SYNTHESIS AND ANISOTROPIC PROPERTIES OF LIQUID CRYSTAL DIMERS CONSISTING OF ESTER AND DISULPHIDE BRIDGING GROUPS

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by

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3.0 **RESULTS AND DISCUSSION**

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LIST OF ABBREVIATION AND SYMBOL

%	Percent
$\Delta S_{NI}/R$	Entropy change of nematic-isotopic transition per gas constant
$\Delta S_{N*I}/R$	Entropy change of chiral nematic-isotropic transition per gas constant
$\Delta S_{SmAI}/R$	Entropy change of smectic A-isotropic transition per gas constant
°C	Degree Celcius
°C min^{-1}	Degree Celcius per minute
^{1}H-NMR	Proton nuclear magnetic resonance
^{13}C-NMR	Carbon nuclear magnetic resonance
Å	Angstrom
alternate SmC	Alternate smectic C phase
$Br(CH_2)_nBr$	1,n-Dibromoalkane
$CDCl_3$	Deuterated chloroform
CHN	Carbon, Hydrogen and Nitrogen
CH_2Cl_2	Dichloromethane
CH_3OH	Methanol
CH_3COCH_3	Acetone
Conc.HCl	Concentrated hydrochloric acid

$COOH(CH_2)_5Br$	6-Bromohexanoic acid
COSY	Correlation spectroscopy
Cr	Crystal
d	Layer spacing
DCC	N,N-Dicyclohexylcarbodiimide
DCM	Dichloromethane
DEPT	Distortionless enhancement by polarization transfer
DMAP	4-Dimethylaminopyridine
DSC	Differential scanning calorimetry
FT-IR	Fourier transform infrared
FT-NMR	Fourier transform nuclear magnetic resonance
H_2O	Distilled water
H_2O_2	Hydrogen peroxide
HMQC	Heteronuclear multiple quantum correlation
HMBC	Heteronuclear multiple bond correlation
I	Isotropic phase
J	Coupling constant
K_2CO_3	Anhydrous potassium carbonate
KI	Potassium iodide

$kJmol^{-1}$	Kilojoule per mole
KSAc	Potassium thioacetate
L	Molecular length
LC	Liquid crystal
m	Multiplet
MHz	Megahertz
n	Number of methylene units
N	Nematic phase
N*	Chiral nematic phase
NaI	Sodium iodide
NaOH	Sodium hydroxide
POM	Polarizing optical microscope
s	Singlet
SmA	Smectic A phase
SmB	Smectic B phase
SmC	Smectic C phase
SmC*	Chiral smectic C phase
t	Triplet
T	Transition temperature

R.T	Room temperature
THF	Tetrahydrofuran
TMS	Tetramethylsilane
T_{NI}	Nematic-isotropic transition temperature
T_{SmAI}	Smectic A-isotropic transition temperature
XRD	X-ray diffraction
δ/ppm	Chemical shift in part per million unit
v/cm^{-1}	Wavenumber in centimetre unit

SINTESIS DAN SIFAT ANISOTROPIK BAGI DIMER HABLUR CECAIR MENGANDUNGI KUMPULAN TITIAN ESTER DAN DISULFIDA

ABSTRAK

Empat siri dimer baru yang mengandungi kumpulan titian ester dan disulfida telah disintesis dan sifat anisotropik bagi setiap dimer telah dicirikan. Siri ini terdiri daripada dua dimer bukan simetri iaitu α-{4-[(4-tertukarganti-fenilimino) metil]karbonil)fenoksik]fenoksik}-ω-[4-(4-(*R,S*)-2-metilbutiloksikarbonilfenil)fenoksik]heksanoat, **X-E6-*RS*MB** dan α-{4-[(4-tertukarganti-fenilimino)metil]karbonil) fenoksik]fenoksik}-ω-[4-(4-(*S*)-2-metilbutiloksikarbonilfenil)-fenoksik]heksanoat, **X-E6-*S*MB** serta dua dimer simetri (6-{4-[(4-tertukarganti-fenilimino)metil] fenoksik}heksil)disulfida, **X-6-SS-6-X** dan (6-{4-[(4-bromofenilimino)metil]fenoksik}alkil)disulfida, **Br-*n*-SS-*n*-Br**. Perbezaan antara dua siri dimer bukan simetri ini adalah disebabkan oleh kehadiran pelbagai penukargantian dan pengenalan pusat kiral dan rasemik pada fragmen bifenil. Bagi dua siri dimer yang simetri pula perbezaan ini boleh disebabkan oleh kepelbagaian kepanjangan spaser dan kumpulan penukargantian.

Struktur molekul bagi sebatian dimer ini telah dikaji melalui CHN, spektroskopi FT-IR, ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC dan ^{1}H-^{13}C HMBC serta kajian terhadap sifat anisotropik bagi semua dimer telah dijalankan dengan menggunakan POM, DSC dan XRD. Kesemua dimer ini mempamerkan pelbagai fasa antaranya fasa nematik (N), fasa nematik kiral (N*), smektik A (SmA), smektik C (SmC), smektik C alternat, smektik C kiral (SmC*), smektik B mosaik

(SmB) dan smektik G mosaik (SmG). Dimer **X-E6-*RS*MB** dan **X-E6-*S*MB** yang mempunyai penukargantian kumpulan etil mempamerkan pelbagai fasa. Ransangan kiraliti pada dimer bukan simetri **X-E6-*S*MB** mencirikan fasa kiral seperti N* dan SmC*. Tambahan pula kedua-dua dimer dengan penukargantian bromo mempamerkan suhu penjernihan (T_c) yang tinggi berbanding penukargantian yang lain.

Kedua-dua dimer simetri seperti **X-6-SS-6-X** (kepelbagaian penukargantian terminal) dan **Br-*n*-SS-*n*-Br** (kepelbagaian kepanjangan spaser) menunjukkan kehadiran disulfida dapat meningkatkan fleksibiliti spaser yang menggalakkan kestabilan mesofasa dan kepelbagaian penukargantian terminal mencirikan fasa-fasa yang berbeza. Salah satu ciri yang menarik perhatian di dalam siri **X-6-SS-6-X** adalah sebatian yang mengandungi penukarganti bromo mempamerkan fasa SmA yang enantiotropik. Siri yang lain **Br-*n*-SS-*n*-Br** dengan penukarganti bromo telah disintesis dan dikaji. Kepanjangan spaser dipelbagaikan dari $n = 3$ hingga $n = 8$. Suatu ciri penting yang perlu dikemukakan di dalam siri ini ialah kesan ganjil-genap yang ketara dapat dilihat dalam suhu peralihan (T_m dan T_c) serta nilai perubahan entropi smektik A-isotropik ($\Delta S_{SmAI}/R$). Hasil kajian ini boleh dihubungkaitkan dengan sudut kilasan dari C−S−S−C mempunyai kesesuaian nilai pada 90°.

