translational freedom. Conversely, in the isotropic liquid phase, only a short-range order dominates. Since the molecular axes are able to tumble freely, the molecules are mobile and have no orientation with respect to each other. The LC phase (mesophase) shares properties of both the crystal and liquid phases. It possesses an intermediate molecular order between the perfect three-dimensional long-range positional and orientational order found in crystals and the absence of long-range order found in isotropic liquids. Although the molecules are not constrained within a lattice, the molecular axes tend to be oriented in a preferred direction, on average, defined as the director (**n**) (Singh,

2000). Hence, throughout the LC phase, the mesogens (materials able to sustain mesophases) are fluids and at the same time, have anisotropic physical properties which are known as tensor properties due to their dependence on the orientation. Some examples of anisotropic properties are birefringence, alignment in electric and magnetic fields (electrical permittivity and magnetic susceptibility), elasticity, viscosity and conductivity (Photinos, 2001).

1.2 History Of Liquid Crystals

The discovery of LCs in the year 1888 was attributed to the Austrian botanist F. Reinitzer. Reinitzer observed a “double melting” behaviour for cholesteryl benzoate (Figure 1.1). The crystals of this material melted at 145.5 ^{o}C into a cloudy fluid, which upon further heating to 178.5 ^{o}C became clear. Further investigations of this phenomenon were carried out in the year 1900 by a German physicist, O. Lehmann who first named this mesomorphic state as liquid crystal state (Collings and Hird, 1998).

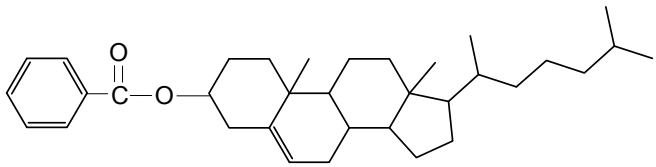
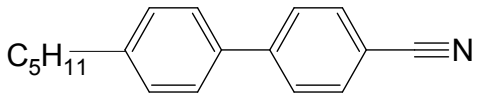


Figure 1.1: Structure of the first liquid crystal, cholesteryl benzoate.

Following these observations and discoveries, scientists in the relevant fields turned their attention towards a growing number of compounds, which displayed liquid crystalline properties. In order to establish a relationship between molecular structure and the exhibition of liquid crystalline properties, systematic modifications of the structures of mesogens were undertaken in

1973, leading to the discovery of the most technologically and commercially important class of LCs to date: the 4-alkyl-4'-cyanobiphenyl (**CB**) of which an example, 4-pentyl-4'-cyanobiphenyl (**5CB**) is illustrated in Figure 1.2 (Gray *et al.*, 1973).



5CB

Cr $\xrightarrow{24\ ^{o}C}$ **N** $\xrightarrow{35\ ^{o}C}$ **I**

Figure 1.2: Structure and phase transition of 4-pentyl-4'-cyanobiphenyl (**5CB**) (Gray *et al.*, 1973).

These materials still constitute the simple common displays found in calculators or mobile phones. Since numerous and increasingly sophisticated applications which rely on the use of liquid crystalline materials require such complex superior properties to achieve improved device performance, the quest for ever new LCs has grown enormously over the last three decades. Nowadays, LCs play a dominant role in a large part of the display technology.

1.3 Types Of Liquid Crystals

Different types of molecules can form liquid crystalline phases. The two most important types are:

i. thermotropic LCs, whose mesophase formation are temperature dependent, and

ii. lyotropic LCs, whose mesophase formation are concentration and solvent dependent.

This research focused on calamitic thermotropic LCs. However a brief discussion on lyotropic LCs is also given in the following section.

1.3.1 Lyotropic Liquid Crystals

Lyotropic LCs are two-component systems where an amphiphile is dissolved in a solvent. Thus, lyotropic mesophases are concentration and solvent dependent. The amphiphilic compounds are characterized by two distinct moieties, a hydrophilic polar “head” and a hydrophobic “tail”. Examples of these kinds of molecules are soaps [Figure 1.3 (a)] and various phospholipids like those present in cell membranes [Figure 1.3 (b)] (Belloni, 2002).

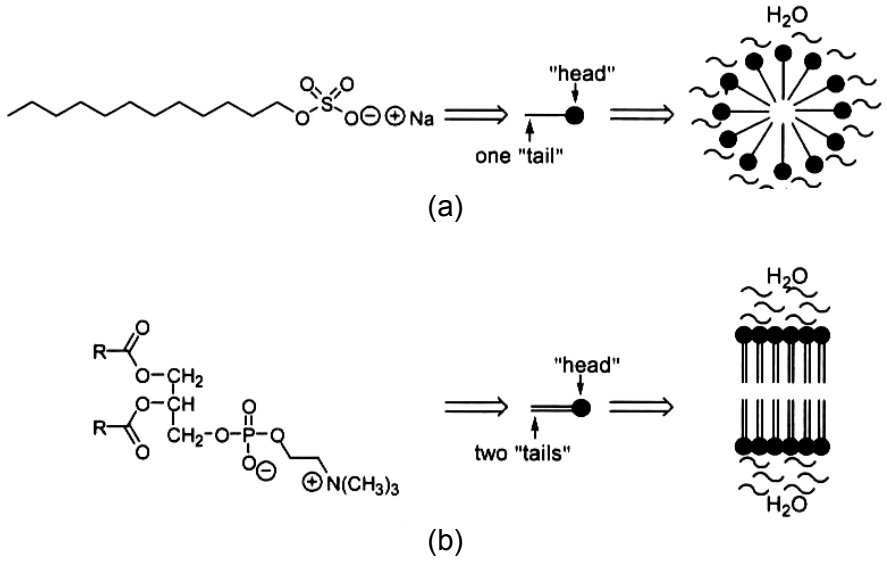


Figure 1.3: (a) Illustration of sodium dodecylsulfate (soap) forming micelles.
(b) Illustration of phospholipids (lecithine) forming bilayer lyotropic liquid crystal as present in cell membranes (Belloni, 2002).

