

**SYNTHESIS OF V-SHAPED LIQUID CRYSTALS
CONTAINING AZO CHROMOPHORES**

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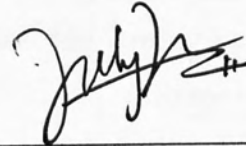
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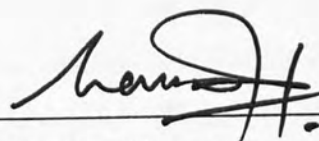
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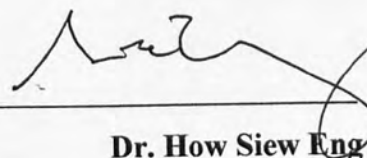
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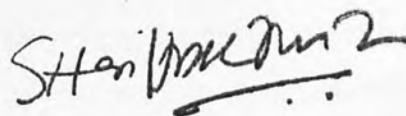
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ABSTRACT

The main objective of this study was to synthesize V-shaped liquid crystals materials containing azo chromophores. The starting material, methyl-4-aminobenzoate, was used to undergo diazonium salt coupling reaction with phenol to obtain methyl-4-(4-hydroxyphenylazo)benzoate. The next step of the reaction was Williamson's ether synthesis, whereby hexadecyl bromide was added to the diazonium salt to give methyl-4-(4-hexadecyloxyphenylazo)benzoate. The ester functional group (benzoate) of this compound was then hydrolyzed with sodium hydroxide, yielding 4-(4-hexadecyloxyphenylazo)benzoic acid. Lastly, the benzoic acid was reacted with catechol in the presence of DCC and DMAP for the Fischer esterification reaction. As the result, 15.78 % of yellow V-shaped liquid crystals, 1,2-phenylene-bis[4-(4-hexadecyloxyphenylazo)benzoate], with a melting point ranging from 198 – 202 °C was obtained. The molecular structures and characteristics of the intermediates and target compound were further confirmed by spectroscopic methods and thermal analysis including FT-IR, ¹H-NMR and DSC. From the FT-IR spectra of all intermediates and the final compound, the functional groups that present in each compound were shown and were identified as alkyl, aryl, ether, ester, carboxylic acid, etc. for each spectrum. ¹H-NMR spectrum of the final compound showed the types of protons as in the projected molecular structure of the V-shaped target molecule with the presence of some impurities. DSC thermogram showed the phase transition temperatures of crystalline to isotropic (Cr-I) at 198.39 °C for endothermic while for exothermic, isotropic to crystal (I-Cr) phase appeared at 148.53 °C. However, from the DSC thermogram analysis, the synthesized compound did not show liquid crystal mesophase but crystalline phase.



SINTESIS HABLUR CECAIR BERBENTUK V YANG MENGANDUNGI KUMPULAN BERFUNGSI AZO KROMOFOR

ABSTRAK

Objektif utama bagi penyelidikan ini adalah untuk mensintesis hablur cecair berbentuk V yang mengandungi azo kromofor. Bahan permulaan, iaitu metil-4-aminobenzoat, telah digunakan untuk menjalani tindak balas penduaan garam diazonium dengan fenol untuk menghasilkan metil-4-(4-hidroksifenilazo)benzoat. Langkah seterusnya ialah tindak balas Williamson, di mana heksadesil bromida ditambahkan kepada garam diazonium untuk memberi metil-4-(4-heksadesiloksifenilazo)benzoat. Kumpulan berfungsi ester (benzoat) kompaun ini kemudian dihidrolisis dengan natrium hidroksida, menghasilkan asid benzoik 4-(4-heksadesiloksifenilazo). Akhirnya, asid benzoik telah bertindak balas dengan katekol dalam kehadiran DCC dan DMAP untuk tindak balas pengesteran Fischer. Keputusannya, 15.78 % hablur cecair yang berwarna kuning, 1,2-fenilin-bis[4-(4-heksadesiloksifenilazo)benzoat], dengan takat lebur pada sekitar 198 - 202 °C didapati. Struktur molekul dan sifat kompaun pertengahan serta kompaun sasaran dikenalpasti dengan kaedah spektroskopi dan analisis termal yang merangkumi FT-IR, ¹H-NMR and DSC. Daripada spektra FT-IR bagi semua kompaun, kumpulan berfungsi yang hadir dalam setiap kompaun telah ditunjukkan dan dikenali sebagai alkil, aril, eter, ester, karboksilik dan lain-lain. Spektrum ¹H-NMR bagi kompaun terakhir menunjukkan jenis proton seperti yang terdapat dalam struktur molekul sasaran berbentuk V dengan kehadiran bahan asing. Termogram DSC menunjukkan suhu perubahan fasa hablur dengan fasa isotropik pada 198.39 °C bagi endotermik manakala untuk eksotermik, fasa isotropik dengan fasa hablur ialah 148.53 °C. Namun, didapati bahawa hasil daripada termogram DSC menunjukkan kompaun yang disintesis ini tidak mempunyai mesofasa seperti yang ada pada hablur cecair tetapi fasa kristal sahaja.



