# SYNTHESIS OF V-SHAPED LIQUID CRYSTALS HAVING NITRO GROUPS AS TERMINAL

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#### ABSTRACT

The main objectives of the study were to synthesized V-shaped liquid crystals materials with mesogenic properties. 4-Nitroaniline was used as a starting material for the synthesis. The peripheral cores were prepared from 4-Nitroaniline in which the amino group was diazotized by sodium nitrite and the obtained diazonium salt was coupled with phenol to yield 4-(4-nitrophenylazo)phenol. The obtained compound was used for the Williamson ether synthesis to obtained 1-bromo-4-(4nitrophenylazo)phenoxyhexane. The target molecule 1.2-bis-[{4-(4nitrophenylazo)phenoxy}hexyloxy]benzene prepared by 1-bromo-4-(4was nitrophenylazo)phenoxyhexane was used to dialkylate catechol in the presence of potassium carbonate and potassium iodide. Melting point of the final compound was in the range between 68 °C to 74 °C. From the obtained IR spectra, the functional groups in both compounds, 1-bromo-4-(4-nitrophenylazo)phenoxyhexane and 1,2-bis-[{4-(4-nitrophenylazo)phenoxy}hexyloxy]benzene was compared. The spectrum showed that the synthesized compound had all the functional groups as in the projected molecular structure. The mesomorphic properties of final compound were investigated by differential scanning calorimetry (DSC). However, from the DSC study, the compound did not show liquid crystal phase.



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#### ABSTRAK

Objektif utama disertasi ini adalah untuk mensintesis hablur berbentuk V yang menunjukkan sifat mesogenik. Bahan permulaan yang digunakan untuk sintesis ini ialah 4-Nitrofenilamina. Langkah permulaan bagi sintesis ini melibatkan tindak balas penggabungan garam diazonium dengan fenol untuk menghasilkan 4-(4nitrofenilazo)fenol. Seterusnya, bahan yang dihasilkan menjalani sintesis eter Williamson dan menghasilkan 1-bromo-4-(4-nitrophenylazo)phenoxyhexane. Seterusnya, bertindak balas dengan catechol dengan kehadiran kalium karbonat dan kalium iodida untuk menghasilkan 1.2-bis-[{4-(4nitrophenylazo)phenoxy}hexyloxy]benzene sebagai hasil terakhir dengan julat takat didih di antara 68 °C – 74 °C. Melalui perbandingan kedua-dua spektum inframerah 1-bromo-4-(4-nitrophenylazo)phenoxyhexane bagi dan 1,2-bis-[4-(4nitrophenylazo)phenoxyhexyloxy]benzene, didapati bahawa bahan yang disintesiskan mempunyai kesemua jenis kumpulan berfungsi seperti yang dijangkakan. Sifat mesomofik hasil itu dikaji dengan menggunakan differential scanning calorimetry (DSC). Namun, didapati bahawa hasil tersebut tidak menunjukkan mesophase.



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## LIST OF SYMBOLS

$S_A$	Smectic A phase
$S_{\mathrm{B}}$	Smectic B phase
S <sub>B(cry)</sub>	Smectic B crystal phase
$\mathbf{S}_{\mathrm{C}}$	Smectic C phase
Sc*	chiral Smectic C phase
$S_{L}$	Smectic L phase
$\mathbf{S}_{\mathrm{F}}$	Smectic F phase
$\mathbf{S}_{\mathbf{I}}$	Smectic I phase
SE	Smectic E phase
$\mathbf{S}_{\mathrm{G}}$	Smectic G phase
$S_{\mathrm{H}}$	Smectic H phase
N	Nematic phase
N*	chiral nematic phase



#### **CHAPTER 1**

#### INTRODUCTION

#### 1.1 Introduction

Liquid crystal is a substance that flow like a liquid but has some order in its arrangement of molecules. There are a few of type of thermotropic liquid crystals, such as rod-like molecules, disc-shaped molecules, bent-shaped molecules, V-shaped molecules, banana-shaped molecules and so on.

