SYNTHESIS AND CHARACTERIZATION OF ROD-SHAPED LIQUID CRYSTALS WITH AZOBOZENZENE AS MESOGENIC CORES

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ABSTRACT

Rod shaped liquid crystals is probably the most important type of liquid crystals nowadays. This is because, rod shaped liquid crystals serve as the cores of the most complicated liquid crystals which means that it can be used to synthesized other types of liquid crystals. In this study four types of organic reactions were conducted in order to obtain the target liquid crystals molecule. The first reaction is the Diazonium coupling reaction. The starting material which is 4-Aminoacetophenone was coupled with phenol to yield compound 1 which is 4-(4-Hydroxyphenylazo) acetophenone. The second reaction is the Williamson’s ether synthesis reaction. In this reaction, compound 1 was reacted with Ethyl-6-bromohexanoate to produce compound 2 which is 6-[4-(4-Acetylphenylazo) phenoxy] hexanoate. The third reaction is the alkaline hydrolysis reaction. In this reaction, compound 2 was reacted with potassium hydroxide to yield 6-[4-(4-Acetylphenylazo) phenoxy] hexanoic acid, compound 3. The last reaction done was esterification reaction. Compound 3 was reacted with resorcinol in the presence of DCC and DMAP to yield the target molecule which is {4-(4-Acetylphenylazo) phenoxy} pentyl} benzoate, compound 4. The percentage yield of the target compound obtained was calculated to be 51.02%. The functional group of the intermediates and the target compound was determined using FT-IR. The phase transition temperature and phase transition enthalpy of the target compound was determined using DSC. The Phase transition temperatures are 123.88 °C for endothermic and 99.97 °C for exothermic. From the DSC thermogram, it can be observed that the target compound has mesophase characteristic which means that the target compound has liquid crystals phase.
SINTESIS DAN PENCIRIAN HABLUR CECAIR BERBENTUK ROD DENGAN AZOBENZENA SEBAGAI TERAS MESOGENIK.

ABSTRAK

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LIST OF SYMBOLS

N  Nematic phase.
Sm  Smectic phase.
SmA  Smectic A phase.
SmB  Smectic B phase.
SmC  Smectic C phase.
T  Temperature.
Tg  Glass transition temperature.
H  Enthalpy
%  Percentage.
°C  Celcius.
g  Gram.
ml  Millimeter.
Mw  Molecular weight.
Mmol  Milimol
TLC  Thermotropic liquid crystals.
MBBA  n-(p-methoxybenzylidene)-p-butyllanilene.
DCC  Dichloroethylcarbodiimide.
DMAP  4-\(N,N\)-dimethylaminopyradine.
P  Pitch.
CHAPTER 1

INTRODUCTION

1.1 Introduction to Liquid Crystals

Liquid crystal science is a science of human knowledge that was discovered and started to bloom at the end of the 19th century. An Austrian botanist, Friedrich Reinitzer accidentally discovered liquid crystal when he was doing microscopic observation about the unusual thermal behavior of molten sample of cholesterol benzoate. This first observation of optical anisotropies phenomena in organic compound opened a new and fascinating class of soft materials (Ritter et al., 2006).

Liquid crystals are systems that have the ability to self organized due to mesogenic groups which show short and long range collective interaction among them. This is the origin of interesting liquid crystals properties which were exploited extensively in the early 70's, mostly in TN-LC technology (Ritter et al., 2006). The molecular self-organization and self assembly at a nanometer and micrometer scale are useful strategies in the development of novel function materials and are currently exciting areas of intense research. Liquid crystalline materials are known to be able to self-assemble by nature and can offer a very elegant and effective way of controlling and tuning the physical properties that ultimately define the self-organization and self-assembly process (C.Zhang et al., 2008).
1.2 Application of liquid Crystals.

Nowadays, liquid crystals have been most extensively used as display materials. Some are applied as liquid crystals display for calculators, sentences display, word processors, portable notebook computers, speedometer, mobile phones, wave plates, polarizers and full-color TV display. Polymer liquid crystals (PLC) for image storage materials, has also been reported by several groups, etc (Silong et al., 2001).

![Figure 1.1 Example of the usage of liquid crystals; display screen of Playstation Portable.](image)

Liquid crystals technology has dominated the display market due to their compactness, low weight, low-voltage operation, and lower power consumption. In our technological society, liquid crystal displays gives an interface between human and machines and are expected to play an even bigger role in the future as the need of displaying information grows.
The urgency to develop liquid crystals materials, batteries, polarizers, electrodes, semiconductors, compensation films spacers and etc, has been the most essential driving force behind liquid crystals research.

