SYNTHESIS OF BENT-SHAPED LIQUID CRYSTALS CONTAINING NITRO AS TERMINAL GROUP

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ABSTRACT

The main objectives of the study were to synthesized bent-shaped liquid crystal that containing nitro as terminal groups. 4-nitroaniline was used as a starting material for the synthesis. The initial step of the synthesized was diazonium coupling reaction with phenol to obtain 4-(4-nitrophenylazo)phenol. The obtained compound was used for the Williamson ether synthesis to obtain 1-bromo-4-(4-nitrophenylazo)phenoxyhexane. The targeted molecule 1,3-bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene was prepared by 1-bromo-4-(4-nitrophenylazo)phenoxyhexane was used to resorcinol in the present of potassium carbonate and potassium iodide.The melting point of the final compound was in the range between 75°C to 80°C. From the obtained IR spectra, the functional groups in both compounds, 1-bromo-4-(4-nitrophenylazo)phenoxyhexane and 1,3-bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene were compared. It showed that the synthesized compound had all the functional groups as in the projected molecular structure except a band of hydroxyl group in the 1,3-bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene .
The mesomorphic properties of the final compound were investigated by differential scanning calorimetry (DSC). It showed the enthalpy changes of transition were 67.7076 Jg^{-1} when heating and -44.2609 Jg^{-1} when cooling.

PROSES SINTESIS BAGI BENT-SHAPED LIQUID CRYSTAL MENGANDUNGI NITRO SEBAGAI TERMINAL

ABSTRAK

Objektif tesis ini adalah untuk menyintesiskan bent-shaped liquid crystals di mana mengandungi kumpulan nitro sebagai terminal. Pengunaan 4-Nitroaniline untuk memulakan sintesis ini. 4-Nitroaniline ini melalui tindak balas penduaan garam diazonium dengan fenol telah menghasilkan 4-(4-nitrophenylazo)phenol. Bahan hasilan ini akan digunakan untuk menjalankan tindak balas eter Williamson dengan 1,6-dibromohexane untuk mendapatkan 1-Bromo-4-(4-nitrophenylazo)phenoxyhexane. Kemudian, 1-Bromo-4-(4-nitrophenylazo)phenoxyhexane menjalankan tindak balas eter Williamson sekali lagi dengan resorcinol. Akhirnya, 1,3-Bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene didapati dan sebagai hasilan terakhir dengan takat lebur pada sekitar 75°C - 80 °C. Selain itu, dengan adanya FT-IR spectrum bagi 1-Bromo-4-(4-nitrophenylazo)phenoxyhexane dan 1,3-Bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene telah memudahkan perbandingan kumpulan berfungsi antara satu sama lain. Dengan adanya Differential Scanning Calorimetry, takat lebur dan takat didih bagi compound 1,3-Bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene dapat diketahui iaitu 67.7076 Jg^{-1} *semasa pemanasan dan -44.2609* Jg^{-1} *semasa penyejukan.*

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CHAPTER 1

INTRODUCTION

1.1 Discovery of Liquid Crystals

The study of liquid crystal began in 1888, Fredrick Reinitzer, an Austrian botanist discovered that an organic compound called cholesteryl benzoate had interesting and unusual properties. When the substances heated, it melted at 145°C to form a milky liquid and at 179°C milky liquid suddenly become clear. Reinitzer's work represents the first systematic report of what now we called liquid crystals. A liquid crystal mesophase is a state of matter intermediate between a solid and liquid (Brown *et al*., 1994).

There are few types of classification for liquid crystal mesogen, namely calamitic mesogen, discotics mesogens, pyramidic mesogens, and the bent-core mesogen that also known as banana shaped mesogen depending on the shape of the mesogen (Collyer, 1992). Nowadays, liquid crystals composed of bent-shaped are very interesting subject which have recently attracted much attention. In bent-shaped liquid crystals consisting of azo linkages and exhibited different type of smectic phases such as smectic A, smectic B, and smectic C (Prasad, 2000).