SYNTHESIS AND ANISOTROPIC PROPERTIES OF LIQUID CRYSTAL DIMERS CONSISTING OF ESTER AND DISULPHIDE BRIDGING GROUPS

ABSTRACT

Four new series of dimers consist of ester and disulphide bridging groups have been synthesized and the anisotropic properties for each dimer characterized. These series comprise of two non-symmetric dimers which are α-{4-[(4-substituted-phenylimino)methyl]carbonyl)phenoxy]phenoxy}-ω-[4-(4-(*R,S*)-2-methylbutyloxy carbonylphenyl)phenoxy]hexanoate, **X-E6-*RS*MB** and α-{4-[(4-substituted-phenyl imino)methyl]carbonyl)phenoxy]phenoxy}-ω-[4-(4-(*S*)-2-methylbutyloxycarbonyl phenyl)phenoxy]hexanoate, **X-E6-*S*MB** and also the other two symmetric dimers (6-{4-[(4-substituted-phenylimino)methyl]phenoxy}hexyl)disulphide, **X-6-SS-6-X** and (6-{4-[(4-bromophenylimino)methyl]phenoxy}alkyl)disulphide, **Br-*n*-SS-*n*-Br**. The differences between the two series of non-symmetric dimers can be attributed to the presence of various terminal substituents and the introduction of chiral and racemic centres at the biphenyl fragments. For both series of symmetrical dimers the differences can be attributed to the variety of the spacer length and terminal substituents.

The molecular structure of these dimers were elucidated by CHN, FT-IR, ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC spectroscopy and the investigation of the anisotropic properties for all dimers was performed using POM, DSC and XRD. All of these dimers exhibit variety of mesophases such as nematic phase (N), chiral nematic phase (N*), smectic A (SmA), smectic C (SmC), alternate smectic C, chiral smectic C (SmC*), mosaic smectic B (SmB) and mosaic

smectic G (SmG). **X-E6-*RS*MB** and **X-E6-*S*MB** dimers that possess ethyl substituted analogue exhibit variety of phases. The induction of chirality to the non-symmetric dimer of **X-E6-*S*MB** promotes the chiral phase such as N* and SmC*. In addition both of these dimers with bromo substituent exhibit higher clearing temperature (T_c) than other terminal substituent.

Both of the symmetric dimers such as **X-6-SS-6-X** (variety of terminal substituents) and **Br-*n*-SS-*n*-Br** (variety of the spacer length) shows that the presence of disulphide can increase the flexibility of the spacer which enhances the stability of mesophase and various terminal substituents can exhibit different phases. One of the notable features in the **X-6-SS-6-X** series is bromo substituted compound exhibits enantiotropic SmA phase. Another series of **Br-*n*-SS-*n*-Br** with bromo substituent have been synthesized and studied. The spacer length are varied from n = 3 to n = 8. It is important to mention that in this series a significant odd-even effect can be observed in the phase transition temperature (T_c and T_m) as well as the entropy changes of smectic A-isotropic ($\Delta S_{SmAI}/R$). This study can be related with the torsional angle of C−S−S−C at a preferable value of 90°.

1.0 INTRODUCTION

1.1 Liquid crystals

Liquid crystals (LCs) have been explored since 1888 and it was discovered by an Austrian Botanist, Fridrich Reinntzer and he had found a strange behaviour of a material known as cholesteryl benzoate extracted from carrots (Reinitzer, 1888). He found that this cholesteryl benzoate obviously has two different melting points. This substance has initially melted into cloudy fluid at 145.5 °C. It has subsequently turned into a clear solution at 178.5 °C. Three important character of cholesteric liquid crystals were discovered and described by Reitnizer (this name was designed 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, 1997). He was able to make observations of these properties by polarized light, and his microscope was equipped with a hot stage enables the observation at high temperature. In a later version, with polarisers added, it became a standard equipment in every liquid crystal research laboratory (Ici.kent, 2010). It has well been accepted that liquid crystals are substances which display a phase of matter that has properties between those of a conventional liquid and those of a solid, as shown in Figure 1.1.

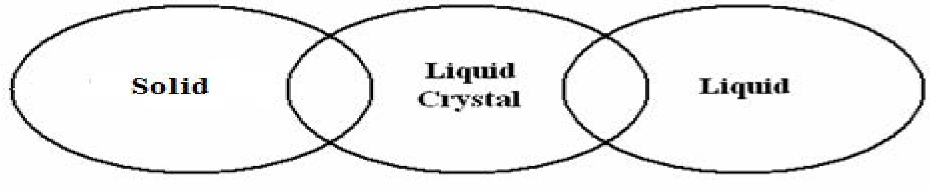


Figure 1.1: Overlap of the properties of liquid crystals with conventional solid and liquid.

In a solid state, molecules are arranged very close to each other with no translational freedom as shown in Figure 1.2 (a) while the molecules in a liquid as shown in Figure 1.2 (c) do not have fixed position and can move freely. In contrast, the molecules in a liquid crystal have an arrangement of that in between solid and a liquid as shown in Figure 1.2 (b) in which the molecules possess some orientational order and little or no positional order and have ability to move freely but remain oriented to a common axis, called a director.

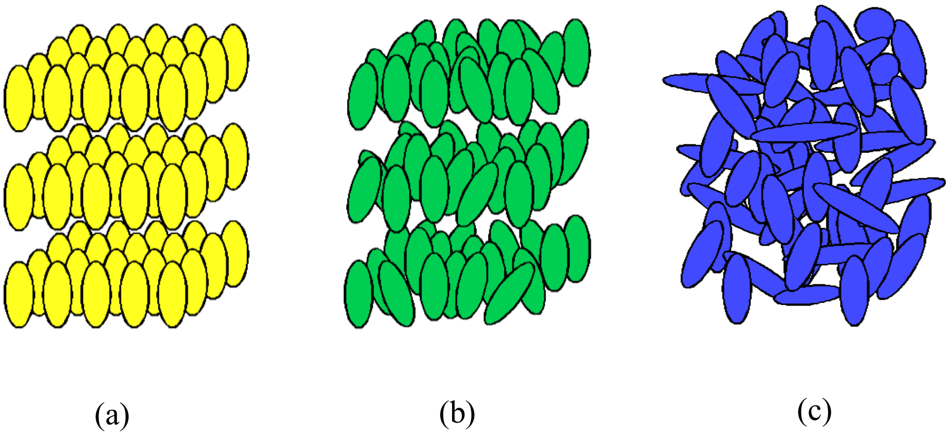


Figure 1.2: (a) Arrangement of molecules in a crystalline solid, (b) arrangement of molecules in a liquid crystal and (c) arrangement of molecules in a liquid (Shakhashiri, 2007).