1.3.2 Thermotropic Liquid Crystals

The essential requirement for a molecule to be a thermotropic LC is a structure consisting of a rigid central core (often aromatic) and a flexible peripheral moiety (generally aliphatic groups). These structural requirements lead to two general classes of LCs which are calamitic and discotic LCs.

1.3.2.1 Calamitic Liquid Crystals

Calamitic or rod-like LCs are mesomorphic compounds that possess an elongated shape as depicted in Figure 1.4. The result of the molecular length (L) being significantly greater than the molecular breadth (B) is responsible for the anisotropy of the structure (Collings and Hird, 1998).

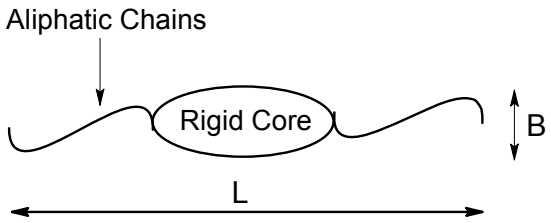
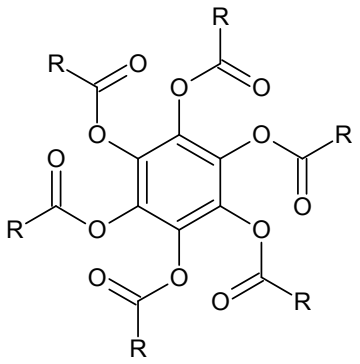


Figure 1.4: General shape of calamitic liquid crystals, where L>>B.

1.3.2.2 Discotic Liquid Crystals

In the year 1977, a second type of mesomorphic structure based on a discotic (disc-shaped) structure was discovered. The first series of discotic compounds to exhibit mesophase belonged to the hexa-substituted benzene derivatives (Figure 1.5) reported by Chandrasekhar *et al.* (1977).

Similar to calamitic LCs, discotic LCs possess a general structure comprising a rigid planar (usually aromatic) central core surrounded by a flexible periphery, represented by pendant chains (usually four, six, or eight), as illustrated in Figure 1.6. As can be seen, the molecular diameter (D) is much greater than the disc thickness (T), imparting the anisotropy to the structure.



where R = C_4H_9 to C_9H_{19}

Figure 1.5: Structure of the first series of discotic LCs discovered: the benzene-hexane-*n*-alkanoate derivatives (Chandrasekhar *et al.*, 1977).

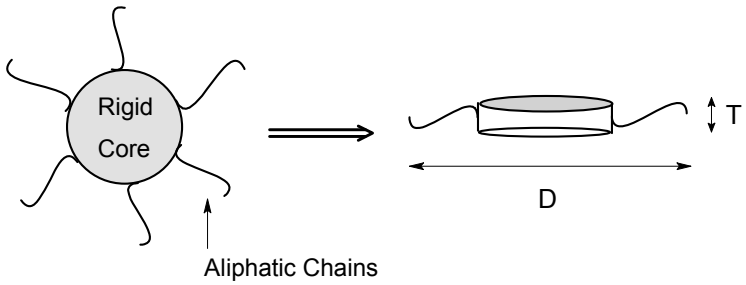


Figure 1.6: General shape of discotic liquid crystals, where D>>T.

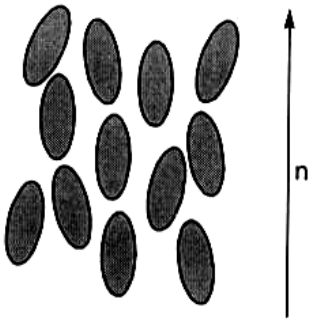
Discotic LCs can show several types of mesophases with varying degrees of organization. The two principle mesophases are nematic discotic and columnar phases.

1.4 Phase Structures Of Calamitic Liquid Crystals

Two types of mesophases commonly exhibited by calamitic LCs are the nematic and smectic phases.

1.4.1 Nematic Phase

The least ordered mesophase (the closest to the isotropic liquid state) is the nematic (N) phase, where the molecules only have an orientational order. The long molecular axis points on average in one favoured direction referred to as the director (Figure 1.7) (Singh, 2000). A classical example of a LC displaying a nematic mesophase is **5CB** (Figure 1.2).



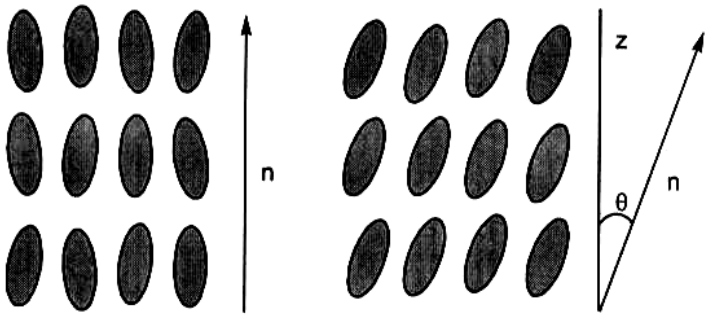
Note: The arrow points to the director, **n**

Figure 1.7: Structure of nematic phase.

