

PREPARATION OF ROD-SHAPED MOLECULE FOR LIQUID CRYSTALLINE
PROPERTIES

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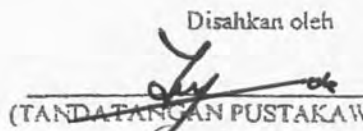
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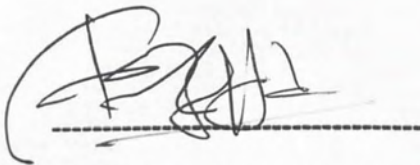
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DECLARATION

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



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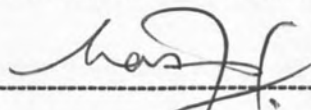
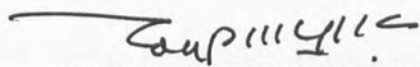
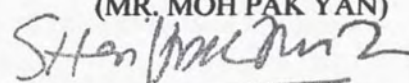
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ABSTRACT

A rod-shaped molecule of liquid crystal was synthesized. The molecule has a typical shape of rod liquid crystal molecule. The molecule has core units (benzene), terminal moieties (hexyl group) and linked by a nitro group, the linking group. To determine the functional groups presence in the molecule, FT-IR was used. Three final compounds were determined. The expected 4-(4-Hexyloxy-phenylazo)-benzoic acid did not show any absorbance between $1780-1650\text{cm}^{-1}$ showing that this is not an acid compound. H NMR spectrometer was used to determine the structure of the molecule. The H NMR spectra did not show a good series of signals due to impurities. The presence of water was detected at 4.5ppm with a very intense peak. The thermotropic properties of the final compound was finally analyzed using Differential Scanning Calorimetry (DSC). The compound crystallization temperature, or T_c was at 126.91°C . And the melting temperature was found at 102.18°C .



ABSTRAK

Mensintesis Molekul Kristal Cecair Berbentuk rod dan Mengkaji Sifat Termotropik Molekul

Molekul kristal cecair yang berbentuk rod disintesis. Proses mensintesis molekul ini banyak menggunakan persamaan-persamaan kimia organik. Molekul ini mempunyai struktur molekul yang biasa bagi kristal cecair berbentuk rod. Molekul ini mempunyai unit kerak (benzena), kumpulan heksil di bahagian terminal dan juga mempunyai unit penyambung iaitu kumpulan nitro. FT-IR digunakan untuk mengkaji tentang kehadiran kumpulan berfungsi di dalam molekul. Tiga hasil terakhir dianalisa menggunakan FT-IR. IR spektra untuk 4-(4-Heksiloksi-fenilazo)-asid benzoik tidak menunjukkan kehadiran kumpulan berfungsi asid karboksilik menunjukkan sebatian itu bukan sebatian asid yang dijangka. Spektrometer H NMR digunakan untuk mengkaji struktur hasil akhir. Spektra H NMR tidak menunjukkan signal spektra yang baik. Kehadiran molekul air dapat dikesan pada 4.5 ppm dengan peyerapan yang sangat kuat. Sifat-sifat termotropik sebatian akhir dianalisa menggunakan kalorimetri analisis pembezaan. Suhu mengkristal adalah pada 126.91⁰C manakala suhu pencairan adalah pada 102.18⁰C.



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SYMBOL LIST

ppm	part per million
$^{\circ}\text{C}$	degree celcius
g	gram
mJ	milijoule
g/J	gram per joule



CHAPTER 1

INTRODUCTION

1.1 Liquid crystal

In considering the liquid crystal state, it is important to know that it represents a discrete state of matter, lying between the solid and the liquid states and therefore possessing properties characterization of each. Liquid crystals are fluid like liquids, but at the same time still maintain the partial translational and/or orientational order; reminiscent of solids (Bruce, 1993). The consequences of having both fluidity and order mean that the fluids are anisotropic.

A number of different types of molecules form liquid crystal phases. The most common type of molecule that forms liquid crystal phases is a rod-shaped molecule. Such compounds are called calamitic liquid crystals and many different phases are available (Collings *et al.*, 1997).



1.2 Liquid crystal display

Organic molecules and liquid crystals (LC) are known to be favorable to photonic and nonlinear optical device applications because of their large optical nonlinearity and rapid optical response (Ozder *et al.*, 2005). Liquid crystal displays consist of a thin liquid crystal layer sandwiched in two glass plates. The liquid crystal layer in these devices is exclusively the calamitic liquid crystals composed of rod-shaped liquid crystal. The twisted nematic and supertwisted nematic display devices have dominated commercial displays since their invention.