1.2 Types of liquid crystals

Liquid crystals exhibiting mesophases can be divided generally into two categories: lyotropic and thermotropic liquid crystals (LCs). In lyotropic LCs the mesomorphism depends on the action of solvents on amphiphilic molecules. However, in thermotropic LCs the transition will be brought by the action of heat. Since the present study will focus on thermotropic LCs and hence, lyotropic LCs will not be discussed further. The important requirement for a material to behave as a thermotropic liquid crystal is that it should have rigid (hard) and soft (flexible) regions. Aromatic or non-aromatic cores can be used as an example of molecules for hard regions while aliphatic chains account for soft region of the molecule. Besides, the combination of these two distinct regions is to obtain molecules featuring pronounced shape anisotropy, which plays an essential role in the stabilization of different types of liquid crystal phases. Melting point is the transition from crystal to mesophase while clearing point is the transition between mesophase to the isotropic liquid. Liquid crystal which exhibits phases during both heating and cooling cycles are enantiotropic and in term of monotropic phase, the liquid crystal phase will only be exhibited during the cooling cycle due to hysteresis crystallization. Through the shape of molecules, these thermotropic LCs can be divided into two groups: conventional and non-conventional liquid crystals.

1.3 Shape of molecules and their mesophases

1.3.1 Conventional shaped liquid crystals

Calamitic LCs and discotic LCs are the two types of conventional liquid crystals. These two types of conventional liquid crystals are classified based on mesophase as shown in Figure 1.3.

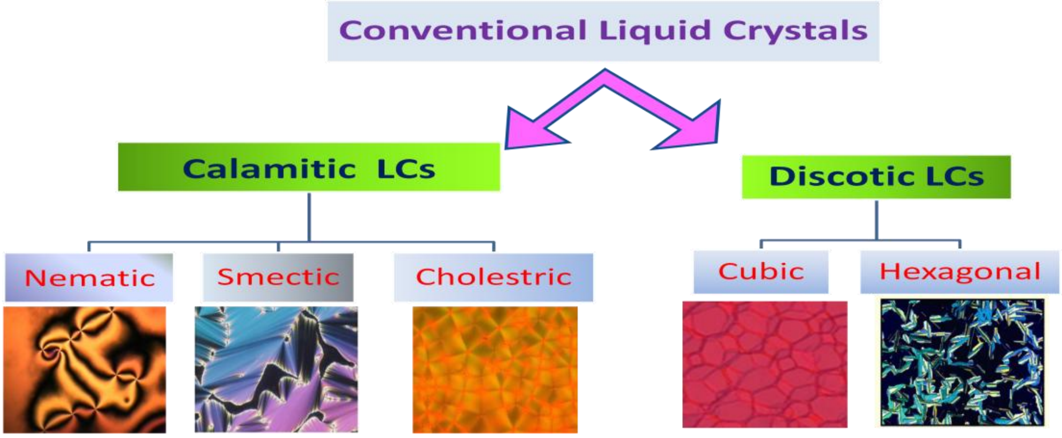
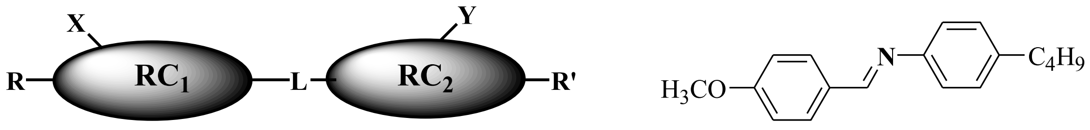


Figure 1.3: Schematic representation for classification of conventional LCs.

1.3.1.1 Calamitic liquid crystals

Calamitic LCs are the most commonly known liquid crystals (LCs). It possesses rod-like molecules with one molecular axis longer than the other two axes. A general template that describes the structure of calamitic liquid crystal is shown in Figure 1.4.



(a)

(b) MBBA

Figure 1.4: (a) A general template describing the structure of calamitic LCs and (b) an example of a calamitic LCs.

The RC$_1$ and RC$_2$ from the above figure are referred to the rigid cores often to aromatic in nature such as 1,4-phenyl, 2,5-pyrimidinyl and 2,6-naphthyl or they can also be alicyclic with *trans*-4-cyclohexyl and cholesteryl cores. Generally, these two cores are interconnected via a covalent bond or linking groups L such as -COO-, -CH$_2$-CH$_2$-, -CH=N and -N=N-. The terminal substituents R and R' are usually either alkyl or alkoxy chains or the combination of these two. In many cases one of the terminal units is a polar substituent of CN, F, Cl and Br. In some special cases lateral substituents X and Y such as F, Cl, CN, CH$_3$, C$_2$H$_5$ and OCH$_3$ are incorporated to account for the special property. In Figure 1.4(b) 4-methoxybenzylidene-4-n-butylaniline (MBBA) shows a typical example of calamitic LCs (Tschierske and Dantlgraber, 2003, Ros *et al.,* 2005). However, the introduction of chirality in rod-like molecules furnished optically active LCs and exhibited a variety of fascinating mesophases (Meyer *et al.,* 1975).

1.4 Mesophases

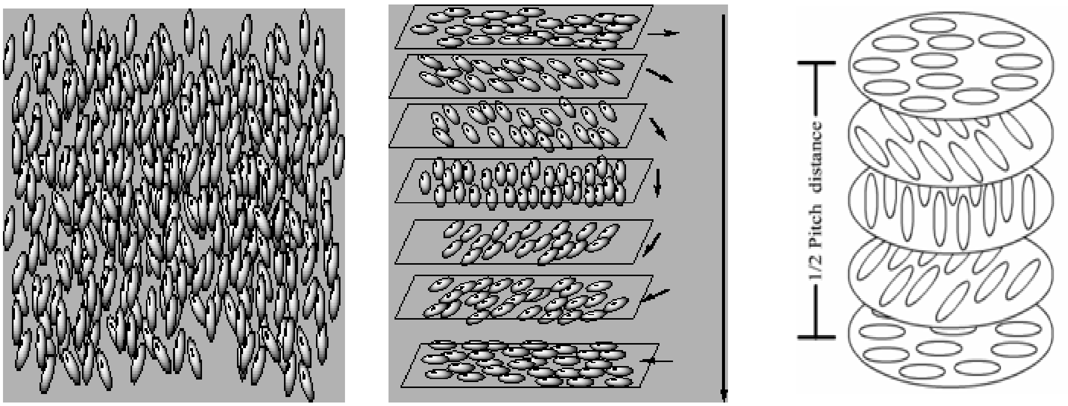
In general, conventional achiral rod-like molecules exhibit nematic and/or smectic phases. Whereas, chiral rod-like molecules organize themselves to form macroscopic helical structures that results in mesophases such as the chiral nematic (N*) and/or chiral smectic C (SmC*) phases. They also stabilize highly frustrated structures like blue phase (BP) and twist grain boundary (TGB) phases.