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LIST OF SYMBOLS

N	Nematic phase
Sm	Smectic phase
SmA	Smectic A phase
SmC	Smectic C phase
T_g	Glass transition temperature
T_m	Melting point
T_c	Crystallization point
ΔH	Enthalpy change
I	Isotropic phase
Cr	Crystalline phase
π	π



CHAPTER 1

INTRODUCTION

1.1 Background

The study of liquid crystals (LC) has begun since 1888 by an Austrian botanist, Friedrich Reinitzer on the solid sample of cholesteryl benzoate, which was found to have two distinct melting points (Virga, 1994). When heated, the substance melts at 145.5 °C to form a milky liquid, and at 178.5 °C the milky liquid suddenly becomes clear. When the substance is cooled, the reverse processes occur (Brown *et al.*, 2000). According to Demus *et al.* (1999), Reinitzer also noted the range of spectral colours reflected as the temperature decreased until crystallization occurred and the complementary nature of the coloured light when the sample was viewed in transmission.

On the other hand, Singh (2002) also reported that a German physicist Professor Otto Lehmann observed that the samples of cholesteryl benzoate flow like liquids and exhibit optical properties like that of a crystal. The subsequent studies established that these observed intermediate phases represent a new thermodynamic state of matter that are quite distinct from the isotropic liquid. The mechanical and symmetry properties of these phases are intermediate between those of a crystalline



solid and an isotropic liquid. Lehmann first referred to them as flowing crystals and later used the term “liquid crystals”.

In 1922, the French scientist Georges Friedel presented the real seal of acceptance of liquid crystals for what they are, i.e., a fascinating and distinct state of matter with the first classification of liquid crystals into types, namely, nematic, smectic and cholesteric (Friedel, 1922).

In the early years, Friedel strongly objected to Lehmann’s term liquid crystal, on the basis that liquid crystals were neither true liquids nor true crystals. He preferred the term mesomorphic to describe the liquid crystal state, and the associated term mesophase, reflecting the intermediate nature of these phases between the crystalline and isotropic liquid states. All terms are widely used today and coexist happily, simply because the juxtaposition of two contradictory terms carries an element of mystery and attraction in Lehmann’s terminology and a useful word mesogen springing in Friedel’s nomenclature used to describe a material that is able to produce mesophases (Demus *et al.*, 1999).

Conventionally, thermotropic LCs are formed by anisometric mesogens that are either rod-shaped (calamitic LCs) or disc-shaped (discotic LCs). By employing these two anisometric moieties, many conventional low molar mass (monomers) as well as high molar mass (polymers) liquid crystalline systems have been designed and synthesized (Yelamaggad *et al.*, 2004).



However, many other types of low molecular mass compounds with unconventional molecular structures have been shown to exhibit liquid crystalline properties. It was assumed that a linear molecular shape is a mesogenic pre-requisite when a compound contains two mesogenic units until the discovery of banana-shaped LC materials, i.e. mesogenic compounds with a bend in the middle of the molecules (Prasad, 2001). Some other examples on 'non-conventional LCs' are oligomeric LCs, bent-core V-shaped molecules, polycatenars and dendrimers (Yelamaggad *et al.*, 2004).