Bent-core V-shaped is also known as fused twins or U-shaped. The first synthesis of bent-core molecules was discovered by Vorlander and Apel (Yelamaggad *et al.*, 2004). It can be classified into two categories, like V-shaped and banana-shaped (Yelamaggad *et al.*, 2004). Yelamaggad *et al.* (2004) has reported the first bent-core V-shaped synthesized by Vorlander and Apel is 1,2-phenylene bis[4-(ethoxyphenylazoxy)benzoate] which show a nematic phase. Bent core V-shaped molecules are formed two mesogenic segments attached covalently to a benzene ring in the 1,2-positions (Yelamaggad *et al.*, 2004). Prasad (2001a) reported a number of azobenzene-based bent-core V-shaped molecules exhibit nematic, smectic A, and



crystal E phases. V-shaped liquid crystals exhibits mesophases are used in many device applications. A study of liquid crystals composed of bent-shaped molecules reveals that compounds with azo linkages have surprising advantages. Azo compounds are thermally very stable and bring in a new dimension to photochromism (Prasad, 2001a, 2001b).

Liquid crystals (LCs) with rod-like molecules shows nematic and/or smectic mesophases, while liquid crystals with flat disc-shaped molecules exhibit nematic and/or columnar mesophases (Yelamaggad *et al.*, 2004). The most ordered phase is the smectic phase, which molecules are aligned parallel to one another in regular layer (Whittaker *et al.*, 2001). Besides that, the smectic phase where found at lower temperature than the nematic which form well-defined layers that can slide over one another like soap. Thus, the smectic is positional ordered along one direction. The molecules are oriented along the layer normal in the Smectic A phase, while, in the Smectic C phase, they are tilted away from the layer normal. In the nematic phase, the simplest LC, the molecules are aligned parallel to one another, but are no longer arranged in layers (Whittaker *et al.*, 2001).

The cholesteric phase is characterized by ordered layers in which the molecules are aligned with respect to one another within each layer, but the layers are no longer ordered with respect to one another. In all these phases, the material flows like a liquid, but shows optical properties akin to those of a solid crystal. The typical operating range for liquid crystals is between -5° C and 70° C. Below this range, the material is true crystalline solid, and above this range, all order is lost and the material behaves as an isotropic liquid (Whittaker *et al.*, 2001). The common application of



liquid crystal is liquid crystal displays (LCDs), dyes, and liquid crystal thermometer and so on.

#### 1.2 RESEARCH OBJECTIVES

- To synthesis a V-shaped liquid crystal material which exhibit mesogenic properties.
- To analyze the structure of the liquid crystal materials using Fourier Transform Infra Red Spectroscopy (FTIR) and Nuclear Magnetic Resonance Spectroscopy (NMR).
- To determine the phase transition using Differential Scanning Calorimetry (DSC).

#### 1.3 SCOPE OF THE STUDY

The synthesis focuses only on the organic synthesis of the V-shaped liquid crystals and the determination of liquid crystals properties. The physical properties of liquid crystals can be determined by using FTIR, NMR and DSC.



#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Liquid Crystals

A phase of matter whose order is intermediate between that of a liquid and that of crystals are known as liquid crystals. Generally, there are several common characteristics of liquid crystal materials, such as a rod-like molecular structure, rigidness of the long axis, and strong dipoles and or easily polarizable substituents.

The tendency of the molecules (mesogens) to pint along a common axis is the distinguishing characteristic of the liquid crystalline state which is known as director. This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state.



Singh (2002) reported that the molecules in a crystal are ordered whereas in liquid they are not. The following possibilities exist at the melting point when a molecular material composed of anisotropic molecules is heated from the solid phase (Figure 2.1):

a) Both types of order (positional and orientational) disappear simultaneously and the resulting phase will be an "isotropic liquid (IL)" possessing  $T(3) \times O(3)$ symmetry.



a. Crystalline solid



b. Isotropic liquid

â





d. Liquid crystal

Figure 2.1 Schematic arrangements of molecules in various phases (Singh, 2002).

b) Only orientational order disappears leaving the positional order intact and the corresponding phase is called a "plastic crystal (PC)". The materials in this phase



are exhibit rotator phases; the molecules freely rotate along one or more of their molecules axes, whereas their centers of mass are fixed in a lattice.

c) The positional order either fully or partially disappears while some degree of orientational order is maintained. Thus, the phase is called as "liquid crystal (LC)". Another term in use is mesophase (intermediate phase) or mesomorphic phase. In this phase, the unique axes of the molecules remain, on average, parallel to each other leading to a preferred direction in space. To describe the local direction of alignment by a unit vector  $\hat{\mathbf{n}}$ , the director, this gives at each point in a sample the direction of preferred axis. A compound that exhibits a mesophase is called a mesogenic compound (Singh, 2002).