1.4.1 Nematic phase

Molecules in the nematic phase possess long range orientational order but lack of positional order as shown in Figure 1.5(a) (Wright and Mermin, 1989). These molecules are oriented parallel in a certain domain of a sample or all aligned towards a similar direction referred to as the director (Singh, 2000).

1.4.1.1 Cholesteric phase

The cholesteric phase is also called chiral nematic (N*) phase in which the N phase is induced by chiral molecules. The molecules in different layer orient at a slight angle relative to each other. Each consecutive molecule is rotated slighltly relative to the one before it. Therefore, instead of the constant director of the nematic, the cholesteric director rotates helically throughout the sample shown in Figure 1.5(b). The helix may be right- or left-handed depending on the molecular chirality. The pitch is the distance after which the molecules have the same average orientation as shown in Figure 1.5(c) (Collings and Hird, 1998).



(a) (b) (c)

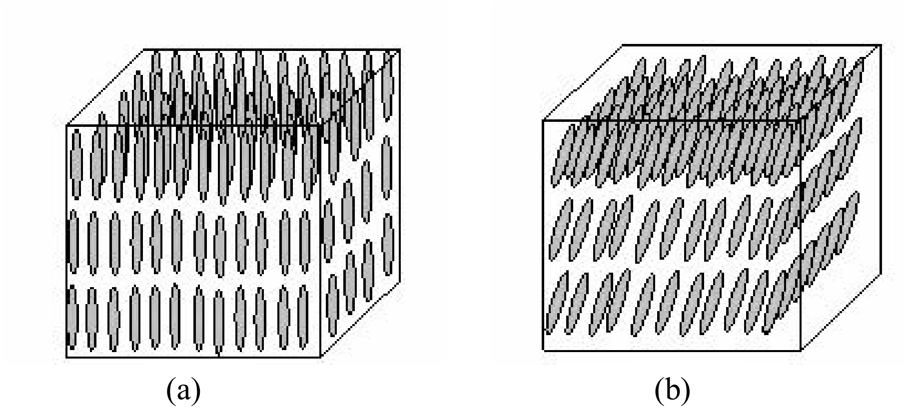
Figure 1.5: Diagram representation of (a) N, (b) N* phases and (c) the pitch distance after the molecules have the same average orientation (Collings and Hird, 1998)

1.4.2 Smectic phase

The smectic state is another distinct mesophase of liquid crystal substances. Molecules in this phase show a degree of translational order not present in the nematic phase. The molecules maintain the general orientational order of nematics, but also tend to align themselves in layers in the smectic state. Motion is restricted within these planes, and separate planes are observed to flow past each other. The smectic state is more "solid-like" than the nematic phase upon increasing the order in layers.

1.4.2.1 Smectic A phase

Molecules in smectic phases are ordered in layers and the translation of molecules from one layer to another is limited. A variety of molecular arrangements is possible within the layered systems. In most cases, there is no positional order in the smectic A (SmA) phase (Figure 1.6(a)) (Devi and Bhattacharjeen, 2010) within each layer and the long axes of the molecules are on average positioned perpendicular to the layers. Despite this partial ordering of the molecular positions, the substance still flows and is therefore a liquid.



(a) (b)

Figure 1.6: (a) Molecular arrangement in (a) SmA and (b) SmC phases (Devi and Bhattacharjeen, 2010)

1.4.2.2 Smectic C phase

The smectic C (SmC) phase is different from SmA phase. It can be differentiated by the molecular arrangement in which the director in the SmC phase makes a tilt angle with respect to the smectic layer. Hence, this angle rotates from layer to layer forming a helix. Normally, the tilt angle increases when the temperature decreases.

1.4.2.3 Chiral smectic phase

In a chiral smectic phase such as chiral smectic C (SmC*) phase, the molecules exhibit a helical structure. Contrary to the cholesteric phase, the subsequent layers with the tilted molecules are slightly rotated with respect to each other (Figure 1.7). The molecules of SmC* form soft layer planes with an alternating high and low density of molecular cores separated by regions of highly mobile hydrocarbon chains. In these materials, the orientation of the tilt can be influenced by an electric field and thus in theory, the application of SmC* displays can be switched much faster than conventional nematic displays.

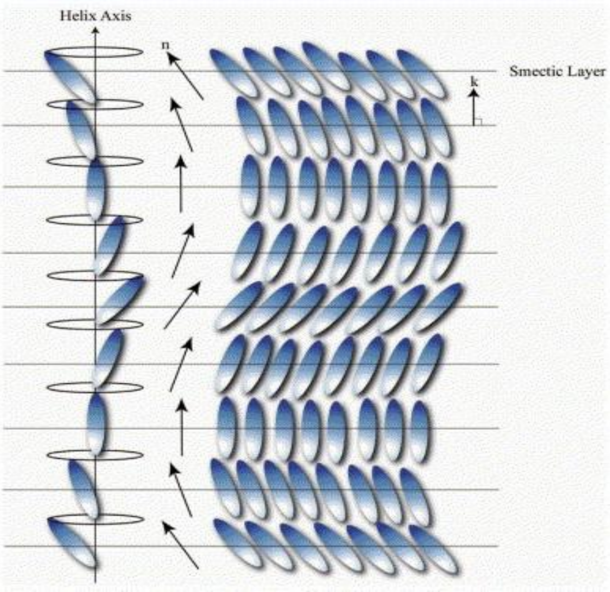


Figure 1.7: Molecular configuration of one pitch of the chiral smectic C phase showing the layer planes, the layer normal k, the director n and the helix axis (Ford *et al.,* 2006).

1.5 Liquid crystal oligomers

In the early 1980s, research activity in liquid crystal oligomers can be traced back especially on the development of semi-flexible main chain liquid crystal polymers (Ober *et al.,* 1984). LC oligomers consist of mesogenic units attached by flexible spacers, most commonly alkyl chains, and the focus of intense research activity arising not only because of their technological potential (Attard, 1993) but also on a more fundamental level because they exhibit a range of unusual liquid crystalline behaviour. The description on the simplest oligomers namely dimers will be given in the following section.