According to Yelamaggad (2004), bent-core V-shaped compounds are also known as fused twins or U-shaped molecules. Vorlander and Apel were the first to report a bent-core V-shaped molecule, namely 1,2-phenylene-bis[4-(ethoxyphenylazoxy)benzoate] and recently shown to exhibit a nematic phase. Kato *et al.* described the nematic behaviour of bent-core molecules formed as a result of hydrogen bonding between phthalic acid and stilbazole. However, Prasad (2001) has reported a number of azobenzene-based bent-core V-shaped molecules were found to exhibit N, SmA and crystal E phases.

1.2 Applications of liquid crystals

From the time of the discovery in 1888 until about 30 years ago, liquid crystals were largely a laboratory curiosity. They are now widely used as pressure and temperature sensors and in the displays of electrical devices (LCDs) such as digital watches, calculators, and laptop computers, relying on the interaction of polarized light with the liquid crystalline substance (John and Robert, 1998). 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 temperature, pressure, and electromagnetic fields (Brown *et al.*, 2000).

Organic compounds that exhibit a variety of interesting optical, electrical, photoelectrical, and magnetic properties in the solid state have found widespread use in a growing number of practical applications, including their utility as emitters in light-emitting diodes, laser dyes, photoconductors, optical switches, and optical data storage devices (Cristiano *et al.*, 2007).

The ability to control the orientation of the molecules in a liquid crystal allows us to produce materials with high strength or unique optical properties. High-strength applications involve the use of polymers with superior mechanical properties in the direction of the long molecular axis. Sporting equipment, supersonic aircraft parts, and the sails used in the America's Cup races are fabricated from these polymeric materials (Silberberg, 2006).

Cholesteric liquid crystals are used in applications involving colour changes with temperature. The example for this application is liquid crystal thermometers that include a mixture of substances to widen their range of temperatures. Newer and more important uses include "mapping" the area of tumor, detecting faulty connections in electronic circuit boards, and non-destructive testing of materials under stress (Silberberg, 2006).



1.3 Objectives

The objectives of this study were:

- a. To prepare V-shaped liquid crystals containing azo chromophores.
- b. To determine the functional groups of the compounds using Fourier Transform Infrared (FT-IR) spectrometer.
- c. To identify the molecular structure of the compound using Nuclear Magnetic Resonance ($^1\text{H-NMR}$) spectrometer.
- d. To determine the mesomorphic properties of the compound using Differential Scanning Calorimetry (DSC) method.

1.4 Scope of study

The study focused mainly on the organic synthesis of V-shaped liquid crystals containing azo chromophores. The procedures involved in the synthesis process were refluxes, hydrolysis, recrystallization, filtration, and etherification by specific chemicals such as DCC, DMAP, catechol and hexadecyl bromide. The molecular structural identification of the intermediates and the final compound were done by using Fourier Transform Infrared Spectrometer (FT-IR) and Nuclear Magnetic Resonance Spectrometer ($^1\text{H-NMR}$), while the mesomorphic properties of the final compound was determined by using Differential Scanning Calorimeter.



CHAPTER 2

LITERATURE REVIEW

2.1 Liquid crystals

Liquid crystals are wonderful materials (DeGennes, 1974) because they are mesophases or intermediate states of matter (Virga, 1994). Instead of passing directly from the solid to the liquid phase when heated, some substances, such as cholesteryl benzoate, pass through an intermediate liquid-crystalline phase that has some of the structure of solids and some of the freedom of motion possessed by liquids (Brown *et al.*, 2000). Thus, they can flow like nearly incompressible viscous fluids, and yet retain several features, especially optical characteristics of crystals (Virga, 1994).

Like crystalline solids, liquid crystals are packed at the molecular level with a high degree of positional and orientational orders (Silberberg, 2006) but they adopt the shape of their container. Meier (1975) therefore define liquid crystals as “condensed fluid phases with spontaneous anisotropy”.

Because of the partial ordering, liquid crystals may be very viscous and possess properties intermediate between those of the solid and liquid phases. The region in which they exhibit these properties is marked by sharp transition



temperatures (Brown *et al.*, 2000). Figure 2.1 shows that the liquid crystalline phase is in between the solid and liquid phases.