To obtain liquid crystals in this synthesis, there were several process had been undergoes included diazo coupling reaction and Willamson Ether Synthesis. In the diazo coupling reaction, aromatic amines reacted with nitrous acid to form diazonium salts. On the other hand in Williamson Ether Synthesis, a phenoxide ions acts as a nucleophile reacting with a primary alkyl halide in bimolecular nucleophilic substitution (S_N2) reaction (Zanger and Mckee, 1995).

An electro-optic display industry depends on liquid crystalline materials and their properties for TV screens, watch and calculator displays and light-shutters. These uses of liquid crystals result from the fact that the weak intermolecular forces that hold the molecules together in a liquid crystal are easily affected by changes in temperatures, pressure and electromagnetic field (Brown *et al.*, 1994).

1.2 Research Objectives

- To synthesize a bent-shaped liquid crystals containing nitro group as terminal.
- To determine phase transition temperatures of synthesized materials using differential scanning calorimetry (DSC).
- To examine chemical structures of the bent-shaped liquid crystals by ^{1}H NMR.

- To determine the functional groups of the bent-shaped liquid crystals using Fourier Transform Infra Red Spectroscope (FTIR).

1.3 Scope of Research

The project focused only on the organic synthesis of liquid crystals and the determination of liquid crystal properties.

CHAPTER 2

LITERATURE REVIEW

2.1 Definition Liquid Crystals

A liquid is a collection of molecules not positioned and oriented in space in any regular manner. A crystal is a collection of molecules or atoms positioned and oriented in a space in a regular and repeated manner. In liquid crystals molecule exhibit orientation with respect to each other and in some type of liquid crystals, exhibit position with respect to each other (Hecke, 1997).

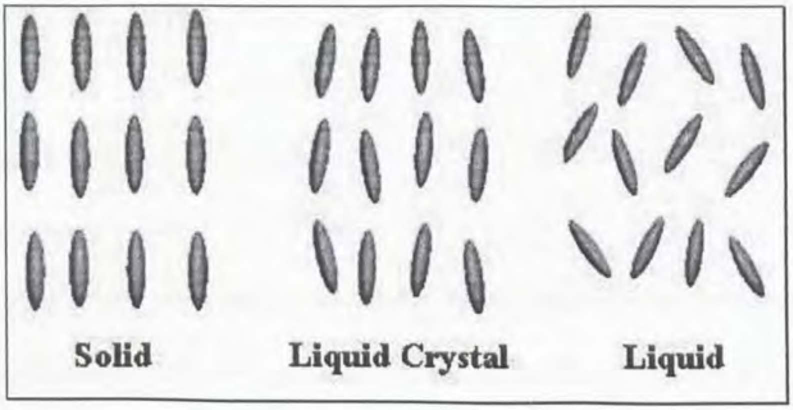

Figure 2.1 Diagram of average alignment of the molecules for each phase (Anon, 2006).

Strictly, the liquid crystal is made up of number of orientationally ordered phases that occur between the breakdown of positioned ordering of the molecules in a solid and the formation of the amorphous liquid. The breakdown in ordering on passing from a crystal to a liquid can be achieved other by changing the temperature of the material or by dissolving in a liquid (Goodby, 1995).

In contrast, crystalline solids have a high degree of order among their particles, the properties of a crystal do depend on direction, so a crystal is anisotropic. Liquid crystals are also anisotropic in that several physical properties, including the electrical and optical properties that lead to their most important applications, differ with direction through the phase (Silberberg, 2000). This anisotropy can achieve in two ways: either the molecules have one molecular axis, which is very different from the other ones, or the molecules possess part with very different solubility. The liquid crystal obtained by the first method are called "thermotropics" where as those obtained by the second are "lyotropic" (Demus and Richter, 1978).

2.2 Thermotropic Liquid Crystals

Thermotropic mesophase are indefinitely stable at defined temperatures and pressures. Moreover, a thermotropic liquid- crystalline material exhibit reversible phase transitions at well-defined temperature. The way, or sequence, in which thermotropic transition occur is defined in the following ways. The liquid crystal to isotropic liquid transition is called to the clearing or isotropization point, and this transition, like those between liquid crystal phases, is essentially reversible and occurs with little hysteresis in temperature (Goodby, 1995).