The major disadvantage of these types of devices is the narrow and nonuniform viewing cone. The great emphasis toward higher quality of wide viewing angle LCDs has fostered numerous development efforts such as multidomain technique, the introduction of an optical compensator to reduce the amount of light linkage in the dark state, and also the application of electric field parallel to the plane of the substrates (Kumar *et al.*, 2001).

1.3 Types of liquid crystal

Organic liquid crystals can be divided into thermotropics and lyotropics. Thermotropics are further sub-divided into calamitic and discotic which are made-of rod-like and disk-like molecules, respectively (Nozaki *et al.*, 1996). They are called thermotropic liquid crystals because the liquid crystal phase is stable for a certain temperature interval.



Compared to the large number of calamitic molecules with a nematic phase, the number of disc-shaped molecules with a discotic nematic phase is low (Kumar *et al.*, 2001).

Lyotropic liquid crystals only form the liquid crystal phases when mixed with a solvent of some kind. The last types of molecules that form liquid crystal are polymers. Sections of the polymer must be rigid in order for it to be liquid crystalline (Collings *et al.*, 1997).

1.4 Significance of study

Liquid crystals are the fascinating condensed state of soft matter with unique electrical, optical, and mechanical properties. The anisotropic properties of liquid crystals make them very attractive materials, which can be found in many practical technological applications such as displays (Vasconcelos *et al.*, 2005). Also liquid crystals with azo linkage group, either low molar mass or polymeric in nature, have attracted tremendous attentions as a result of their unique photoswitchable properties induced by light (Le *et al.*, 2005). These materials are very interesting and promising for practical applications. It can be suitable for fast electro-optical displays like switches, guest host display and many others (Ozder *et al.*, 2005).



1.5 Scope of study

This study will be focused only on the rod-shape molecule, the type of molecule that forms calamitic liquid crystal. The properties of azo compounds are also to be considered since there is an azobenzene in the structure. After synthesizing the liquid crystal, the thermotropic phase transition behavior of the compounds will be examined using DSC to determine the phases of the liquid crystal.

1.6 Objectives of study

The objectives of this study are to synthesize a new rod-like liquid crystal molecule and then determine the phase transition behavior of the liquid crystal using differential scanning calorimetry.



CHAPTER 2

LITERATURE REVIEW

2.1 Rod-shape liquid crystal

Rod-shaped molecules containing rigid core have traditionally been regarded as the most suitable geometry to give rise to mesogenic behavior (Wan *et al.*, 1998). A typical schematic diagram describing the features necessary in a calamitic (rod-like) molecule is shown below in figure 2.1 (Bruce, 1993).

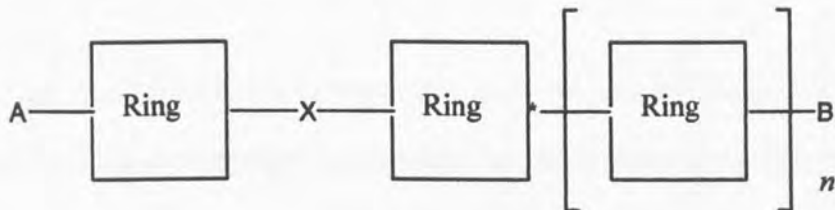


Figure 2.1 A typical feature of rod-shaped molecule of liquid crystal

Traditionally, the most common liquid crystal is based on aromatic core because of the relative ease of synthesis (Collings *et al.*, 1997). The following factors have been found affect the nematic-to-liquid transition temperature of liquid crystals: (a) nonpolarity of cores; (b) large amplitude motion of phenyl rings; (c) length of linking units; and (d) additional intermolecular interactions due to atomic charge of coordinated oxygen atom (Tsuji *et al.*, 2001).

The synthesis of molecular and supramolecular rodlike liquid crystals which exhibit conventional calamitic mesophases requires at least two aromatic, cycloaliphatic, or a combination of one aromatic and one cycloaliphatic groups interconnected either directly or through a suitable linking unit (Johansson *et al.*, 1997).