1.4.2 Smectic Phase

The next level of organization is classified as smectic (Sm), whereby in addition to the orientational order the molecules possess positional order, such that the molecules organize in layered structures.

Generally, the smectic phase which is characterized by the least order is the orthogonal smectic A (SmA) phase, where the layers are perpendicular to the director [Figure 1.8 (a)]. When the director is tilted at an angle (θ) other than 0^o to the normal [layer (z)], the result is the smectic C (SmC) phase [Figure 1.8 (b)] (Singh, 2000).



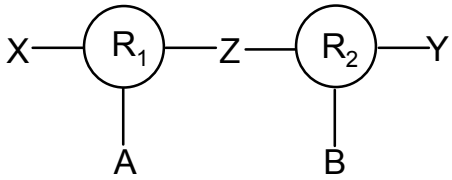
(a) (b)

Note: The arrow points to the director, **n**

Figure 1.8: Structures of (a) SmA and (b) SmC phases.

1.5 Structure Of Calamitic Liquid Crystals

LCs derived from rod-like molecules have been comprehensively studied. The general templates which are used to describe the structure of calamitic mesogens are illustrated in Figure 1.9 (Collings and Hird, 1998).



where Z = connecting group
R_1 and R_2 = ring systems
X and Y = terminal substituents
A and B = lateral substituents

Figure 1.9: General structural templates for calamitic mesogens.

These rod-like structures consist of a rigid rod formed by two rings (R_1 and R_2) that are joined together by a connecting group Z, with two tails (X and Y) called the terminal groups or chains placed in such a position (usually *para* to the central group) to give a linear molecule. Usually, at least one of the terminal groups must be a flexible chain. A lateral substituent (A or B) is attached to the core of a mesogen, mostly to the ring (R_1 or R_2), in a position that is not along the molecular axis. Usually, the lateral substituent depresses both the melting and clearing temperatures by broadening the core of the mesogen (Neubert, 2001a).

In the following sections, the effect exerted by the connecting group, Z and the terminal groups, X and Y of the molecules on their mesogenic properties will be discussed.

1.5.1 Connecting group (Z)

Numerous functional groups have been used as connecting groups. Some of the more common examples are shown in Figure 1.10 (Neubert, 2001a).

To be successful in facilitating mesophase generation, a connecting group must maintain the linearity of the core, whilst increasing the length and polarizability of the core (Collings and Hird, 1998). Thus, with an alkene (Z = C=C) where two isomers (*cis* and *trans*) can exist, only the *trans* isomer is mesogenic. Even if the *trans* isomer is prepared, it can convert to the *cis* isomer under certain conditions such as heat. For the same reason, connecting

groups with an odd number of atoms such as -O- and -CH_2- do not produce mesophases. Generally, fairly rigid connecting groups give the best mesogens, but the more flexible groups such as -OCH_2- and -CH_2CH_2- do show mesomorphic properties (Neubert, 2001a).

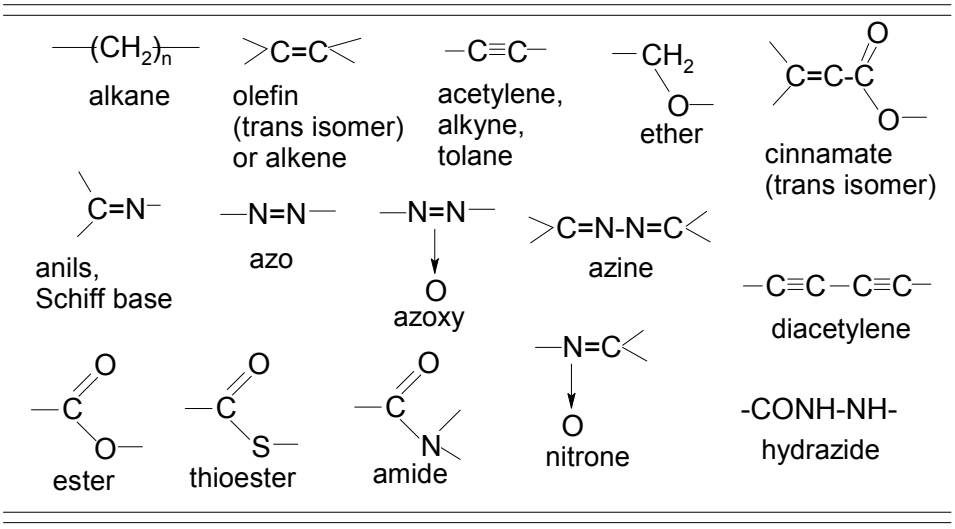
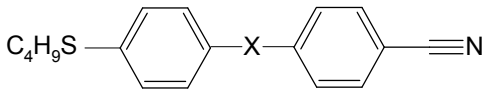


Figure 1.10: Connecting groups and their common names (Neubert, 2001a).