1.5.1 Liquid crystal dimers

LC dimers are composed of molecules containing two mesogenic units connected by a flexibe spacer, most commonly an alkyl chain. Liquid crystal dimers have been attracting a great deal of interest in recent years both in theoretical and experimental studies due to their unusual properties as compared to conventional low molar mass liquid crystals. They serve also as model compounds for semi flexible main chain liquid crystal polymers. In general, LC dimers can be classified into two categories: (i) symmetric dimers and (ii) non-symmetric dimers. A symmetric dimer possesses two identical mesogenic moieties connected by a flexible spacer while a non-symmetric dimer is formed by two different mesogenic units joined up by a flexible spacer.

1.6 Structure-property relationship of liquid crystal dimers

1.6.1 Phase behaviour in liquid crystal dimers

A liquid crystal dimer consists of molecules with chemically distinct regions and therefore, smectic phase behaviour would be predicted. Symmetric LC dimers have been noted to have an unusual property which is the decreasing tendency to exhibit smectogenic properties upon increasing spacer length (Date *et al.,* 1992). In many dimeric LCs, the smectic phase behaviour was also found to be suppressed when their mesogenic moieties (monomers) are smectogenic (Griffin and Britt, 1981). This phenomenon has been attributed to the increase in the overall molecular flexibility.

Dimers with long terminal tails are able to promote smectic behaviour regardless of the spacer length (Luckhurst and Gray, 1979). The first family of symmetric liquid crystal dimers to exhibit rich smectic polymorphism was reported as α,ω-bis(4-*n*-alkyl-anilinebenzylidine-4’-oxy)alkanes (Date *et al.,* 1992). This study revealed a simple relationship relating to the observation of smectic phase to the molecular structure especially for the molecules to exhibit smectic behaviour, the terminal chain length must be greater than half the spacer length. X-ray diffraction studies have also showed that all the smectic phase possess a monolayer structure in symmetric LC dimers. The spacers and terminal chains are added in such a way that all the mesogenic units in one layer are attached to a mesogenic unit in the same adjacent layer to give monolayer arrangement (Figure 1.8 (a)). There are effective domains composed of either the mesogenic units, the spacers or the terminal chains in this arrangement (Imrie and Henderson, 2007).

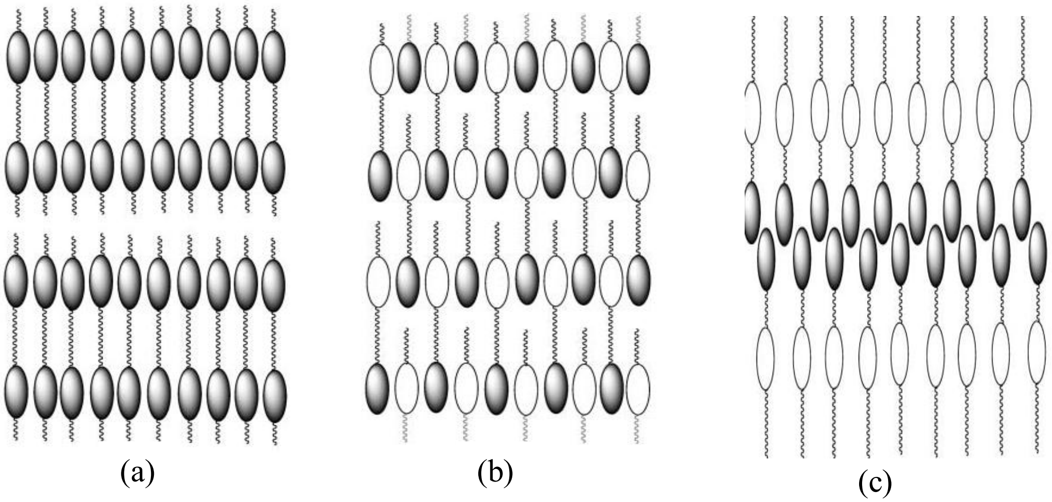

(a) (b) (c)

Figure 1.8: (a) Diagram representation of SmA arrangement in dimeric liquid crystals: (a) Monolayer, (b) intercalated and (c) interdigitated (Imrie and Henderson, 2007).

1.6.2 Layer arrangement of smectic phase in liquid crystal dimers

Generally, symmetric dimers exhibit monolayer smectic phase and in this monolayer variant the layer spacing should be approximately the molecular length. The terminal chain length must be greater than half the spacer length for monolayer smectic phases to be observed. To rationalise this observation, it was suggested that the interaction between a spacer and a terminal is unfavourable one and destabilise the intercalated arrangement (Imrie and Henderson, 2007).

In non-symmetric dimers, molecules tend to arrange in intercalated (Figure 1.8 (b)) or interdigitated (Figure 1.8 (c)) smectic phases (Attard *et al.,* 1994; Blatch and Luckhurst, 2000). The first and most extensively studied family of non-symmetric compounds were the α-(4-cyanobiphenyl-4’-yloxy)-ω-(4-n-alkylanilinebenzylidine-4’-oxy)alkanes (Hogan *et al.,* 1988; Attard *et al.,*1994; Attard *et al.,* 2006; Imrie *et al.,* 2006). In the intercalated smectic phase, the smectic layer periodicity, d is approximately half the molecular length, L ($d/L \approx 0.5$). A specific interaction between the unlike mesogenic units is one of the factors contributing to the intercalated arrangement and this arrangement is induced by an entropy gain resulting from the homogeneously mixing of such groups (Blatch *et al.,* 1997). Another possible factor stabilizing the intercalated arrangement is the electrostatic quadrupolar interaction between the different mesogens having quadrupole moments of opposite signs (Blatch *et al.,* 1995). However, in some cases, the symmetric dimers are also known to exhibit intercalated mesophases (Watanabe *et al.,* 1993). Interdigitated smectic phase is different from intercalated smectic phase because the layer thickness of this arrangement is more than the length of one molecule but less than the length of two molecules, $L < d < 2L$. This means when the terminal chain length is much longer than the spacer the interdigitated smectic A would be predicted. The formation of interdigitated phase is not only limited to the presence of two unlike mesogenic units in the structure but also electrostatic interactions between the groups like polar and polarisable cyanobiphenyl groups in

1-(cholest-5-en-3β-oxy)-ω-(4-cyanobiphenylyl-4'-oxy)alkanes which play an important role in enhancing the interdigitation phase (Marcelis *et al.,* 2003).

