SYNTHESIS OF DISC-SHAPED LIQUID CRYSTALS HAVING SIX ALKYL CHAINS AS PERIPHERAL

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DECLARATION

I hereby declare that this dissertation is based on my original work, except for quotations and references which have been fully acknowledged.

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ABSTRACT

A novel symmetrical liquid crystalline material comprised of a disc-shaped triphenylene unit as central core and six alkyl substituted chains as peripheral has been synthesised. This final compound, 2,3,6,7,10,11-hexakis{[4-(4-acetylphenylazo) phenoxy]hexyloxy}triphenylene was synthesised from alkylation of 2,3,6,7,10,11-hexahydroxytriphenylene with 1-bromo[4-(4-acetylphenylazo)phenoxy]hexane in the presence of potassium carbonate as base and potassium iodide as catalyst. Spectroscopic analysis which are nuclear magnetic resonance (NMR) and fourier transform infrared spectroscopy (FT-IR) were utilised to identify the molecular structure of final triphenylene compound. The ^{1}H NMR and FT-IR spectra show the presence of triphenylenes, aliphatic alkyl chains, azobenzene moieties and acetyl functional groups for this disc-shaped molecule. The phase transition temperatures and enthalpies were measured by thermal analysis of differential scanning calorimetry (DSC). The result of thermogram reveals two lower exothermic cooling points at 96.27 °C and 70.23 °C for crystallisation of compound.

SINTETIK KRISTAL BERBENTUK DISK YANG MEMPUNYAI ENAM RANTAI ALKIL SEBAGAI PERSISIAN

ABSTRAK

Satu kristal berhablur cecair bersimetri yang baru mengandungi satu sebatian trifenilin unit sebagai pusat teras bulatan dan enam rantai alkil yang bercabang di sekelilingnya telah disintesiskan. Sebatian akhir ini, 2,3,6,7,10,11-heksakis{[4-(4-asetilfenilazo)fenoksi]heksiloksi}trifenilin disintesiskan daripada akilasi sebatian 2,3,6,7,10,11-heksahidroksitrifenilin dengan 1-bromo[4-(4-asetilfenilazo)fenoksi] heksana dalam kehadiran kalium karbonat sebagai bahan bes dan kalium iodat sebagai pemangkin. Analisis spektroskopi iaitu nuklear magnetik resonan (NMR) dan forier transfom inframerah (FT-IR) digunakan untuk mengenalpasti struktur molekul sebatian trifenilin akhir. Spektra ^{1}H NMR and FT-IR menunjukkan kehadiran kumpulan-kumpulan berfungsi trifenilin, rantai alkil alifatik, azobenzin dan asetil bagi molekul berbentuk bulat ini. Suhu dan entalpi fasa peralihan diukur oleh analisis terma melalui diferensia skaning kalorimetri (DSC). Keputusan termogram menunjukkan dua takat beku eksotermik yang rendah pada suhu 96.27 °C and 70.23 °C bagi proses kristalisasi sesuatu sebatian .

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CHAPTER 1

INTRODUCTION

1.1 Introduction to Liquid Crystals

The study of liquid crystals began in 1888 when an Austrian botanist named Friedrich Reinitzer observed that a material known as cholesteryl benzoate had two distinct melting points (Reinitzer, 1888). In his experiments, Reinitzer increased the temperature of a solid sample and watched the crystal change into a hazy liquid at 145.5 °C (Reinitzer, 1888). As Reinitzer increased the temperature further up to 178.5 °C, the material changed again into a clear and transparent liquid (Reinitzer, 1888).

Further investigations of this phenomenon were carried out by the German physicist Otto Lehmann who observed and confirmed, using the first polarized optical microscope (Lehmann, 1889). In 1922, the French scientist Georges Friedel produced the first classification scheme of liquid crystals, dividing them into three different types of mesogens which are nematic, smectic and cholesteric (Friedel, 1922). Following these first observations and discoveries, the scientist research turned attention towards a growing number of compounds which displayed liquid crystalline properties (Belloni, 2002).