The melting point of a material is usually a constant, but the recrystallization process can be subject to supercooling. Mesophases formed on the first heating cycle of a material are thermodynamically stable are called enantiotropic phases, whereas phases that are formed below the melt point on cooling cycles, and are revealed because of the supercooling of the crystal state, are metastable and termed monotropic phases (Goodby, 1995).

Thermotropic means a change of phase with fluctuation of temperature. This happens when a solid crystalline is heated. Molecules will leave their lattice sites when energy is provided but the intermolecular interaction are still strong enough to keep the molecules aligned with each other along their axis (Silberberg, 2000).

2.3 Characterization of Liquid Crystals Mesophase

2.3.1 Nematic Phase

The molecules of nematic liquid crystal closely resemble whose typical dimension is 5Å by 20Å. The nematic phase manifests itself when the interaction between neighboring molecules tends to make them parallel to one another, so as to induce a partial orientational order at the microscope scale. Nematic liquid crystal are completely free to flow, the positions in space of their molecules are free from any constraint (Virga, 1994). In nematic phase, the phase looks like a rectangular volume of the phase where the molecules lie in the general direction but theirs end are not aligned. Nematic phase is the phase with least orderly arranged mesogens of liquid crystal phase (Silberberg, 2000).

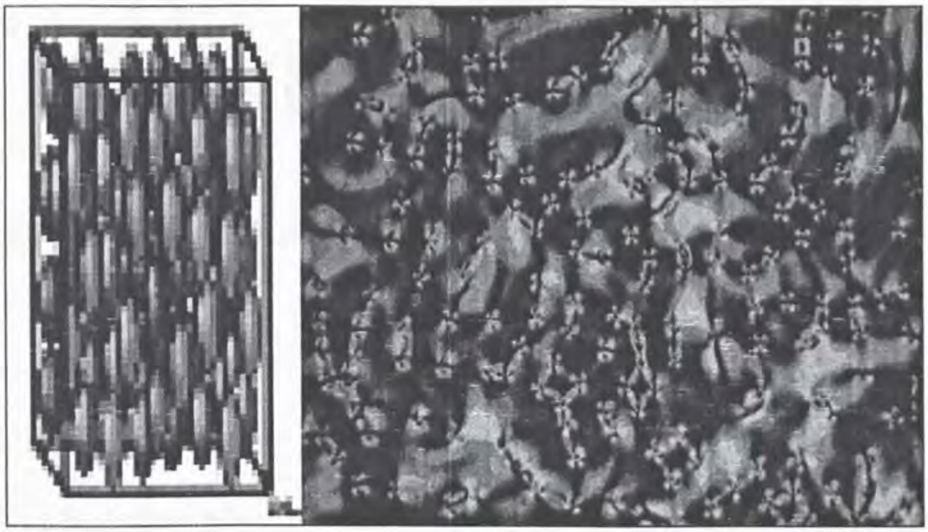

Figure 2.2 Diagram for the molecules point in nematic phase (Anon, 2006).

2.3.2 Smectic Phase

Smectic liquid crystals are essentially different from both nematics and cholesterics. Smectic liquid crystals exhibit a close interplay between positional and orientation ordering of molecules. The intermolecular forces are strong enough to favor preferred positioned of the molecules, besides preferred orientation of their axis. Such as feature gives the substances some stiffness and yet they are able to flow (Virga, 1994).