An example of the effect of a connecting group on the mesomorphic properties is illustrated by 1,4-phenyl derivatives containing butylsulfanyl and cyano groups with various linking groups (Seed *et al.*, 1995a and Seed *et al.*, 1995b and Cross *et al.*, 2000). The clearing temperatures (T_c) (temperature when the compound turns into isotropic liquid or known as clearing point) of the 1,4-phenyl derivatives are displayed in Table 1.1.

Table 1.1: Clearing temperatures (T_c) of compounds with various connecting groups (X) in 1,4-phenyl derivatives



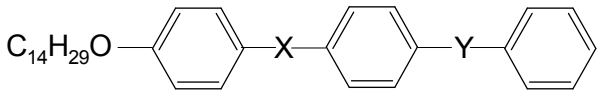
Compound	Connecting group, X	T_C / ^oC	Reference
1	-	64.8	Seed *et al.*, 1995a
2	-CH=CH-	96.7	Cross *et al.*, 2000
3	-C≡C-	80.3	Cross *et al.*, 2000
4	-COO-	82.2	Seed *et al.*, 1995b
5	-C≡C-COO-	78.4	Cross *et al.*, 2000

Table 1.1 shows that the T_c of compounds **2** to **5** are higher than compound **1**. For compound **2** to compound **5**, each of the connecting group consists of at least one *sp* or sp^2 hybridized atom that which allows conjugation interaction with the aromatic rings. For compound **1**, the two aromatic rings in core center are linked together by a single bond without any bridging group. The presence of an additional connecting group in compounds **2** to **5** increases the molecular length as well as the molecular polarizability, hence increasing the T_c of compounds **2** to **5**. In conclusion, the geometry of the connecting group affects the stability of the mesophase.

Another factor that could influence mesomorphic properties is the conjugative interaction between the connecting group, the core and the terminal groups. Two mesogens containing two carboxyl groups are compared in Table 1.2 (Sakurai *et al.*, 1989). Phenyl 4-(4-tetradecyloxybenzoyloxy)-benzoate (compound **6**) and 4-tetradecyloxyphenyl 4-benzoyloxybenzoate (compound **7**) differ only in the orientation of the COO groups. If the oxygen

atom of the alkoxy group in a mesogen has the chance to come into conjugative interaction with the C=O of the ester group, the mesogen will have the more stable mesophase. This interaction caused the polarity of the carbonyl oxygen to increase. It can be apparently seen from Table 1.2 that compound **6** has a wider mesophase length and a higher clearing point in comparison to compound **7** owing to the conjugative interaction. In addition, compound **6** possessed more ordered mesophase properties than compound **7** wherein compound **6** exhibited the more ordered SmA phase and compound **7** exhibited the less ordered nematic phase.

Table 1.2: Transition temperatures and phase ranges (ΔT) of phenyl 4-(4-tetradecyloxybenzoyloxy)benzoate (compound **6**) and 4-tetradecyloxyphenyl 4-benzoyloxybenzoate (compound **7**) (Sakurai *et al.*, 1989)

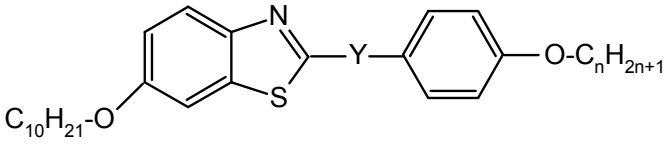


Compound	X	Y	Transition temperature/ °C		ΔT/ °C
			Cr-M[a]	M[a]-I	
6	COO	COO	113	133	20
7	OOC	OOC	117	120	3

[a] compound **6**: M = SmA phase, compound **7**: M = nematic phase

Influence of the polarity of a connecting group can also be inferred from the three series of benzathiazol unit–containing compounds reported by Belmar (1999a). The structures of the compounds are shown in Figure 1.11. Compounds in Series A and C showed very similar mesomorphic behaviour wherein these compounds exhibited nematic and smectic phases. However, only smectic phase was observed for the compounds in Series B. These

observations can be explained by taking into account the formation of intermolecular hydrogen bonding by the NHCO group. The hydrogen bonding caused the molecules to arrange in a parallel order and this arrangement in turn would encourage smectic mesomorphism as both positional and orientational orders were established.



where n = 6 to 10

Series A: Y = N=CH
Series B: Y = NHCO
Series C: Y = N=N

Figure 1.11: Structure of compounds containing benzathiazol unit (Belmar, 1999a).

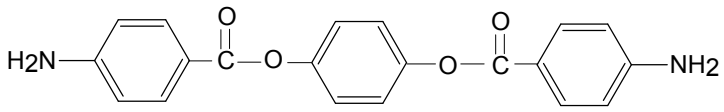
1.5.2 Terminal Substituents (X, Y)

The core of a mesogen, by establishing the primary shape of the molecule and its rigidity, determines (i) the approximate temperature range where mesophases will occur and (ii) the types of mesophases which are possible. However, a rod-like rigid core rarely produces mesophases. Thus, terminal substituents are needed to balance this rigidity with flexibility (Neubert, 2001a). In standard systems with two rings, mesogens are rarely observed even when one of the substituent is an aliphatic chain and the other one is simply a hydrogen atom. However, the addition of another benzene ring, such as in the esters ($R\text{-}C_6H_4COOC_6H_4C_6H_5$ where R = aliphatic chain) can produce mesophases (Sadashiva, 1979). Replacing the hydrogen atom with a polar substituent can also lead to the emergence of mesogenic properties.