1.2 Objectives of Research

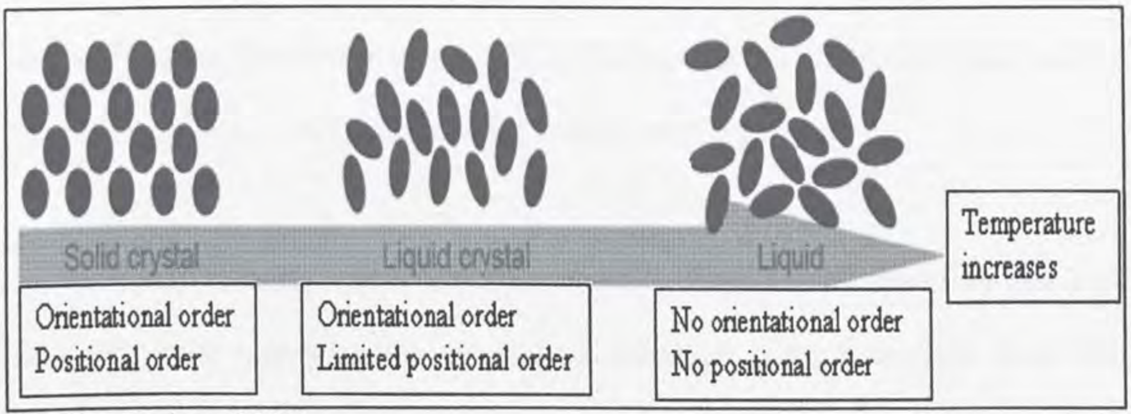
- **i.** To synthesis the hexaalkoxytriphenylene compound having six alkyl chains at the periphery,
- **ii.** To determine the molecular structures of the intermediates and the final compound by using nuclear magnetic resonance spectroscopy (NMR) and fourier transform infrared spectroscopy (FT-IR), and
- **iii.** To determine the phase transition properties of the final compound by using differential scanning calorimetry (DSC).

CHAPTER 2

LITERATURE REVIEW

2.1 Liquid Crystals

Liquid crystals are substances that exhibit a phase of matter that has properties between those of an anisotropic solid and those of an isotropic liquid (Kadam, 2004). They are systems with orientational order while lacking complete positional order (Figure 2.1) (Kadam, 2004).



(Source: Kadam, 2004)

Figure 2.1 Schematic melting behavior of a liquid crystal.

Thus, a liquid crystal may flow like a liquid, but have the molecules in the liquid arranged and oriented in a crystal-like way (Kadam, 2004). On the basis of their appearance, liquid crystals are divided into two different classes which are calamitic mesogens characterised by a rod-like molecule and discotic mesogens characterised by a disc-like core of the molecule (Fechtenkötter, 2001).

2.2 Applications of Discotic Liquid Crystals

Today, discotic liquid crystals play a dominant role in a large part of the liquid crystal display technology (Kadam, 2004). These are produced in huge numbers and used for various applications such as calculators, watches, mobile phones, laptop computer displays, digital clocks, microwave ovens, CD players and many other electronic devices (Kadam, 2004).

Mesophases formed by discotic liquid crystals are now well-recognised to be suitable for many device applications (Boden *et al.*, 1996). The potential uses of these materials as one-dimensional conductors (Arikainen *et al.*, 1995; Boden *et al.*, 1996), photoconductors (Henderson *et al.*, 1995; Simmerer *et al.*, 1996) and light emitting diodes (Stapff *et al.*, 1997) are attracting considerable attention.

It was recently discovered that discotic liquid crystal materials can self-assemble to be highly ordered hexagonal columnar mesophases and have high mobility of charges and energies (Adam *et al.*, 1994; Lehmann *et al.*, 2005; Van de Craats and Warman, 2001; Van de Craats *et al.*, 1996; Warman *et al.*, 2004). The charge carrier mobility of such materials organised in self-assembled columnar liquid crystal phases renders them also of potential interest as organic semiconductors such as photovoltaic cells (Gregg *et al.*, 1990) and optical data storage (Fox *et al.*, 1993; Liu *et al.*, 1993).