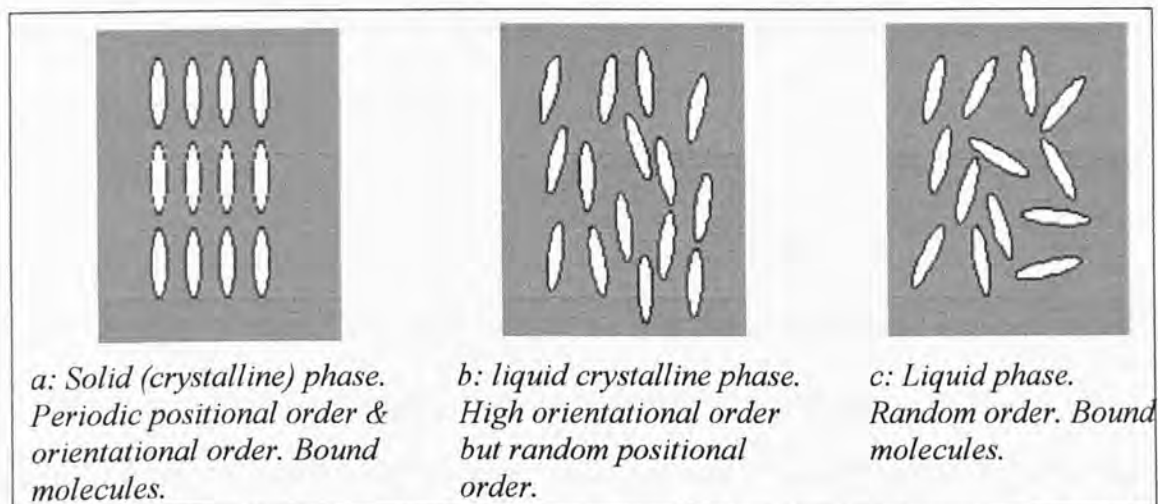


Figure 2.1 An illustration of the difference in positional order between the solid, liquid crystal and liquid phases. The effect of thermal fluctuations is neglected in the sketch of the solid state.

According to Silberberg (2006), the molecules that form liquid crystal phases in most cases have two characteristics: a long, cylindrical shape and a structure that allows intermolecular attractions through dispersion and dipole-dipole or H-bonding forces, but that inhibits perfect crystalline packing. Mostly, liquid crystal molecules form rodlike shapes with the presence of certain groups such as flat, benzene-like ring systems that keep the molecules extended. Many of these types of molecules also have a molecular dipole associated with the long molecular axis. A sufficiently strong electric field can orient large numbers of these polar molecules in approximately the same direction, like compass needles in a magnetic field.

The viscosity of a liquid crystal phase is lowest in the direction parallel to the long axis. Like moistened microscope slides, it is easier for the molecules to slide along each other because the total attractive force remains the same, than it is for them to pull apart from each other sideways. As a result, the molecules tend to align while the phase flows (Silberberg, 2006).

The most commonly occurring liquid crystal molecules are aromatic, and, if they contain benzene rings, they are often referred to as benzene derivatives. In general, aromatic liquid crystal molecules comprise a side chain R, two or more aromatic rings A and A', connected by linkage groups X and Y, and at the other end connected to a terminal group, R' (Figure 2.2) (Virga, 1994).

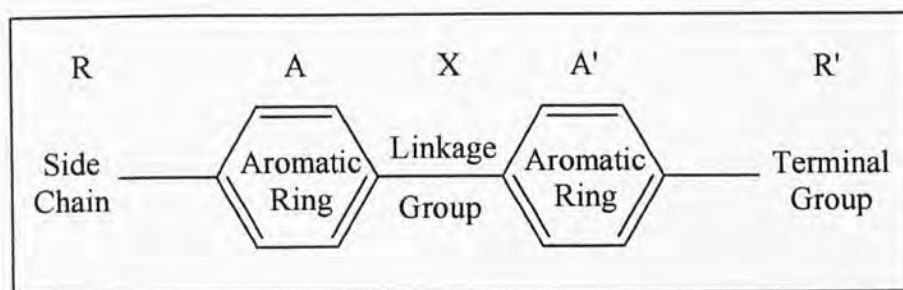


Figure 2.2 Molecular structure of a typical liquid crystal (Virga, 1994).