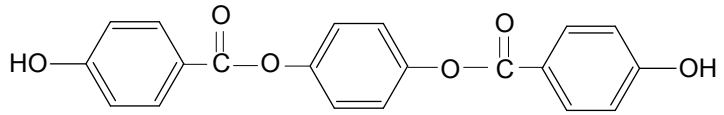
Terminal substituents tend to be used to fine-tune mesomorphic properties wherein they are used to raise or lower transition temperatures (for example, alkoxy or branched chains), create dipoles along or across the molecular axis (for example, CN or F substituents), produce chiral mesogens (for example, chiral branched chains) or enhance the preference for a specific mesophase (for example, short alkyl chain favours nematic).

1.5.2.1 Polar Groups

It has been claimed that mesogens must consist of a terminal polar group (Kelker and Hatz, 1980). However, compounds with terminal groups such as OH and NH_2 do not have the tendency to form mesophases. These groups tend to form polymeric hydrogen bonding that increases the melting point (Gray, 1962). Nevertheless, Schroeder and Schroeder (1974) reported that both *p*-phenylene di-*p*-aminobenzoate and *p*-phenylene di-*p*-hydroxy-benzoate exhibited mesomorphic properties. The structures of the compounds are shown in Figure 1.12.



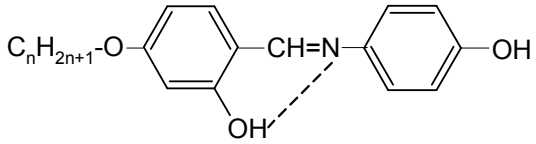
(a)



(b)

Figure 1.12: Structures of (a) *p*-phenylene di-*p*-aminobenzoate and (b) *p*-phenylene di-*p*-hydroxybenzoate (Schroeder and Schroeder, 1974).

Schroeder and Schroeder (1974) also suggested that phenolic compounds must have three benzene rings in order to exhibit mesomorphic properties. Another criterion is the molecules must be able to form intramolecular hydrogen bonding. Sakagami and Takase (1995) also supported the claim but in addition, they also claimed that phenolic compounds with two benzene rings (Figure 1.13) could also exhibit mesomorphic properties. However, an additional OH group must be present at the *ortho* position of the aldehyde moiety so that the formation of zwitterions via intramolecular hydrogen bonding can occur.

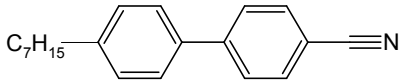
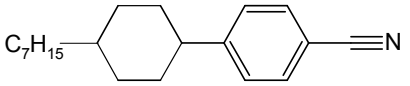
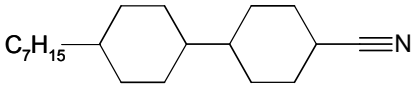


where n = 1-18

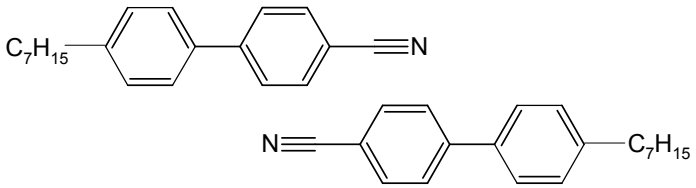
Figure 1.13: Intramolecular hydrogen bonding in 2-hydroxy-4-*n*-alkyloxybenzylidene-4'-hydroxyanilines (Sakagami and Takase, 1995).

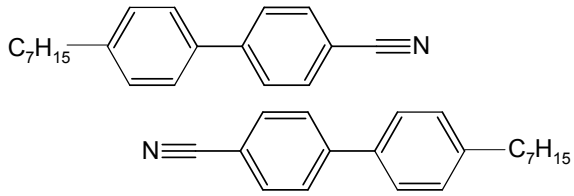
Compounds containing certain polar groups show tendency to form dimers. Through dimerization, the length of the molecule is increased. It is known that the length to breadth ratio controls the clearing point of a mesogen (Collings and Hird, 1998). The correlation between the molecular length to breadth ratio and the clearing point can be substantiated by a study of three biphenyl analogous compounds with CN as the terminal substituent (Ibrahim and Haase, 1981). The structures and their clearing temperatures are shown in Table 1.3.

Table 1.3: Structures and clearing temperatures (T_c) of biphenyl analogous compounds with CN group (Ibrahim and Haase, 1981)

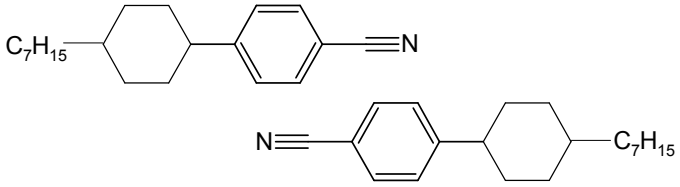
Compound	Structure	T_c/ ^oC
8		42.2
9		56.8
10		83.3

As can be seen in Table 1.3, compounds **8-10** differ in their core structure, giving rise to different types of dimers. The cyclohexane ring differs from the benzene ring by being more bulky in shape and being non-aromatic. These in turn caused a strong decrease in the intermolecular interaction. The sketches of the possible dimers in order to illustrate the different effective length to breadth ratio are shown in Figure 1.14. The dimerization occurs either by the interaction of a CN group with a benzene ring [Figure 1.14 (a) and (b)] or the interaction of two CN groups [Figure 1.14 (c)]. Comparison among compounds **8** to **10** showed that compound **10** has the highest length to breadth ratio and therefore, has the highest clearing point.