Most of the compounds exhibiting columnar phases investigated for these applications have been triphenylene derivatives due to their high tendency to form the required columnar phases and the presence of the large conjugated aromatic molecular core with a large delocalised π-electron system (Cross *et al.*, 1998). Hence, several research groups have been working on the synthesis of functionalised triphenylene-based discotic liquid crystals and their potential applications (Boden *et al.*, 1997; Goodby *et al.*, 1994; Kumar *et al.*, 1999).

Besides, discotic columnar liquid crystals have some advantages compared to those of other materials. These columnar liquid crystalline molecules have a π electron-rich aromatic core attached by flexible alkyl chains, which attracting particular attention for potential molecular electronics in which aromatic part act as transport electrons or holes and alkyl chains act as insulating parts (Chandrasekhar, 1993). The advantages of these liquid crystalline conductors are their anisotropy, processibility, and self-healing characteristics for structural defects when it is compared to nematic and smectic liquid crystalline conductors (Chandrasekhar, 1993).

2.3 Mesophase Characterisation

There are three main techniques to identify the liquid crystalline properties of a compound. The first technique is based on the birefringence of the mesophase and is called hot-stage polarizing optical microscopy (POM) (Thomas, 2006). It is used to look at the optical textures that are typical for a given mesophase (Thomas, 2006). The second technique that is used to complimentary to POM is differential scanning calorimetry (DSC) (Thomas, 2006). DSC reveals the phase transition temperature as well as transition enthalpies (Thomas, 2006). A third way to study mesogenic behaviour is by using X-ray powder diffraction (XRD) (Thomas, 2006). When an X-ray beam interacts with the typical structure of the mesophase, a characteristic diffraction pattern is observed, which allows identification of the mesophase (Thomas, 2006).

Besides, there are two types of spectroscopy methods which are nuclear magnetic resonance (NMR) and fourier transform infrared (FT-IR), commonly used for the determination of molecular structure of one organic compound such as liquid crystals and polymers. The NMR spectroscopy is used to describe the elucidation of molecular structure based on the interpretation of nuclear magnetic resonance spectra for simple compounds (Silverstein *et al.*, 1974). The IR spectroscopy is used to describe the elucidation of molecular structure based on the identification of bonds and functional groups (Silverstein *et al.*, 1974).

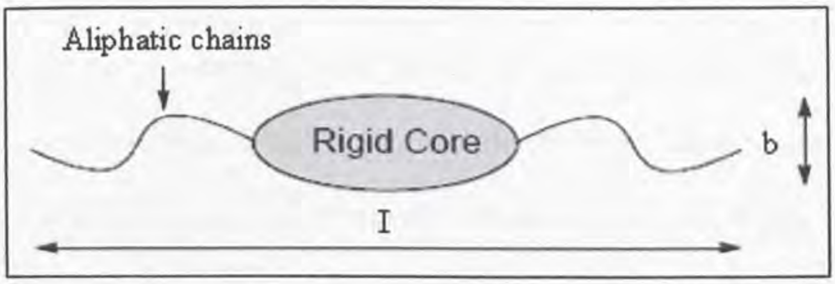
2.4 Thermotropic Liquid Crystals

Thermotropic liquid crystals are a structure consisting of a central rigid core and a flexible peripheral moiety whose mesophase formation is temperature dependent (Belloni, 2002). If the temperature is raised too high, thermal motion will destroy the delicate cooperative ordering of the liquid crystal phase, pushing the material into a conventional isotropic liquid phase (Belloni, 2002). If the temperature is decreased too low, most liquid crystal materials will form a conventional anisotropic crystal (Belloni, 2002).

Many thermotropic liquid crystals exhibit a variety of phases when temperature is changed (Belloni, 2002). For instance, a particular mesogen may exhibit various smectic and nematic and finally isotropic phase as temperature increases (Belloni, 2002). This structural requirement leads to two general classes of .liquid crystals which are calamitic liquid crystals and discotic liquid crystals, meanwhile both of which have other molecular subclasses (Belloni, 2002).