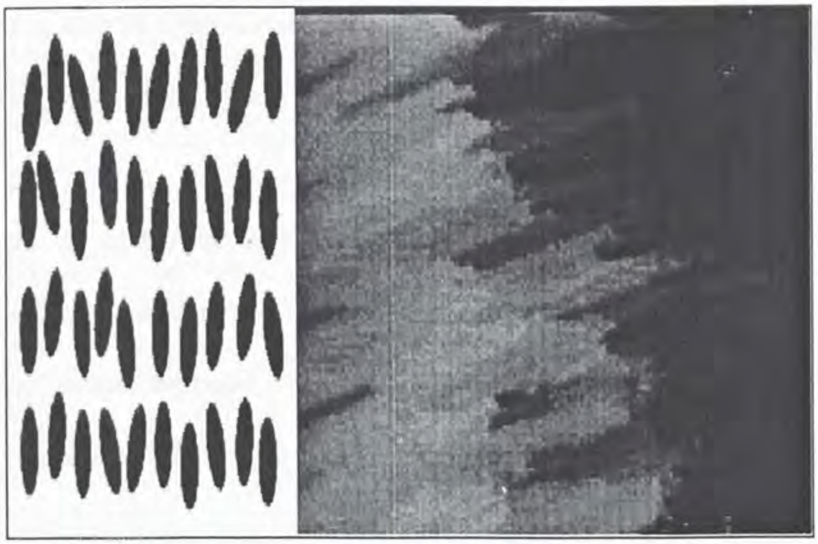

Figure 2.3 The smectic phase by using polarizing microscope (Anon, 2006).

a. Smectic A

Smectic A (S_A) phase where the molecules of each layer are randomly distributed, but their long axes tend to be aligned orthogonally to the layer (Virga, 1994). The mesogens in smectic A phase involve the parallel arrangement of the rod-like molecules, with their ends inline, forming layers with long-axis of the molecules that tends to be orthogonal to the layer planes. Molecules in the layers can rotate freely, with the absence of long-range regularity of packing of the centers of gravity of the mesogens in the planes of the smectic layers (Collyer, 1992).

This smectic A phase are therefore more liquid-like in nature, with the movement of molecules from one layer to another occurring frequently. Furthermore, the layers are able to slide over one another freely. The layer thickness is often less than the length of the molecules calculated from standard bond lengths and angles under the assumption of an all-trans confirmation (Collyer, 1992).

Smectic A phase is confirmed from the microscopic observation of the characteristic focal-conic texture in slides treated for planar orientation, and a dark field of view in slides treated for homeotropic orientation. When untreated slides are used, both the focal-conic and pseudoisotropic texture are observed (Yelamaggad *et al.*, 2004).

S_A phase is the less ordered smectic phase. When a compound exhibits smectic polymorphism, the S_A phase precedes all other smectic modifications upon cooling either the isotropic liquid or cholesteric phase (Collyer, 1992).

b. Smectic B

Smectic B phase show the molecules tend to occupy specific positions like teaser in a mosaic (Virga, 1994). The molecules in smectic B phase are arranged hexagonal close-packing array within the layers with the molecular long axis perpendicular to the layer planes. Furthermore, there is an existence of long-range hexagonal order within the layers (Collyer, 1992).

c. Smectic C

Smectic C phase are like smectic A but their molecules are titled at a definite angle to the normal of each layer (Virga, 1994). Smectic C phase is the titled analogue of the smectic A phase. In which it has the same properties as those of smectic A phase but the molecules are titled with respect to the layer planes. Consequently, the material is optically biaxial (Collyer, 1992).

When smectic C phase occurs in the presence of other phases, smectic phase always occur lower in temperature scale than either a smectic A phase or nematic phase, but higher in the scale than a more ordered smectic phase. Smectic C phase can easily be twisted by the addition of optically active molecules (Collyer, 1992).

2.3.3 Cholesterics Phase

Molecules in a cholesterics liquid crystal can be form by optically active compound or optically active mixture. Locally a cholesteric is very similar to a nematic material. Again, the molecular centers of gravity have no long-range order but the molecules tend to be parallel to some common axis which defines the director (Collyer, 1992).

An important characteristic of the cholesterics mesophase is the pitch. The pitch, p, is defined as the distance it takes for the director to rotate one full turn in the helix as illustrated in the above animation (http://www.iq.usp.br). This analogy p, makes it easier

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