#### 2.2 General Types of Liquid Crystals

The liquid crystals can be grouped into several types according to their geometrical structure of the mesogenic molecules. The liquid crystals that formed from the rod-shapes molecules (one axis is much longer than the other two) are called "calamitics". The mesophases derived from the disc-like molecules (one molecular axis is much shorter than the other two) are known as "discotics" (Ericksen, 1970). Intermediate between rod-like and disc-like molecules are the lath-like species (Singh, 2002).



The liquid crystals are categorized in two different ways; thermotropic liquid crystals, shows mesophases by thermally and lyotropic liquid crystals, exhibits mesophases by the influence of solvents (Demus and Richter, 1978).

Nematic and smectic mesophases is the main subdivision of calamitics thermotropic liquid crystals. There are many types of smectic phases, which indicated as  $S_A$ ,  $S_B$ ,  $S_C$ , and  $S_L$ , which differ in the orientation of the preferred direction of the molecules with the respect to the layer normal and the distribution of the centers of the molecules within the layer (Singh, 2002).

## 2.3 Physical Properties of Liquid Crystals

The physical properties of liquid crystals can be distinguished into two categories, scalar and nonscalar properties. The thermodynamics transition parameters are called scalar properties, such as transition temperature, transition enthalpy, entropy changes, transition density, and fractional density changes, whereas, the most important nonscalar properties are the dielectric, diamagnetic, optical, elastic, and viscous coefficients (Singh, 2002).

Besides that, the liquid crystalline also can be characterized through their orientational, positional, and conformational orders. Orientational order refers to a measure of the tendency of the molecules to align along the director on a long-range basis, which is presents in all the liquid crystal phases and usually is the most important (Singh, 2002). The positional order is to characterize the various mesophases (nematic, smectic A,



smectic C, etc.) and also can be investigated by their textures or their X-ray diffraction patterns which allow a determination of the layer thickness. The conformational order is to measure how the rings, fractional groups and end chains within a molecule are oriented and arises because of the short-range intramolecular and intermolecular forces (Singh, 2002).

#### 2.4 Liquid Crystal Phases

The liquid crystal state is a distinct phase of matter observed between the crystalline (solid) and isotropic (liquid) states. There are many types of liquid crystal states, depending upon the amount of order in the material. Most thermotropic liquid crystals will have an isotropic phase at high temperature. That is, heating will eventually drive them into a conventional liquid phase characterized by random and isotropic molecular ordering (little to no long-range order), and fluid-like flow behavior.

Under other conditions (for instance, lower temperature), a liquid crystal might inhabit one or more phases with significant anisotropic orientational structure and longrange orientational order while still having an ability to flow. The orientational order may be quasicrystalline. This section will explain the phase behavior of liquid crystal materials.



#### 2.5 Thermotropic Liquid Crystals

Thermotropic transactions occur in most liquid crystals, and they are defined by the fact that the transitions to the liquid crystalline state are induced thermally. That is, one can arrive at the liquid crystalline state by raising the temperature of a solid and/or lowering the temperature of a liquid.

Thermotropic liquid crystals can be classified into two types: enantiotropic liquid crystals, which can be changed into the liquid crystal state from either lowering the temperature of a liquid or raising of the temperature of a solid, and monotropic liquid crystals, which can only be changed into the liquid crystal state from either an increase in the temperature of a solid or a decrease in the temperature of a liquid, but not both. In general, thermotropic mesophases occur because of anisotropic dispersion forces between the molecules and because of packing interactions.

#### 2.5.1 Nematic Phases

The word "nematic" is derived from Greek: *nematos*, thread-like (Murell *et al.*, 1994). The nematic liquid crystal phase is characterized by molecules that have no positional order but tend to point in the same direction (along the director). The nematic phase is essentially a one-dimensionally ordered elastic fluid in which the molecules are orientationally ordered (Goodby, 1998). The molecules in nematic phase (Figure 2.2) point vertically but are arranged with no particular order.



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