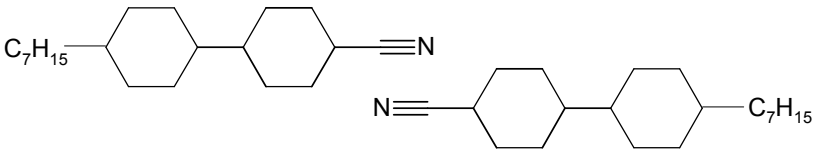




(a)



(b)



(c)

Figure 1.14: Possible associates in polar biphenyl analogous compounds.
(a) Two different types of possible dimerization for compound **8**.
(b) The possible dimerization for compound **9**.
(c) The possible dimerization for compound **10**.

1.5.2.2 Straight Alkyl/Alkoxy Chains

Other common terminal substituents are the alkyl and alkoxy groups. The length of the carbon chain in both of the groups affects the mesomorphic properties. As the length of the alkyl chain is increased, the lateral attraction is increased. However, the terminal attraction becomes relatively weaker or remains unchanged. The illustration for both of the attractions is shown in

Figure 1.15. As a result, the nematic property decreases but the tendency of a compound to exhibit smectic phase increases as a particular series ascends (Collings and Hird, 1998).

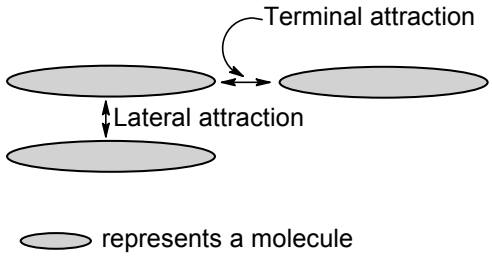
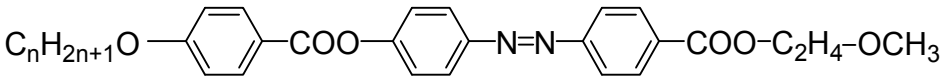


Figure 1.15: Illustration of the terminal and lateral attractions between molecules.

As an example, Prajapati and Pandya (2005) have synthesized 2-methoxyethyl [4-(4'-*n*-alkoxybenzoyloxy)phenylazo]-4"-benzoates (Figure 1.16) and found that for the lower members (n = 1 to 8), the azomesogens showed nematic phase while for the higher members (n = 10 to 16), the azomesogens displayed both nematic and smectic phases.

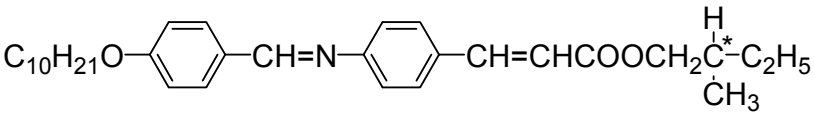


where n = 1-8, 10, 12, 14 and 16

Figure 1.16: Structure of 2-methoxyethyl [4-(4'-*n*-alkoxybenzoyloxy)-phenylazo]-4"-benzoates (Prajapati and Pandya, 2005).

1.5.2.3 Branched Alkyl/Alkoxy Chains

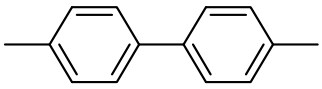
The discussion in Section 1.5.2.2 only focused on straight carbon chains. There are many compounds with branched terminal substituents, particularly chiral materials. Since the ferroelectric liquid crystal (FLC), 2-methylbutyl 4-(4-*n*-decyloxybenzylideneamino)cinnamate (Figure 1.17) was reported by Meyer *et al.* (1975), and a bistable and fast switching electro-optical device based on the properties of FLCs was reported by Clark and Lagerwall (1980), the synthesis of optically active smectic liquid crystal materials for display applications has received considerable interests (Maltase, 1992 and Walba, 1995).



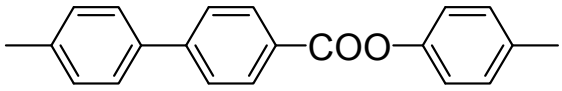
where * denotes the chiral centre

Figure 1.17: Structure of 2-methylbutyl 4-(4-*n*-decyloxybenzylidene-amino)cinnamate (Meyer *et al.*, 1975).

A FLC material used in a display should exhibit smectic phase over a wide temperature range, including room temperature (Adams and Sinta, 1989). General guidelines have been established for the synthesis of FLC materials and the primary requirement is the materials must exhibit tilted chiral smectic phases such as chiral smectic C (SmC*) (Goodby and Gray, 1978). Besides that, FLC mesogens must consist of at least two rigid aromatic groups. A biphenylene group is preferred in comparison to a phenylene group. The structures of the common biphenylene groups that are present in FLCs are shown in Figure 1.18 (Chiellini *et al.*, 1993).