2.4.1 Calamitic Liquid Crystals

Calamitic or rod-like liquid crystals are those mesomorphic compounds that posses an elongated shape, responsible for the formanisotropy of the molecular structure, as the result of the molecular length (I) being significantly greater than the molecular breadth (b) (Figure 2.2) (Belloni, 2002). In general, calamitic liquid crystals can exhibit three common types of mesophases which are nematic, smectic and cholesteric phases.

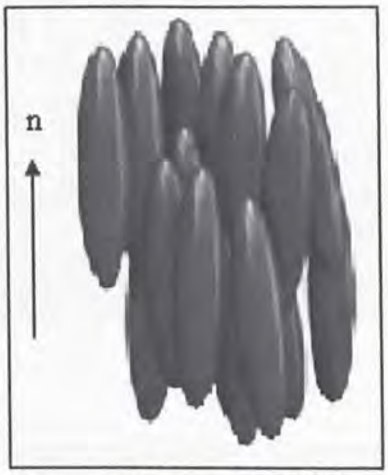


(Source: Belloni, 2002)

Figure 2.2 General shape of calamitic liquid crystals.

a. Calamitic Nematic Phase

The calamitic nematic phase is the least ordered liquid crystal phase with molecules only possessing orientational order and no positional order, but tend to point in the same direction along the director (Date *et al.*, 2003). Thus it is usually the least viscous mesophase (Date *et al.*, 2003). In the following diagram, notice that the molecules point vertically but are arranged with no particular order (Figure 2.3) (Date *et al.*, 2003).



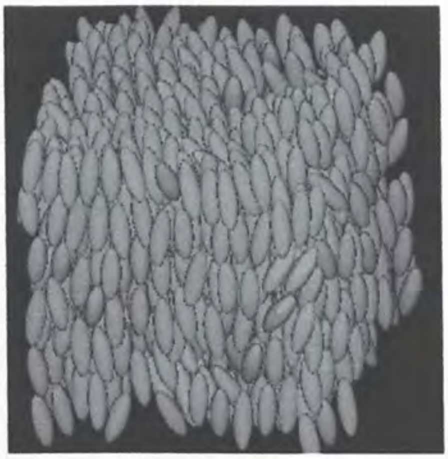
(Source: Date *et al.*, 2003)

Figure 2.3 Molecular structure of calamitic nematic phase.

b. Calamitic Smectic Phase

The word "smectic" is derived from the Greek word for soap. This seemingly ambiguous origin is explained by the fact that the thick and slippery substance often found at the bottom of a soap dish is actually a type of smectic liquid crystal (Belloni. 2002). The smectic state is another distinct mesophase of liquid crystal substances.

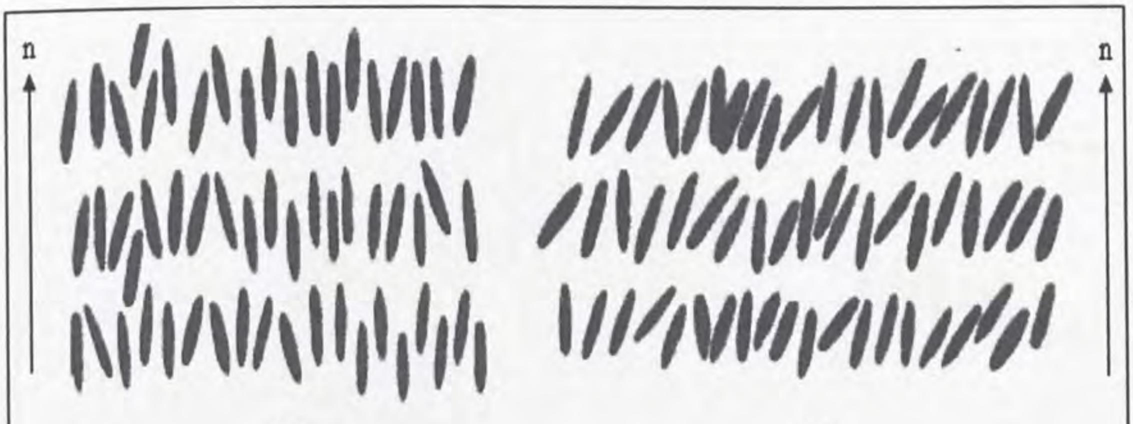
In the smectic phase, the molecules maintain the general orientational order of nematic but possess positional order organised in the layer structures (Date *et al.*, 2003). Because of the motion is restricted within these planes, so that the separate planes are observed to flow past each other (Date *et al.*, 2003). The arrangement of molecular structure in the form of smectic mesophase is shown in the following Figure 2.4.