2.2 Molecular structure of liquid crystals

Considering the geometrical structure of the mesogenic molecules, liquid crystals can be grouped into several types. Liquid crystals derived from the rod-shaped molecules are called “calamitics”, whereas the mesophases formed from disc-like molecules are referred to as “discotics”. Rod-shaped molecules have one axis much longer than the

other two while disc-like molecules have one molecular axis which is much shorter than the other two. Intermediate between rod-like and disc-like molecules are the lath-like species (Singh, 2002) called sanidic, first found in polymeric liquid crystals (Stegemeyer & Guest, 1994).

A typical calamitic mesogen consists of a rigid core unit (aromatic or alicyclic), ensuring the anisotropic character, flexible side chain which provide stabilizing effects within the liquid crystal phases (Khoo, 1977). Discotic compounds consist of flat, rigid cores which are surrounded by flexible chain (alkyl, alkoxy, alkanoyloxy) and the effect of the latter is to lower the melting temperature and to isolate the columns one to another so that a structure with some mobility can be formed (Stegemeyer & Guest, 1994).

2.3 Types of liquid crystals

Liquid crystal phases can arise in two general ways, and, sometimes, either way can occur in the same substance (Silberberg, 2006). The two types of mesomorphisms are thermotropic and lyotropic phases. In general, thermotropic LCs exhibit a phase transition into the LC phase as temperature is changed, whereas lyotropic LCs exhibit phase transition as a function of concentration of the mesogen in a solvent, often water as well as thermal change (Singh, 2002).

According to Kroschwitz and Howe-Grant (1995), the real distinctiveness of thermotropic LCs with lyotropic LCs is the fact that at least two very different species



of molecules must be present in order to form lyotropic LCs, such as amphiphilic molecules with two different parts; hydrophobic and hydrophilic. The order of the lyotropic crystal is broken down by the solvent and the molecules form micelles which then arrange themselves in an ordered way, while allowing fluidity (Demus *et al.*, 1999). Excess of solvent beyond a critical concentration completes the decrease in order and leads to a transformation to an ordinary isotropic liquid (Meier, 1975).

Although there are two types of liquid crystal phases, discussion will only be emphasized on thermotropic LCs since lyotropic LCs are more to biological systems (Meier, 1975) and the surface properties of thermotropic LCs are more well studied (Sonin, 1995).

2.3.1 Thermotropic liquid crystals

Thermotropic liquid crystal phases are formed either on heating crystals or on cooling isotropic liquids, that is, as a consequence of thermal effects (Demus *et al.*, 1999). It develops as a result of a change in temperature (Silberberg, 2006).

As a crystalline solid is heated, the molecules leave their lattice sites, but the intermolecular interactions are still strong enough to keep the molecules aligned with each other along their long axes. Like any other phase, the liquid crystal phase has sharp transition temperatures; however, it exists over a relatively small temperature range. Further heating provides enough kinetic energy for the molecules to become disordered, as in a normal liquid (Silberberg, 2006).

REFERENCES

- Acierno, D. and Collyer, A. A. 1996. *Rheology and Processing of Liquid Crystal Polymers*. Chapman & Hall, United Kingdom.
- Blinov, L. M. and Chigrinov, V. G. 1994. *Electrooptic Effects in Liquid Crystal Materials*. Springer-Verlag New York Inc., USA.
- Brown, M. E. 1995. *Introduction to Thermal Analysis: Techniques and Applications*. (revised) Chapman & Hall, United Kingdom.
- Brown, T. L., Lemay, Jr. H. E. and Bursten, B. E. 2000. *Chemistry The Central Science*. Eighth Edition. Prentice-Hall Inc., New Jersey.
- Bruice, P. Y. 2004. *Organic Chemistry*. Fourth Edition. Pearson Education, Inc., New Jersey.
- Castellion, M. E. and McMurry, J. 1994. *Fundamentals of Organic and Biological Chemistry*. Prentice-Hall, Inc., New Jersey.
- Cheong, K. S. 2004. *Synthesis and Characterization of Bent Shaped Azo Containing Liquid Crystals*. Dissertation Bachelor Degree of Science with Honours, University Malaysia Sabah, Kota Kinabalu (Unpublished).
- Crews, P., Rodriguez, J., Jaspars, M. 1998. *Organic Structure Analysis*. Oxford University Press, Inc., New York.
- Cristiano, R., Westphal, E., Bechtold, I. H., Bortoluzzi, A. J. and Gallardo, H. 2007. Synthesis and Optical/Thermal Properties of Low Molecular Mass V-shaped Materials Based on 2,3-dicyanopyrazine. *Tetrahedron* **63**, 2851-2858.
- DeGennes, P. G. 1974. *The Physics of Liquid Crystals*. Clarendon Press, Oxford.