2.2 Calamitic Liquid Crystal phases

Liquid crystal phases may be classified on some basis. First, by the shape of the molecules which give rise to the phases. The shape may be rod like (calamitic) or disc-like (discotic). Also the method of inducing the mesophase either it is the action of temperature (thermotropic) or of solvent (lyotropic) and whether we are dealing with low- or high molar mass (polymer) (Bruce, 1993).

A large number of calamitic molecules show the nematic phase compared to the low number of disc-shaped molecules with a discotic nematic phase (Kumar *et al.*, 2002). It is the pattern of director fields and degree of orientational order that give rise to the characteristics texture of liquid crystals when viewed between crossed polars in a polarizing optical microscope (Coombs *et al.*, 1997 ; Brostow, 1998).

The nematic phase of calamitic liquid crystal is the simplest liquid crystal phase. In this phase, the molecule with no positional order maintain a preferred orientational order as they diffuse throughout the sample. Two other phases common to calamitic liquid crystals are the smectic A and smectic C. In addition to the



orientational order, there is positional order since the centers of mass are arranged in layers. If the director is perpendicular to the layers in which molecules are likely to be, then it is called a smectic A liquid crystal. If the director makes an angle other than 90° to these layers, it is a smectic C phase (Collings *et al.*, 1997; Bruce, 1993).

In general, all liquid crystals undergo phase transition from nematic to isotropic or from smectic to isotropic directly or through a nematic phase (Kyu *et al.*, 1998).

2.3 Chain length

The longer the terminal chain, the lower the melting points and the wider the liquid-crystalline phases (Wan *et al.*, 1998). The stability of mesophase was found to be controlled by the alkyl length (n). The compound with long alkyl chain length exhibits enantiotropic mesophase which is thermodynamically stable. On the other hand, compounds with short chain length exhibits monotropic mesophase which has unstable behavior (Abbasi *et al.*, 2006).



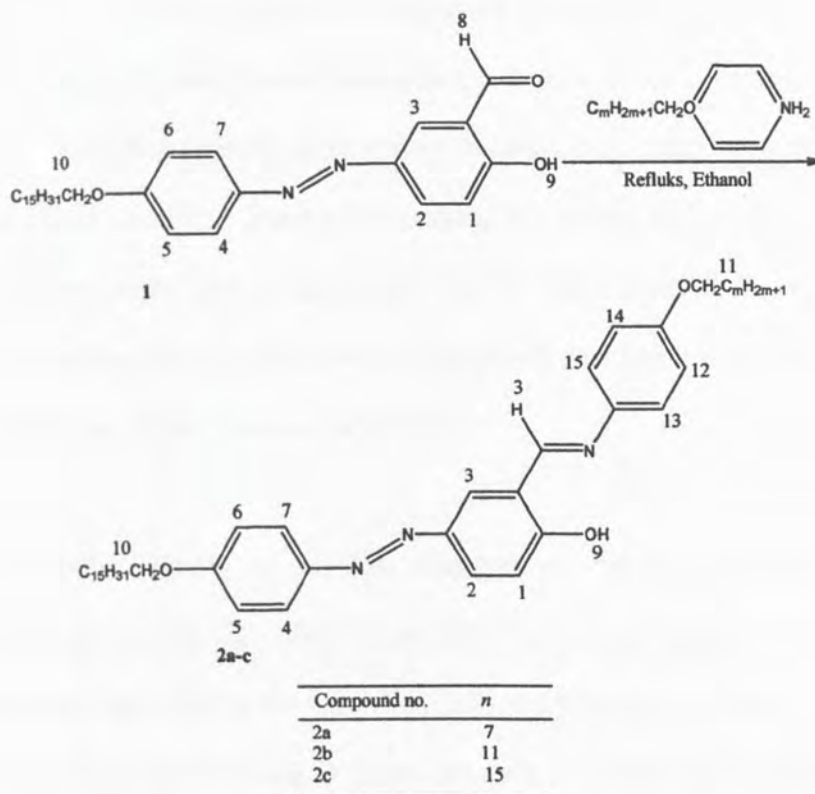


Figure 2.2 A series of Schiff bases 5-((4-nhexadecyloxyphenyl)azo)-N-(4-nalkoxyphenyl) salicylaldehyde (nalkoxy=octyloxy, dodecyloxy, hexadecyloxy)

