SYNTHESIS OF DISC-SHAPED LIQUID CRYSTALS CONTAINING AZO CHROMOPHORES

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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

The objective of this dissertation is to synthesis disc-shaped liquid crystals containing azo chromophores, 2,3,6,7,10,11-hexakis{[4-(4-acetylphenylazo)phenoxy]hexyloxy} triphenylene). This disc-shaped liquid crystal is synthesized from the starting material 4-aminoacetophenone to 4-(4-hydroxyphenylazo)acetophenone via diazo coupling reaction. From 4-(4-hydroxyphenylazo)acetophenone, 1-bromo[4-(4-acetylphenylazo) phenoxy]hexane is synthesized via esterification with the potassium carbonate and the catalyst of potassium iodide. Then 1,2-bis{[4-(4-acetylphenylazo)phenoxy] hexyloxy}benzene is synthesized via esterification from 1-bromo[4-(4-acetylphenylazo)phenoxy]hexane with catechol, potassium carbonate and potassium iodide. Finally the disc-shaped liquid crystal is synthesized ferric chloride oxidative trimerisation of 1,2-bis{[4-(4-acetylphenylazo) phenoxy]hexyloxy}benzene. Melting point of each intermediate is determined by Capillary Melting Point Exterminator. The melting point of compound 1 is in the range or 198-202°C, compound 2 is 120-125°C, and compound 3 is 122-125°C. Fourier Transform Infrared (FT-IR) is used to determine the presence of functional group of each intermediate and the final compound. The functional groups that reveals in the final compound are alkyl, aromatic, ketone, methyl, and ether. ^{1}H-Nuclear Magnetic Resonance (^{1}H-NMR) is utilized to reveal number of magnetically distinct atoms of compound 3. The resulted spectrum produced was not indicates the presence of compound 3 but it was only compound 2. Differential Scanning Calorimetry (DSC) is used to determine the phase transition temperature and enthalpy of the compound 3. The thermogram produced shows only single peak that present in both heating and cooling cycle with melting temperature (T_m) is 123.53 °C and the cooling temperature (T_c) is 102.7 °C.

SINTETIS HABLUR CECAIR BERBENTUK DISK YANG MENGANDUGI AZO KROMOPOR

ABSTRAK

Objektif utama bagi disertasi ini adalah untuk mensintesiskan hablur cecair berbentuk disk yang mengandungi azo kromophor, 2,3,6,7,10,11-heksakis{[4-(4-asetilfenilazo)fenoksi]heksiloksi}trifenilin. Hablur cecair berbentuk disk ini disintesiskan dari bahan permulaan p-aminoasetonfenon kepada 4-(4-hidroksifenilazo)asetonfenon melalui tindak balas penggabungan garam dizaonium. Dari 4-(4-hidroksifenilazo)asetonfenon, 1-bromo[4-(4-asetilfenilazo)fenolsi]heksana dapat dihasilkan melalui sistesis esterifikasi dengan bantuan kalium karbonat dan kalium iodida. Kemudian, 1,2-bis{[4-(4-asetilfenilazo)fenosil]heksilosi}benzene disintesis oleh 1-bromo[4-(4-asetilfenilazo)fenolsi]heksana dengan katekol, kalium karbonat, dan kalium iodida melalui sintesis esterifikasi. Akhirnya, hablur cecair berbentuk disk dapat disintesis melalui ferik klorida pentrimeran pengoksidaan 1,2-bis{[4-(4-asetifenilazo)fenolsi]heksilosi}benzen. Takat lebur bagi setiap perantaraan diukur dengan menggunakan mesin penentu takat lebur berkapilari. Takat lebur bagi kompaun 1 ialah diantara 198 – 202 °C, kompaun 2 ialah antara 120 – 125 °C, dan kompaun 3 ialah antara 122 – 125 °C. Kehadiran setiap kumpulan berfungsi dapat dikesan dengan menggunakan mesin FT-IR. Kumpulan berfungsi yang hadir pada kompaun terakhir ialah alkil, aromatik, keton, metil, dan eter. ^{1}H-NMR digunakan untuk mengesan kehadiran hidrogen pada kompaun 3. Keputusan spetrum dari NMR menunjukan ketidakwujudnya kompaun 3, malah, keputusan yang terhasil menunjukkan kehadiran kompaun 2. Sifat mesomofik kompaun 3 dikaji dengan menggunakan mesin kalorimetri pengimbasan pembezaan (DSC). Keputusan yang dihasilkan oleh DSC menunjukkan bahawa kompaun 3 tidak mempunyai sifat mesomofik. Tetapi takat lebur kompaun 3 tetap dapat diukur. Ia adalah pada 123.53 °C dan takat beku ialah 102.7 °C.