- Demus, D., Goodby, J., Gray, G. W., Spiess, H. -W. and Vill, V. 1999. *Physical Properties of Liquid Crystals*. Wiley-VCH, Federal Republic of Germany.
- Dunemann, U., Schroder, M. W., Pelzl, G., Diele, S. and Weissflog, W. 2005. A New Class of Bent-shaped Mesogens Exhibiting Unusual Mesophase Behaviour. *Liquid Crystals* **32** (2), 151-161.
- Elvers, B., Hawkins, S. and Schulz, G. 1990. *Ullmann's Encyclopedia of Industrial Chemistry* **A15**. Fifth Edition. Wiley-VCH, Federal Republic of Germany.
- Fifield, F. W. and Kealey, D. 2000. *Principles and Practice of Analytical Chemistry*. Fifth Edition. Blackwell Science Ltd., United Kingdom.
- Friedel, G. 1922. The Mesomorphic States of Matter. *Annales de Physique* **18**, 272-274.
- John, M. and Robert, C. F. 1998. *Chemistry*. Second Edition. Prentice-Hall, Inc., New Jersey.
- Khoo, I. C. (eds). 1977. *Liquid Crystals: Physical Properties and Nonlinear Optical Phenomena*. John Wiley & Sons, Canada.
- Kroschwitz, J. L. (eds) and Howe-Grant, M. (eds). 1995. *Kirk-Othmer Encyclopedia of Chemical Technology* **15**. Fourth Edition. John-Wiley & Sons, Inc., New York.
- Lambert, J. B., Shurvell, H. F., Lightner, D. A. and Cooks, R. G. 1998. *Organic Structural Spectroscopy*. Prentice-Hall, Inc., New Jersey.
- Lister, T. and Renshaw, J. 2000. *New Understanding Chemistry for Advanced Level*. Third Edition. Stanley Thornes Publisher Ltd., Cheltenham.



- Lutfor M. R., Yusoff, M., Tschierske, C., Pelz, K., Baumeister, U. and Silong S. 2005a. Nematic and Smectic Mesophase Formation by a Novel Triphenylene-Azobenzene Hybrid Molecule. *Electronic-Liquid Crystal Communications*.
- Lutfor M. R., Tschierske, C., Yusoff, M. and Silong, S. 2005b. Synthesis and Liquid Crystalline Properties of a Disc-Shaped Molecule with Azobenzene at the Periphery. *Tetrahedron Letters* **46**, 2303-2306.
- Maeda, Y., Prasad, S. K., Rao, D. S. S., Nagamani, S. A., Hiremath, U. S. and Yelamaggad, C. V. 2003. Phase Behaviour of Thermotropic Banana-Shaped Compounds Under Pressure. *Liquid Crystals* **30** (11), 1277-1283.
- Meier, G., Sackmann, E. and Grabmaier, J. G. 1975. *Applications of Liquid Crystals*. Springer Verlag, New York.
- Murthy, H. N. S. and Sadashiva, B. K. 2004. Synthesis and Mesomorphic Properties of Unsymmetrical Bent-core Compounds Containing 1,3-phenylene or 2,7-naphthylene as the Central Unit. *Liquid Crystals* **31** (10), 1347-1356.
- Pavia, D. L., Lampman, G. M. and Kriz, G. S. 2001. *Introduction to Spectroscopy*. Third Edition. Brooks/Cole Thomson Learning, Inc., United States of America.
- Prasad, V. 2001. Liquid Crystalline Compounds with V-shaped Molecular Structures: Synthesis and Characterization of New Azo Compounds. *Liquid Crystals* **28** (1), 145-150.
- Sia, S. K. 2007. *Preparation of Fluoro-Substituted Liquid Crystals Containing Azobenzene Moieties*. Dissertation Bachelor Degree of Science with Honours, University Malaysia Sabah, Kota Kinabalu (Unpublished).
- Silberberg, M. S. 2006. *Chemistry: The Molecular Nature of Matter and Change*. Fourth Edition. McGraw-Hill Companies, Inc., New York.