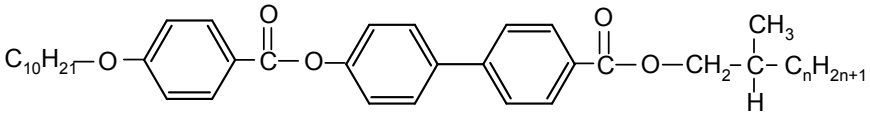
(a)



(b)

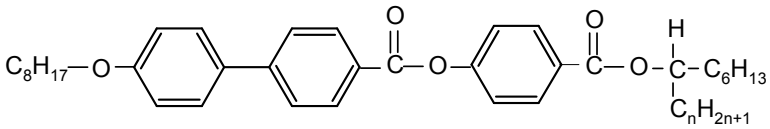
Figure 1.18: Common biphenylene groups that are present in FLCs.
(a) Biphenylene group only.
(b) Biphenylene group attached to a phenylene group by a carboxylate group.

A few examples of FLCs comprising these skeletons are 1-methylalkyl 4'-(4"-*n*-decyloxybenzoyloxy)biphenyl-4-carboxylates [Figure 1.19 (a)] and 4-(1-alkylheptyloxycarbonyl)phenyl 4'-*n*-octyloxybiphenyl-4-carboxylates [Figure 1.19 (b)].



where n = 2, 3, 4, 5 or 6

(a)



where n = 1, 2, 3, 4, 5 or 6

(b)

Figure 1.19: (a) Structure of 1-methylalkyl 4'-(4"-*n*-decyloxybenzoyloxy)-biphenyl-4-carboxylates (Goodby *et al.*, 1992).
(b) Structure of 4-(1-alkylheptyloxycarbonyl)phenyl 4'-*n*-octyloxybiphenyl-4-carboxylates (Ouchi *et al.*, 1995).

1.6 Phase Structures Of Chiral Calamitic Liquid Crystals

Chiral calamitic LCs can exhibit two common types of mesophases; chiral nematic (cholesteric) and chiral smectic phases.

1.6.1 Chiral Nematic (Cholesteric) Phase

The simplest chiral mesophase is the chiral nematic (N*) phase (Figure 1.20) where the local molecular ordering is similar to that of the nematic phase (only orientational order) and additionally the molecules pack to form helical macrostructures in the direction perpendicular to the director. The helicicty depends on the absolute configuration (enantiomer *R* or *S*) of the molecules (Collings and Hird, 1998).

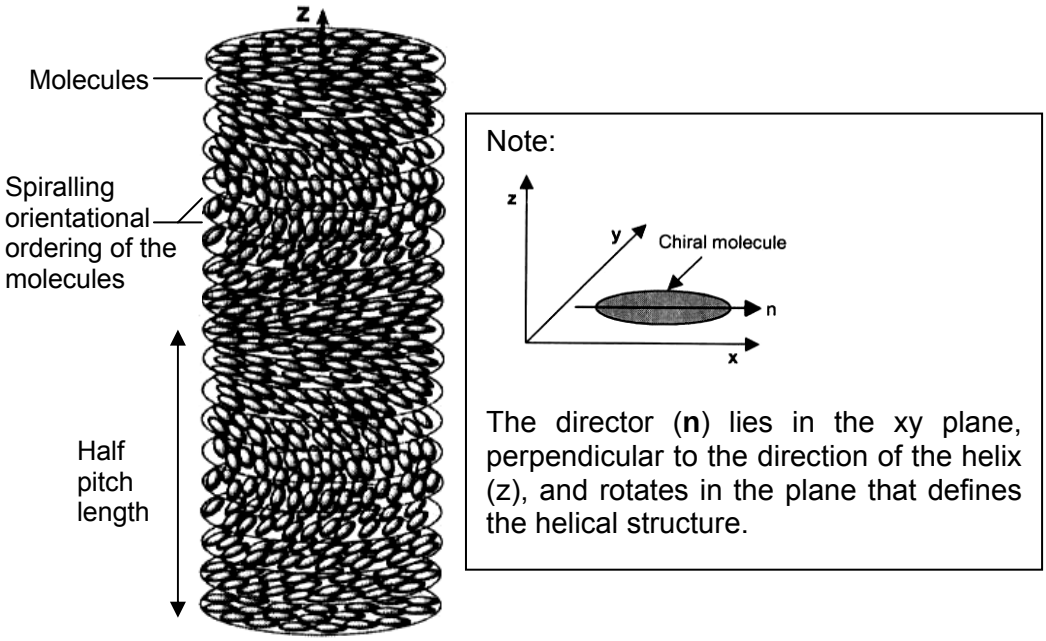


Figure 1.20: Helical structure of the chiral nematic phase (Belloni, 2002).

1.6.2 Chiral Smectic Phase

Chiral smectic phases comprise enantiomerically pure (or at least the concentration of one enantiomer is greater than the other) molecules, which express the chirality in the bulk material by a helical arrangement of the layered structure. The most important chiral smectic phase is the chiral smectic C (SmC*). Here the chiral molecules, like in the SmC phase, are tilted at an angle θ to the normal [the layer (z)] and form spontaneously polarized layers (due to their inherent asymmetry), which additionally give rise to a helical macrostructure (Figure 1.21) (Collings and Hird, 1998).

However, the helical structure of the layers results in the overall polarization (P) being averaged to zero in the bulk.