(Source: Date *et al.*, 2003)

Figure 2.4 Molecular structure of calamitic smectic phase.

There are several different types of smectic mesophases (Sackmann, 1989). The most important ones are smectic-A and smectic-C, the molecules are tilted with respect to the layer plane (Figure 2.5) (Date *et al.*, 2003).



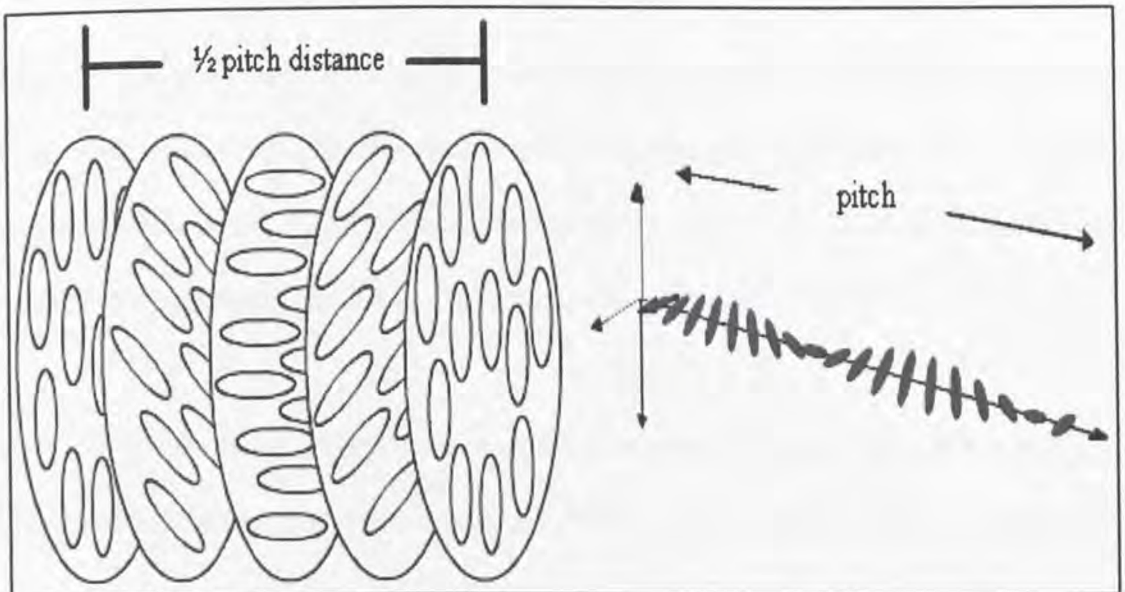
(Source: Date *et al.*, 2003)

Figure 2.5 Molecular structures for (a) smectic-A phase and (b) smectic-C phase.

c. Cholesteric Phase

Cholesteric phases were the first liquid crystals ever observed and for many years were thought to be a separate type of liquid crystal (Gleeson, 1998). The cholesteric or chiral nematic liquid crystal phase is typically composed of nematic mesogenic molecules containing a chiral center which produces intermolecular forces that alignment between molecules at a slight angle to one another (Gleeson, 1998).

This lead to the formation of a structure which can be visualised as a stack of very thin two-dimensional (2D) nematic-like layers with the director in each layer twisted with respect to those above and below (Belloni, 2002). In this structure, the directors actually form in a continuous helical pattern about the layer normal as illustrated by the black arrow director in the following Figure 2.6 (Barón, 2001).



(Source: Barón, 2001)

Figure 2.6 Helical structure of cholesteric or chiral nematic phase.

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