- Silverstein, R. M., Bassler, G. C. and Morrill, T. C. 1974. *Spectrometric Identification of Organic Compounds*. Third Edition. John-Wiley & Sons, Chichester.
- Silverstein, R. M. and Webster, F. X. 1997. *Spectrometric Identification of Organic Compounds*. Sixth Edition. John-Wiley & Sons, New York.
- Singh, S. 2002. *Liquid Crystals: Fundamentals*. World Scientific Publishing Co. Pte. Ltd., Singapore.
- Smith, B. C. 1996. *Fundamentals of Fourier Transform Infrared Spectroscopy*. CRC Press LLC, Florida.
- Smith, B. C. 1999. *Infrared Spectral Interpretation: A Systematic Approach*. CRC Press LLC, Florida.
- So, B. K., Kim, Y. S., Choi, M. M., Lee, S. M., Kim, J. E., Song, H. H. and Park, J. H. 2004. Novel Bent-Shaped Liquid Crystalline Compounds II: Synthesis and Properties of the 1,3-bis{4-[4-(4-alkyloxybenzoyloxy)benzylidene]aminophenoxy}propan-2-ol. *Liquid Crystals* **31** (2): 169-174.
- So, B. K., Kim, H. J., Lee, S. M., Song, H. H. and Park, J. H. 2006. Novel Bent-Shaped Liquid Crystalline Compounds IV. Dimesogenic Compounds Containing 2-hydroxy-1,3-dioxypopylene and Azobenzene Mesogens. *Dyes and Pigments* **70**: 38-42.
- Solomons, G. T. W. 2004. *Organic Chemistry*. Eighth Edition. John Wiley & Sons (Asia) Pte Ltd, Singapore.
- Solomons, G. T. W. and Fryhle, C. 2000. *Organic Chemistry*. Seventh Edition. John Wiley & Sons, New York.
- Sonin, A. A. 1995. *The Surface Physics of Liquid Crystals*. Gordon and Breach Science Publishers SA, Amsterdam.



- Stegemeyer, H. and Guest, E. 1994. *Liquid Crystals*. Volume 3. Steinkopft Darmstard Springer, New York.
- Virga, E. G. 1994. *Variational Theories for Liquid Crystals*. Chapman & Hall, United Kingdom.
- Wade, L. G. Jr. 2006. *Organic Chemistry*. Sixth Edition. Pearson Prentice Hall, United States of America.
- Winikoff, D. and Trikojus, V. M. 1948. *N-diethylsulphanilamide: A Reagent for the Colorimetric Estimation of Thyroxine*. Doctor of Philosophy Thesis. University of Melbourne, Australia.
- Wong, K. H. 2007. *Synthesis of Disc-shaped Liquid Crystals Having Six Alkyl Chains As Peripheral*. Dissertation Bachelor Degree of Science with Honours, University Malaysia Sabah, Kota Kinabalu (Unpublished).
- Yager, K. G. and Barrett, C. J. 2006. Novel Photo-switching Using Azobenzene Functional Materials. *Journal of Photochemistry and Photobiology A: Chemistry* **182**, 250-261.
- Yelamaggad, C. V., I Shashikala, Shankar Rao, D. S. and Krishna Prasad, S. 2004. Bent-core V-shaped Mesogens Consisting of Salicylalimine Mesogenic Segments: Synthesis and Characterization of Mesomorphic Behaviour. *Liquid Crystals* **31** (7), 1027-1036.