Table 2.1 Transition temperature and enthalpy changes of compounds observed

Compound	Transition ^a	T ^b /°C	ΔH ^b /KJ mol ⁻¹
1	K ₁ -K ₂	84.2	1.3
	K ₂ -K ₃	101.9	2.8
	K ₃ -K ₁	122.0	38.2
2a	K ₁ -K ₂	90.1	4.2
	K ₂ -I	115.1	34.7
	(I-S _A) ^c	113.2	1.8
2b	K ₂ -K ₁	92.5	3.8
	K ₂ -I	112.2	35.2
	(I-S _A) ^c	109.7	2.0
2c	K ₁ -S _A	109.1	32.4
	S _A -I	119.3	2.3

^a K : crystal, N : nematic, I : isotropic liquid crystal

^b Data obtained from first DSC cycle

^c monotropic transition

Figure 2.2 shows a series of compounds synthesized using variety of alkyl chain. The transition temperatures and enthalpy change of compounds are shown in Table 2.1. 5-((4-nhexadecyloxyphenyl)azo)-N-(4-phenyl) salicylaldimine did not show any liquid crystalline character on heating or cooling. In the heating cycle, the compound was clearly melted to isotropic liquid. Under examination by polarizing optical microscopy in the cooling scan, the compound was found to crystallize directly from the isotropic liquid (Abbasi *et al.*, 2006).

In the first heating on the DSC measurement, the compound showed three endothermic peaks at 84.2⁰C, 101.9⁰C and 122.0⁰C. The peak at 122.0⁰C is attributed to melting, and other peaks are related to solid-solid phase transitions. The melting peak is narrow and the enthalpy of fusion amounts to 38.2kJ mol⁻¹ which shows the presence of a perfect crystalline state (Abbasi *et al.*, 2006).

Two compounds of 5-((4-nhexadecyloxyphenyl)azo)-N-(4-oxyloxyphenyl) salicylaldimine and 5-((4-nhexadecyloxyphenyl)azo)-N-(4-dodecycloxyphenyl) salicylaldimine show a monotropic liquid crystalline behavior on cooling from the isotropic liquid. This mesophase is stable until the compounds start to crystallize at 100⁰C and 97.2⁰C respectively. The enthalpy changes for 5-((4-nhexadecyloxyphenyl)azo)-N-(4-oxyloxyphenyl) salicylaldimine is 4.2kJ mol⁻¹ and 3.8kJ mol⁻¹ is the enthalpy changes for 5-((4-nhexadecyloxyphenyl)azo)-N-(4-dodecycloxyphenyl) salicylaldimine observed on cooling from isotropic liquid are in agreement with the formation of mesosphere (Abbasi *et al.*, 2006).



5-((4-nhexadecyloxyphenyl)azo)-N-(4-hexadecyloxyphenyl)salicylaldimine shows an enantiotropic liquid crystalline phase behavior. The polarizing microscopy study showed liquid crystalline character on heating and cooling from the isotropic liquid. The texture of its mesophase is similar to those of 5-((4-nhexadecyloxyphenyl)azo)-N-(4-oxyloxyphenyl) salicylaldimine and 5-((4-nhexadecyloxyphenyl)azo)-N-(4-dodecycloxyphenyl) salicylaldimine.

From the DSC thermogram, the mesomorphic behavior was confirmed. When the sample was heated, two endothermic peaks occurred at 109.1⁰C and 119.3⁰C due to crystal to mesophase and mesophase to isotropic liquid were observed. On cooling from the isotropic liquid, the mesophase was formed at 117.2⁰C and crystallized at 105.3⁰C.

On the bases of optical observations and DSC data, they concluded all three compounds of 5 - ((4 - nhexadecyloxyphenyl) azo) – N - (4 – oxyloxyphenyl) salicylaldimine, 5 - ((4 – nhexadecyloxyphenyl) azo) – N - (4 – dodecycloxyphenyl) salicylaldimine and 5 - ((4 – nhexadecyloxyphenyl) azo) – N - (4 – hexadecyloxyphenyl) salicylaldimine exhibit a smectic A mesophase (Abbasi *et al.*, 2006) .

2.4 Intermolecular hydrogen bonding

Many ring-substituted aromatic carboxylic acids form thermotropic liquid crystalline phases as a result of their ability to exist as stable hydrogen bonded dimmers. A stable calamitic liquid crystal phases with lateral intermolecular hydrogen bonding has been



established. The designed molecule has “anchoring” and “spinning” parts. The liquid crystalline compounds consisting of the spinning and anchoring parts could generate stable mesophases effectively with lateral intermolecular hydrogen. Figure 2.3 shows the molecular design and molecular organization generated by intermolecular hydrogen bonding (Kajitani *et al.*, 2004).