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LIST OF SYMBOLS

Cr	Crstalline
N	Nematic
Sm	Smectic
N*	Chiral Nematic or Cholesteric
I	Isotropic

LIST OF UNITS AND ABBREVIATIONS

a. Units

g	gram
g/mol	gram per mol
ml	milliliter
°C	degree Celsius
mmol	milimol
ppm	part per million
MHz	Mega Hertz
$°Cmin^{-1}$	degree Celsius per minute
cm^{-1}	per centimeter

b. Abbreviations

LC / LCs	Liquid Crystal / Liquid Crystals
LCD	Liquid Crystal Display
FT-IR	Fourier Transform Infrared
NMR	Nuclear Magnetic Resonance
DSC	Differential Scanning Calorimetry
POM	Optical Polarizing Microscopy
s	solid
l	liquid
g	gas
TLC	Thermotropic Liquid Crsytal
DLC	Discotic Liquid Crystal
Col	Columnar Liquid Crystal
N_D	Discotic Nematic Phase

CHAPTER 1

INTRODUCTION

1.1 Introduction

Liquid crystal is a matter that found by Friedrich Reinitzer while he was doing his investigations on extracting cholesterol from carrots in 1888 (Demus *et al.*, 1999). The term of liquid crystal was introduced by O. Lehmann back to 1890 (Meier *et al.*, 1975). Liquid crystal has a recommended symbol "LC", is a substance that has both the properties of liquid and solid crystal. This is because liquid crystal can be flow like a liquid yet the molecules are arranged in the form of solid crystal (Sonin, 1995).

The application of matter is first began as the liquid crystal display (LCD) on the calculators and watches right after the discovered of twisted nematic liquid crystals by Schadt and Helfrich in 1971. Then it start to evolve to the display in laptop computer, mobile telephones, and personal digital assistant (PDA), from twisted nematic display (TN) to thin film transitor display (TFT), then supertwisted nematic display (STN), in-plane switching (IPS), and vertical aligned twisted nematic (VA) (Demus *et al.*, 1999).

Shapes of liquid crystals are one of the ways to distinguish the difference of LCs. LCs are made up of rod-shaped, disc-shaped, V-shaped, bend-shaped and banana-shaped. In this project, a disc-like liquid crystal containing azochromophore will be synthesised.

Discotic liquid crystal plays an important role in our daily life. It was found that discotic liquid crystals produced a new class of organic semiconductor and organic photoconductors.

Another ways to distinguish the difference of LCs are through their phase transition, which is nematic, smectic, and chiral nematic.

The disc-shaped liquid crystal will be first synthesised from 4-aminoacetophenone as the starting material to form 4-(4-hydroxyphenylazo)acetone (denoted as compound 1), then followed by the formation of compound 2, 1-bromo[4-(4-acetylphenylazophenoxy)hexane] via Williamson Ether synthesis method. Next is the preparation of aryl ether known as compound 3, 1,2-bis{[4-(4-acetylphenlazo)phenoxy]hexyloxy}benzene from the reaction between catechol and compound 2. Finally the formation of the disc-like core (compound 4) 2,3,6,7,10,11-hexakis{[4-(4-acetylphenoxy)phenoxyl]hexyloxy}triphenylene by ferric chloride oxidative trimerization reaction of compound 3 with catalyst iron (III) chloride and sulphuric acid (Lutfor *et al*., 2005).

The structure of the each intermediate compounds that have been synthezised will be confirmed by introducing it into Fourier Transform Infrared Spectroscopy (FT-IR) and the final compound will be further analyse by using Nuclear Magnetic Resonance (NMR) (Lutfor *et al.*, 2005).

The mesomophic properties of the final compound will be determined by introduce it into the differential scanning calorimeter (DSC) (Lutfor *et al.*, 2005).

1.2 Objectives

The objectives of this study are:

- To synthesize disc-shaped liquid crystals containing azo chromophores.
- To identify the structure of intermediates and final compound by using spectroscopic method.
- To determine the mesomorphic properties of liquid crystal compound by using differential scanning calorimetry method.

1.3 Scope of studies

This project is focus on the synthesis of disc-shaped liquid crystal containing azo chromophores from the starting material of 4-aminoacetophenone to 4-(4-hydroxyphenylazo)acetone, then 1-bromo[4-(4-acetylphenylazophenoxy)hexane], 1,2-bis{[4-(4-acetylphenlazo)phenoxy]hexyloxy}benzene, and finally to 2,3,6,7,10,11-hexakis{[4-(4-acetylphenoxy)phenoxyl]hexyloxy}triphenylene. The identification of the structure of intermediates and the final compound is investigated through spectroscopic method of FT-IR and NMR. Subsequently, the determination of the mesomorphic properties of the final compound is done by using DSC.