The liquid crystals science growth was dependent on the parallel progress and development of the other field of science namely synthetic organic chemistry, electronics, physics and device engineering (Ritter et al., 2006).
1.3 OBJECTIVES OF THE STUDY

The objectives of the study are:

a. to synthesize rod shaped liquid crystals containing azobenzene as mesogenic cores.
b. to determine the mesophase properties of rod-shaped liquid crystals using Differential Scanning Calorimeter (DSC).
d. to identify the functional group of the intermediates and target compound using Fourier Transform Infra Red (FTIR)
1.4 Scope of the Study.

The study was focused on the synthesis of rod shaped liquid crystals having azobenzene mesogenic cores and the characterization of its mesophase properties using Differential Scanning Calorimeter (DSC). It also includes the functional groups identification of the target compound and its intermediates by using Fourier-Transform Infra Red Spectroscopy (FTIR).
CHAPTER 2

LITERATURE REVIEW

2.1 LIQUID CRYSTALS.

Liquid crystals are substances that exhibit a phase of matter that has properties between those of conventional liquid and those of solid crystals. Liquid crystal can be divided into a few phases which are thermotropic, lyotropic and metallotropic phase (Munk and Aminabhavi, 2001) but the most important and most abundant is the thermotrophic phase of liquid crystals.

2.2 THERMOTROPIC LIQUID CRYSTALS, TLC.

The thermotropic phase of liquid crystals appears as a definite region on the phase diagram but is not however thought of as fourth state (the other three are solid, liquid and gas). Thermotropic phase is viewed as a transition between the two states solid and liquid and it is a state in which the molecular order exhibits a size range similar to that of a crystal with the viscosity varying from that of oil to water. The terms mesophase and the mesomorphic state can also be used to define this state. A mesogen is the molecule or a part of it, which gives rise to a mesophase (Guittard et al., 1999).

The mesophase of thermotropic liquid crystals are thermodynamically stable but only partially ordered phases. Each mesophase can be described by its degree of order. If the mesophase have orientational order only, it is called nematic (N), if it has both orientational order and positional order; it is called smectic (Sm) (Silong et al., 2009).

Thermotropic liquid crystals are formed either by cooling isotropic liquid below the point of clarification (clearing point) or by heating solid liquid crystals above the melting point.
These thermotropic liquid crystals can be classified into two types which are enantiotropic and monotropic.

Enantiotropic and monotropic liquid crystals can be reached by both melting and cooling. Enantotropic. If the formation is reversible, the liquid crystals are considered as enantotropic and if the process is irreversible (the liquid crystal phase can only be reached from one direction in thermal cycle), it is considered as monotropic. In a thermotropic mesophase, varying degrees of positional order are lost, giving fluidity, while orientational (supermolecular) order is retain, giving the anisotropy. The consequence of this anisotropy is that the mesophases can have two (or even three) different refractive indices; magnetic susceptibilities and electric permittivities. As a result, some thermotropic molecules can be oriented by applied electric and magnetic fields. This is the basis of their application. Thermotropic then can further be subdivided into calamatic and discotic (Guittard et al., 1999).

In a calamatic liquid crystal, the mesogen (the fundamental unit of a liquid crystal that induces structural order in the crystals) is a rod-like structure composed of two or more aromatic and aliphatic ring connected in one direction. In a discotic liquid crystal, the mesogen is the flat-shaped aromatic core that makes molecules stack in one direction.

Figure 2.1 An example of calamatic liquid crystal.
2.3 Rod-shaped (calamatic) Liquid Crystals

Most of the thermotropic liquid crystals are found to be calamitic structurally. A calamitic mesogen consist of a core, terminal chains and lateral substituents. The core of rod-shaped liquid crystals actually provides rigidity which is required for anisotropy. On the other hand, the terminal chains of the rod-shaped liquid crystals provide flexibility to stabilize the molecular alignment within the mesophase.

The core is usually a linearly linked aromatic ring system and the rings can be directly linked or they may be joined by a linking group. The terminal chain of rod-shaped liquid crystals are either straight alkyl or alkoxy chain, however one terminal unit is often a polar substituent. These calamitic molecules form both nematic and smectic mesophases depending upon the types of substituents and their combinations (Kılıç & Cınar, 2007).
Figure 2.3: Typical structure of a rod-shaped liquid crystal.

Optically, rod-shaped liquid crystals exhibit uniaxial positive birefringence. Birefringence or also known as double refraction is the decomposition of one ray of light into two rays which is ordinary ray and extraordinary ray. When the ray of light passes through material, such as calcite crystals or boron nitride, it will disperse into two rays depending on the polarization of the light. This effect can only occur if the structure of the materials is anisotropic (Wing, 2008).

The rod-shaped liquid crystals can be divided into three main classes of mesophases which are nematic, chiral nematic and smectic.
REFERENCES