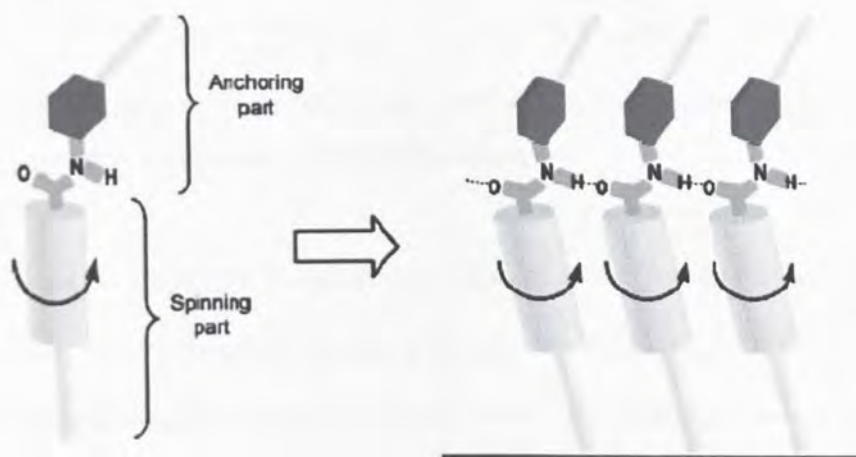


Figure 2.3 Molecular design and molecular organization generated by intermolecular hydrogen bonding

In the smectic phases, spinning of the anchoring part is strongly suppressed by its *m*-alkoxy chain to stabilize the lateral intermolecular hydrogen bonding, while the spinning part rotates independently to stabilize the liquid-crystal phase. Thus, it was initially expected that the molecules maintained the intermolecular hydrogen bonding even in the mesophase bonding (Brostow, 1998).

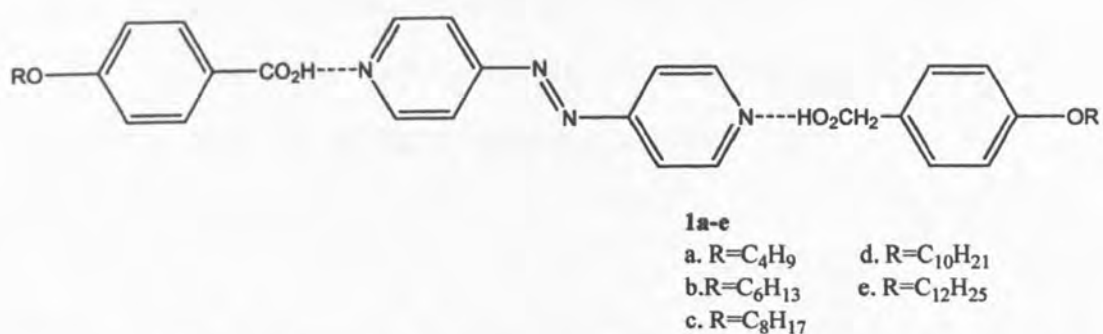


Figure 2.4 Hydrogen bond bind together 4,4'-azabipyridine (ABP) and 4-alkoxybenzoic acids forming a phase of liquid crystal

Figure 2.4 shows the hydrogen bond bind together 4,4'-azabipyridine (ABP) and 4- alkyloxybenzoic acids forming a phase of liquid crystal. To investigate the intermolecular hydrogen bonding in the mesophase, the temperature-variable FT-IR spectra was measured. The typical wavenumber of N-H stretching vibrations of amides in the crystal state is around 3350 cm⁻¹ and that in the isotropic liquid phase is around 3400 cm⁻¹.¹⁰ The N-H wavenumber measured at 170 °C was 3382 cm⁻¹ in the smectic C phase. It increased to 3387 cm⁻¹ during the transition from the smectic C to the smectic A phase, while it slightly increased during the transition from the smectic A to the isotropic phase. These shifts indicated that the intermolecular hydrogen bonding interacted in the smectic C phase, while it was absent or very weak in the smectic A phase (Kajitani *et al*, 2004).

It has been recognized that through noncovalent interactions between molecules possessing the desired complimentary structural elements, liquid crystalline materials can be obtained. Thus, hydrogen bond, ionic, charge transfer, and ion-dipolar interactions between donor-acceptor moieties have been recognized to generate

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