CHAPTER 2

LITERATURE REVIEW

2.1 State of Matter

State of matter is classified by its physical state. There are three common states of matter such as solid (s), liquid (*l*), and gas (g) (Ebbing *et al.*, 2003). These three matters are temperature dependent. It changes from one state to another when the temperature increases or decreases (Figure 2.1). They can be distinguished by their physical properties; shape, compressibility, and their ability to flow (Silberberg, 2006).

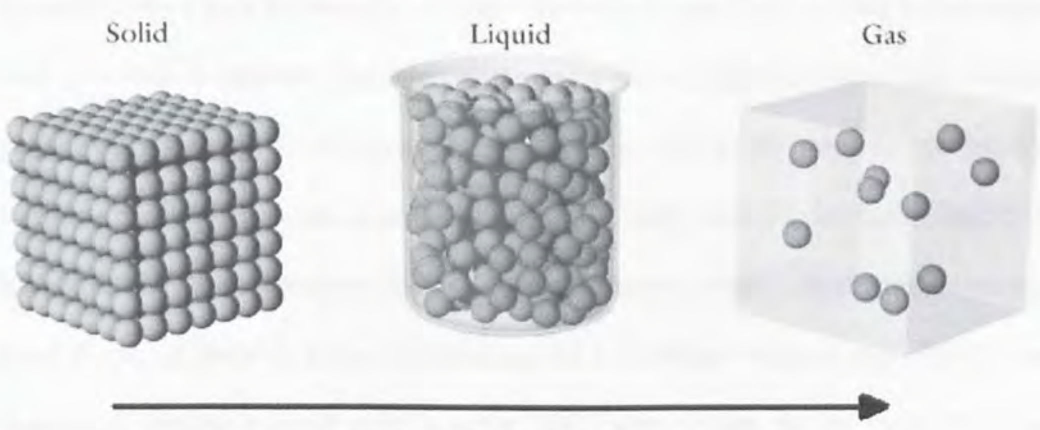

Figure 2.1 Three different states of matter.

2.1.1 Solid State (s)

Solid is defined as the form of matter that characterized by it rigidity; many solid are crystalline. They have strong intermolecular forces that make the arrangement of the tiny, individual particles closely packed (Burns, 2003). As the result, solid's particles are in the fixed position and do not flow significantly (Silberberg, 2006). Besides, it is relatively incompressible and has a fixed volume (Ebbing *et al.*, 2003). An example of the solid state is ice, H_2O, where it has a fixed shape and does not has the ability to flow.

2.1.2 Liquid State (*l*)

Liquid is defined as the form of matter that is a relatively incompressible fluid. The intermolecular forces between the particles are weaker than those in solid but stronger than gas. This is because liquid has an arrangement of particles that is less closely packed compare to solid but more packed than gas. Due to the weak intermolecular force, its particles can slide, slip and glide among each other. Hence these properties have made liquid able to flow (Burns, 2003). Moreover, it has a fixed volume but no fixed shape, its shape is following the shape of it container (Ebbing *et al.*, 2003). An example to picture a liquid state is water, H_2O, where it has the ability to flow but does not has a fixed shape.

2.1.3 Gaseous State (g)

Gas is defined as the form of matter that can be easily compressed. The intermolecular force between the particles is the weakest among the other two states of matter. Since it has the weakest intermolecular force, the particles are far apart. They expanded and filled the entire volume of the container and conformed to the shape of the container. In a closed container, the particles will exert the same pressure on all the walls of the container. The particles arrangement of gas is the least packed compared to the other two states (Burns, 2003). Therefore, it has no definite shape and volume but has the ability to flow (Ebbing *et al.*, 2003). An example that used to represent this state is steam, H_2O, where it has the ability to flow but no fixed shape.

2.1.4 Mesomorphic State

Mesomorphic state is not included as the common states of matter. It is defined as a state of matter in which the degree of molecular order is intermediate between the perfect three-dimensional, long-range positional and orientational order found in solid crystals and the absence of long-range order found in isotropic liquids, gases and amorphous solids (Demus *et al.*, 1998).

2.2 Definitions

2.2.1 Liquid Crystal (LC)

Liquid crystal with a recommended symbol of LC is a substance that exhibit both phase of matter of the liquid phase and the solid phase. LC can flow like an ordinary liquid where it can adopt the shape of its container and has the molecules arranged as in the form of solid crystal. Liquid crystal is also known as mesophase or mesomorphic phase because of its intermediate nature (Sonin, 1995).

2.2.2 Mesophase

Mesophase is a phase that does not possess long-range positional ordered, but does has long-range orientational order. It is a phase occurring over a defined range of temperature, pressure or concentration within the mesomorphic state (Demus *et al.*, 1998).

2.3 Thermotropic Liqud Crystal (TLC)

Thermotropic liquid crystals (LCs) are substances that undergo phase transition when the temperature changes (Sonin, 1995). They exhibit types of LCs as a function of temperature. There are three main classes of TLC, mainly nematic, smectic, and chiral nematic (also known as cholesteric).

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