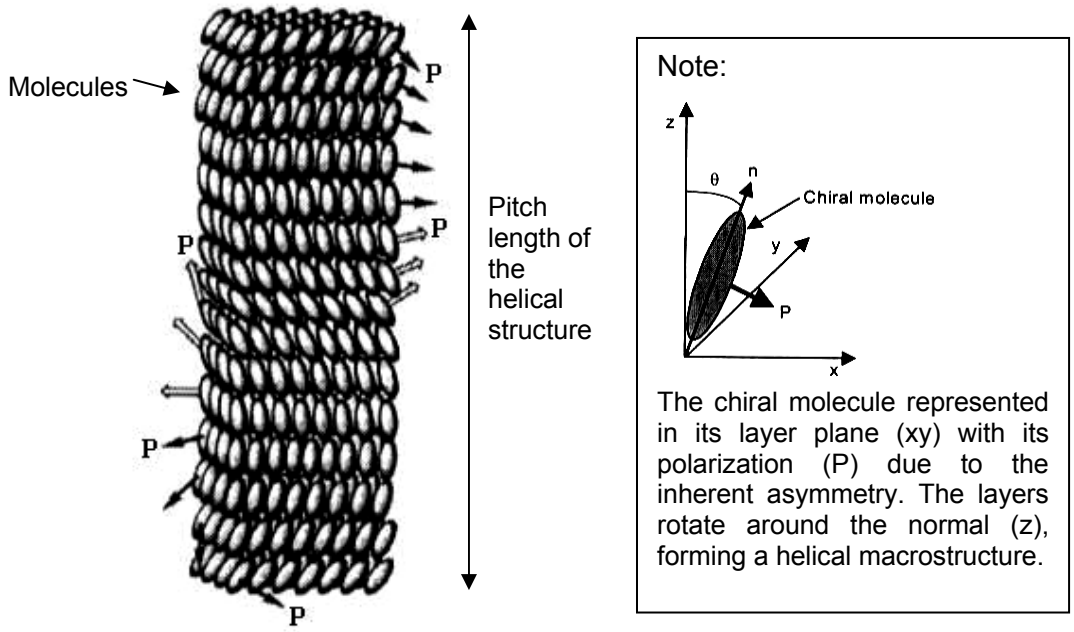


Figure 1.21: Helical macrostructure of the chiral smectic phase (Belloni, 2002).

CHAPTER TWO

LITERATURE SURVEY

2.1 Liquid Crystals Consisting Of Cholesterol, Rod-Like Imine And Biphenyl-4-Carboxylate Components

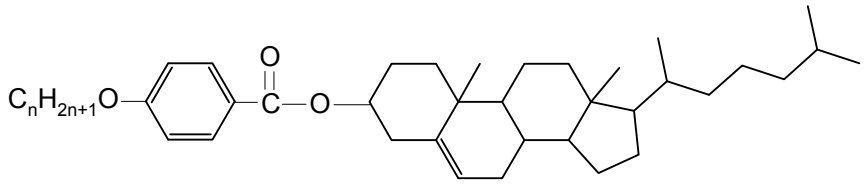
In the current project, three types of calamitic liquid crystals, each with a different core structure were targeted based on the literature review carried out. These include compounds with the cholesterol (Series 1 and 2, in Section 2.1.1), rod-like imine (Series 3 to 6, in Section 2.1.2) and biphenyl-4-carboxylate (Series 7, in Section 2.1.3) components. Altogether, a total of sixty-three compounds were synthesized and characterized. The objectives of this research are outlined in Section 2.1.4.

2.1.1 Liquid Crystals Consisting Of Cholesterol Component

2.1.1.1 Series 1: Cholesteryl 4-*n*-Alkoxybenzoates

In the year 1888, the Austrian botanist Reinitzer discovered the first liquid crystal known as cholesteryl benzoate (Figure 1.1). Later, Dave and Vora (1970) made an expansion of cholesteryl benzoate through the preparation of cholesteryl 4-*n*-alkoxybenzoates ($C_nH_{2n+1}OC_6H_4COOCh$ or **nOACh** where Ch represents the cholesteryl moiety). Dave and Vora characterized thirteen members of the **nOACh** homologous series (where n = 1-10, 12, 16 or 18) by using only elemental analysis. Later, a Russian research group carried out X-ray diffraction analysis on these compounds. They determined the crystal structures of compounds **1OACh**, **2OACh** (Polishchuk *et al.*, 1988), **4OACh**, **5OACh** (Polishchuk *et al.*, 1985b), **6OACh** (Polishchuk *et al.*, 1986a), **8OACh**

(Polishchuk *et al.*, 1985a) and **16OACh** (Polishchuk *et al.*, 1990) in solid state. In addition, Yakubov (1999) also studied the structure of compounds **nOACh** in solid state by using infrared spectroscopy. Apart from that, nuclear magnetic resonance (NMR) is also considered as one of the tools for structure elucidation and conformation studies. NMR spectroscopy characterization of these compounds in solution in a common organic solvent which has not been reported in the literature prior to this work was carried out in the current research. The structures of the compounds which were studied are shown in Figure 2.1.



where n = 6, 8, 10, 12, 14, 16 or 18

Figure 2.1: Structure of cholesteryl 4-*n*-alkoxybenzoates (**nOACh**).

Dave and Vora (1970) also reported the mesomorphic properties of these compounds which were merely based on the liquid crystal textures observed using polarizing optical microscope (POM). Since differential scanning calorimetry (DSC) is another essential method for studying the properties of liquid crystals, the mesomorphic properties of compounds **6OACh**, **8OACh**, **10OACh**, **12OACh**, **14OACh**, **16OACh** and **18OACh** were revised in the current research by using POM with the support of DSC data.