1.6.3 Odd-even effect in liquid crystal dimers

Liquid crystal dimers comprising of two mesogenics units linked by a flexible spacer exhibit transitional behaviour whose dependence on the length and parity of the spacer is strongly important of that observed for polymeric systems (Griffin and Britt, 1981) and have proved useful as model compounds for the oligomers (Luckhurst, 1995). The nematic-isotropic transition temperature, T_{NI} and the associated entropy changes, $\Delta S_{SmAI/R}$ are the one of the example which depends critically on the length and parity of the spacer. The nematic-isotropic transition temperatures exhibit a pronounced alternation and attenuated when increasing the spacer length. The entropy of transition also observes a marked alternation but not attenuated with the increasing chain length. In LCs dimer these example of alternation observes a significant odd-even effect in which the transition temperature and entropies are higher for even membered than for odd membered dimers. These differences in the physical properties can be observed in symmetric and non-symmetric dimers (Heeks and Luckhurst, 1993). The different molecular shapes adopted by the odd and even spacer dimers in the liquid crystal phase together with the coupling between orientational order and conformational distribution can be described and explained through this phenomenon. The molecules with odd-parity spacer tend to presume a bent conformation with the two mesogens tilted and inclined to each other (Figure 1.9(a)) while in even-parity spacer compounds, mesogenic moeities are more likely to have a zigzag conformation in which the mesogenic units are anti-parallel to each other (Figure 1.9(b)) (Imrie and Henderson, 2007; Watanabe *et al.,* 2000). These conformations revealed that LC dimers with odd-parity tend to form SmC-like phases while even-parity forms SmA phases (Niori *et al.,* 1995; Watanabe *et al.,* 1993). Dependence of the mesophase structure on the spacer parity, the ratio of the spacer and terminal chain length are other characteristics which of is considerable interest in liquid crystal dimers. A wide range of dimers have been prepared containing either ether or methylene linking groups as a flexible spacer between the two mesogenic units (Henderson *et al.,* 2001).

Several additional fascinating properties of dimers with flexible alkylene spacer were investigated in 1999 (Choi *et al.,* 1999; Watanabe *et al.,* 1998). These investigations showed that liquid crystals consisting of bent-shaped molecules have switching properties with an odd number of alkylene spacers. An achiral twin dimer with two identical mesogenic units connected by an odd-parity spacer has also been reported to forming a chiral, anticlinic and antiferroelectric smectic phases (Watanabe *et al.*, 1998).

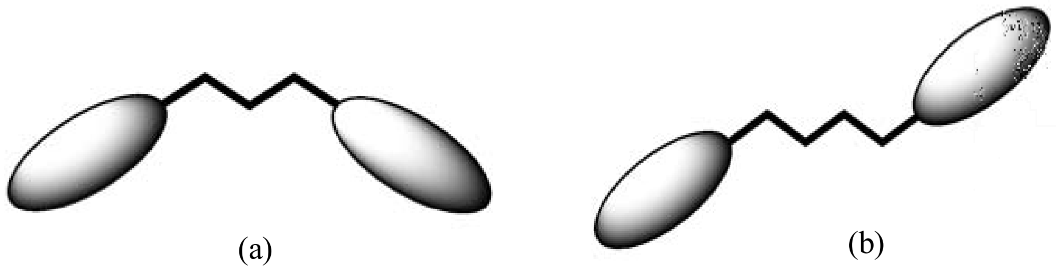

(a) (b)

Figure 1.9: Diagram representation of dimeric molecules with (a) an odd and (b) an even number of flexible units between two mesogenic units (Imrie and Henderson, 2007).

1.6.4 Chirality effect on liquid crystalline properties of dimers

Chirality is one of the most interesting research fields of science and its enantioselectivity have been an important issue in chemistry. In enhancing the materials containing chiral properties, molecules or enzymes of chiral are necessary to used. Various liquid crystal phases such as cholesteric, blue phase, twisted grain boundary (TGB), chiral smectic C (SmC*) and chiral nematic (N*) phases are chiral due to the introduction of chirality by molecules containing chiral carbons. Tilted chiral smectic phases could exhibit spontaneous polarization and thus these mesophases were pyroelectric (Dierking, 2003). Blatch and co-workers reported that the chirality of the chiral phase depends strongly on the length and parity of the spacer which is for non-symmetric series. The odd members exhibited N*-BP transition while the even members showed N*-I phase transition. This behaviour was rationalised in terms of the smaller pitch for the odd relative to the even membered dimers which arises from the smaller twist elastic constant for odd dimers and it is related to their lower orientational order. The helical twisting power of the dimers in a common monomeric N solvent also appears to be solely dependent on the nature of the chiral group. Thus, similar helical twisting powers are observed for both odd-even membered dimers. The properties of a chiral symmetric dimer have also been reported in which the dimers exhibit ferroelectric and antiferroelectric phases with high values of the tilt angle (Nishiyama *et al.,* 2001, 2002). A direct ferroelectric smectic-to-isotropic phase transition was observed along with an isotropic to isotropic transition in the liquid phase. However, for the racemic analogue it exhibited N-SmC phase sequence.

1.7 Liquid crystals dimers incorporating Schiff base moiety

Most thermotropic liquid crystals are rod-like molecules which have a rigid core composed by two or more aromatic rings and one or more flexible terminal chains. Aromatic imines better known as Schiff base, can easily be prepared from corresponding aromatic aldehydes and substituted aniline by acid catalyzed condensation in an inert organic solvent (Heinze, 2001; Jursic *et al.,* 2002). Figure 1.10 depicts a general structure of a Schiff base. It is used as a linking group to connect between core groups and provides a stepped core structure but still maintained the molecular linearity in order to exhibit higher stability and to form mesophases (Collings and Hird, 1998; Singh and Dunmur, 2002). An extensive study on Schiff base core systems have been conducted since the findings of MBBA which has exhibited a nematic phase at room temperature (Kelker and Scheurle, 1969). Several studies on the mesomorphic behaviour of the mesogenic Schiff base derivatives with different number of carbon atoms at the terminal chain have been reported (Sakagami and Takase, 1995). The influence of different substituent located at the terminal axis such as polar and halogen substituents on the mesogenic Schiff base of liquid crystalline compounds have also been documented. This study has become an interesting subject for researcher working on LC dimers (Yeap *et al.,* 2002; Yeap *et al.,* 2006(a, b); Yeap *et al.,* 2011; Yeap *et al.,* 2009). In order to establish the structure-property relationship of Schiff base dimers, four series of dimeric liquid crystalline compounds with various structural modifications have been prepared.

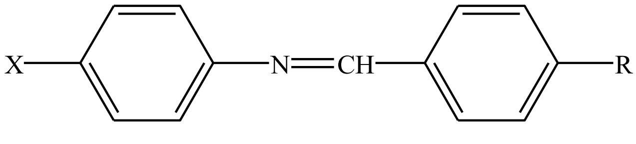


Figure 1.10: A general structure of a Schiff base (imine).

1.8 Objectives of the research

Four series of dimeric liquid crystal compounds with several of structural differences have been synthesized. The overall objectives of present study are:

a) To synthesize and characterize new dimeric compounds with symmetric and non-symmetric aromatic imine mesogenic unit with different length of flexible spacer and variable of terminal groups.

b) To investigate the effect of chirality and non-chirality on the liquid crystalline properties of these dimers.

c) To investigate the structure-property relationship of these dimers by increasing the flexible alkyl spacer and by varying the terminal substituents with the introduction of sulfur-sulfur linking as a bridging group.

d) To elucidate the structure of title compounds by CHN microanalysis, FT-IR, NMR and mass spectral analysis.

e) To study the phase transition and thermal behaviour of title compounds by polarized optical microscopy (POM) and differential scanning calorimetry (DSC).

2.0 EXPERIMENTAL

2.1 Chemicals

Table 2.1. List of chemicals used for the syntheses

Chemicals	Source	Percentage purity (%)
Aniline	Acros Organics (Belgium)	>99
1,6-Dibromohexane	Acros Organics (Belgium)	98
1,8-Dibromooctane	Acros Organics (Belgium)	98
4-Bromoaniline	Acros Organics (Belgium)	99
4-Chloroaniline	Acros Organics (Belgium)	98
4-Ethylaniline	Acros Organics (Belgium)	99
30% Hydrogen peroxide	Acros Organics (Belgium)	-
N,N-Dicyclohexylcarbodiimide	Acros Organics (Belgium)	99
(*R*,*S*)-2-methyl-1-butanol	Acros Organics (Belgium)	99
Potassium metabisulphide	Acros Organics (Belgium)	97
Potassium thioacetate	Acros Organics (Belgium)	98
Sulphuric acid	Acros Organics (Belgium)	96
1,3-Dibromopropane	Fluka (Switzerland)	99
1,4-Dibromobutane	Fluka (Switzerland)	99
(*S*)-(-)-2-methyl-1-butanol	Fluka (Switzerland)	95
Potassium carbonate anhydrous	Fisher Scientific(United Kingdom)	>99
Potassium iodide	Fisher Scientific(United Kingdom)	>99

Sodium hydroxide	Fisher Scientific(United Kingdom)	98
Hydrochloric acid	Fisher Scientific(United Kingdom)	37
Sodium iodide	R&M Chemicals(United Kingdom)	>99
1,5-Dibromopentane	Sigma Aldrich (USA)	97
1,7-Dibromoheptane	Sigma Aldrich (USA)	97
6-bromohexanoic acid	Sigma Aldrich (USA)	97
4-Iodoaniline	Sigma Aldrich (USA)	98
p-Toluidine	Sigma Aldrich (USA)	99
4-Dimethylaminopyridine	Sigma Aldrich (USA)	99
4-(4-Hydroxyphenyl)benzoic acid	Tokyo Chemical Industry (Japan)	>98

2.2 Instruments

(a) Melting points were determined by Gallenkamp melting point apparatus.

(b) CHN microanalyses were performed using a Perkin Elmer 2400 LS Series CHN/O analyzer.

(c) Fourier Transform Infrared (FT-IR) data were recorded by a Perkin Elmer 2000-FTIR spectrophotometer.

(d) 1D and 2D Fourier Transform Nuclear Magnetic Resonance (FT-NMR) were carried out on a Bruker-Avance 300MHz, 400MHz and/or 500MHz ultrashield spectrometers.

(e) Phase transition temperatures and enthalpy values of the synthetic compounds were recorded by differential scanning calorimeter.

(f) Mesophase textures were investigated by polarizing optical microscope.

(g) Layer spacing of dimers during phase transition were determined by X-ray diffraction.

(h) Structural information and molecular formula for symmetrical dimers were obtained using the Electrospray ionisation-time of flight mass spectrometer (ESI-TOF-MS).

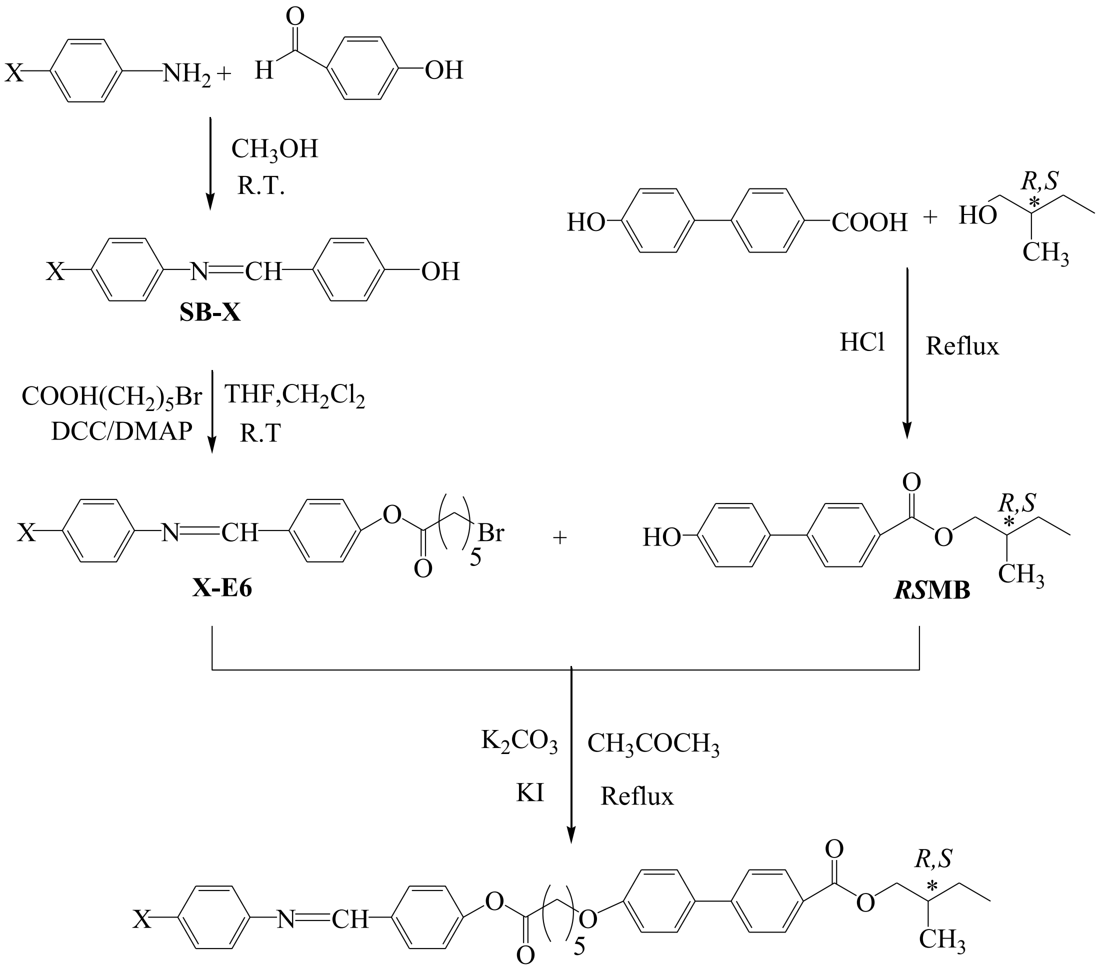
The details of the instruments will be discussed further in Section 2.4 based on different series of **X-E6-*RS*MB**, **X-E6-*S*MB**, **X-6-SS-6-X** and **Br-*n*-SS-*n*-Br**.

2.3 Synthesis

All compounds were synthesized, purified and analyzed at normal atmospheric pressure.

2.3.1 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]carbonyl)phenoxy] -phenoxy}-ω-[4-(4-(R,S)-2-methylbutyloxycarbonylphenyl)phenoxy]hexanoate, X-E6-*RS*MB

The synthesis of the **X-E6-*RS*MB** series in which **X** denotes the terminal substituent, **E** denotes the ester group in the flexible spacer and ***RS*MB** denotes achiral 2-methyl-1-butyl is outlined in Figure 2.1. 4-hydroxybenzaldehyde was reacted with 4-substituted-aniline to afford a series of Schiff bases **SB-X**. The Schiff bases were reacted with 6-bromohexanoic acid via Steglish esterification (Ha *et al.,* 2010b) in order to obtain the intermediate **X-E6.** In subsequent reaction, the 4-(4-hydroxyphenyl)benzoic acid underwent esterification with (*R*,*S*)-2-methyl-1-butanol to afford intermediate ***RS*MB** (Yeap *et al.,* 2009)**.** Finally, Williamson etherification reaction occurred between intermediate **X-E6** and ***RS*MB** in the presence of anhydrous potassium carbonate and catalytic amount of potassium iodide to obtain the desired dimers **X-E6-*RS*MB** (Yeap *et al.,* 2009).



X= H, CH_3, C_2H_5, I, Cl, Br

X-E6-*RS*MB

Figure 2.1. Synthetic route for the preparation of liquid crystal dimers, **X-E6-*RS*MB**.

2.3.1.1 Synthesis of 4-[(4-bromophenylimino)methyl]phenol, SB-Br

4-bromoaniline (1.97 g, 11.45 mmol) was dissolved in absolute methanol. A methanolic solution of 4-hydroxybenzaldehyde (1.40 g, 11.45 mmol) was added dropwise and the mixture was stirred at room temperature for ½ hour. The yellow precipitate thus formed was filtered and washed with methanol to afford the desired Schiff base, **SB-Br**.

2.3.1.2 Synthesis of 4-[(4-substituted-phenylimino)methyl]phenol, SB-X

The same procedure described in section 2.3.1.1 was used to obtain the other homologues of **SB-X** in similar molar ratio of 4-substituted-aniline.

2.3.1.3 Synthesis of 1-{4-[(4-bromo-phenylimino)methyl]phenoxy}-6-bromo-hexanoate, Br-E6

SB-Br (1.00 g, 3.62 mmol) was dissolved in a minimum amount of THF and added to a mixture of 6-bromohexanoic acid (0.71 g, 3.62 mmol) and DMAP (0.22 g, 1.81 mmol) which have been dissolved in dichloromethane (20 mL). DCC (0.75 g, 3.62 mmol) in dichloromethane (5 mL) was added dropwise into the mixture upon stirring at 0 °C for 1 hour. The solution was stirred further at room temperature for another 3 hours. Finally, the mixture was filtered and the excess solvent was removed from the filtrate by evaporation. The white product was washed by ethanol and recrystallized with n-hexane.

2.3.1.4 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]phenoxy}-6-bromohexanoate, X-E6

In order to obtain the other homologues of **X-E6**, the equal amount of molar ratio intermediate compounds **SB-X** was used following the procedure described in section 2.3.1.3.

2.3.1.5 Synthesis of 2-methylbutyl-4-(4-hydroxyphenyl)benzoate, *RS*MB

4-(4-hydroxyphenyl)benzoic acid (2.00 g, 9.34 mmol) was added to (*R*,*S*)-2-methyl-1-butanol (25 mL), which served both as a reactant and the reaction solvent. As the temperature increased to 90 °C, a catalytic amount of concentrated HCl was added dropwise and the reaction mixture was refluxed for 24 hours. The mixture was evaporated under reduced pressure. The precipitate was washed by water and recrystallized from chloroform to afford white precipitate.

2.3.1.6 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]carbonyl)phenoxy]phenoxy}-ω-[4-(4-(*R,S*)-2-methylbutyloxycarbonylphenyl)phenoxy] hexanoate, X-E6-*RS*MB

X-E6 (0.48 g, 1.06 mmol) and ***RS*MB** (0.30 g, 1.06 mmol) were dissolved in stirred acetone (40 mL). Anhydrous potassium carbonate (0.73 g, 5.30 mmol) was added to the solution, together with a catalytic amount of potassium iodide as the temperature was increased. The reaction mixture was refluxed for 18 hours. The mixture was cooled and the solvent was evaporated under reduced pressure. Water (50 mL) was added and the resulting precipitate was filtered. The white precipitate was purified by column chromatography packed with silica gel using $CHCl_3$/n-hexane (8:2) as eluent to afford **X-E6-*RS*MB**.

2.3.2 Synthesis of α-{4-[(4-substituted-phenylimino)methyl]carbonyl)phenoxy] phenoxy}-ω-[4-(4-(*S*)-2-methylbutyloxycarbonylphenyl)phenoxy]hexaneate, X-E6-*S*MB

The synthesis of the **X-E6-*S*MB** series in which **X** denotes the terminal substituent, **E** denotes the ester group in the flexible spacer and ***S*MB** denotes the (*S*)-(-)-2-methyl-1-butyl is outlined in Figure 2.2. The same method was used to describe the formation of intermediates and the title compounds as mentioned in section 2.3.1. In this series the 4-(4-hydroxyphenyl)benzoic acid underwent esterification with (*S*)-(-)-2-methyl-1-butanol to afford intermediate ***S*MB.** Finally, intermediate **X-E6** and ***S*MB** underwent Williamson etherification to afford the non-symmetric dimers **X-E6-*S*MB**.