PREPARATION OF CHLORO-SUBSTITUTED LIQUID CRYSTALS CONTAINING AZOBENZENE MOIETIES

HUI KOK KENG

DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE WITH HONOURS

INDUSTRIAL CHEMISTRY PROGRAMME
SCHOOL OF SCIENCE AND TECHNOLOGY
UNIVERSITY MALAYSIA SABAH

APRIL, 2007

PUMS 99:1

UNIVERSITI MALAYSIA SABAH

BORANG PENGESAHAN STATUS TESIS@

UDUL: Preparation of chloro-substituted liquid crystals containing azobenzene moieties

azah: Ijazah Sarjana Muda Sains (Kepujian)

SESI PENGAJIAN: 2004/2005

ya HUI KOK KENG

(HURUF BESAR)

engaku membenarkan tesis (~~LPS~~/Sarjana/~~Doktor Falsafah~~)* ini disimpan di Perpustakaan Universiti alaysia Sabah dengan syarat-syarat kegunaan seperti berikut:

Tesis adalah hakmilik Universiti Malaysia Sabah.
Perpustakaan Universiti Malaysia Sabah dibenarkan membuat salinan untuk tujuan pengajian sahaja.
Perpustakaan dibenarkan membuat salinan tesis ini sebagai bahan pertukaran antara institusi pengajian tinggi.
**Sila tandakan (/)

☐	SULIT	(Mengandungi maklumat yang berdarjah keselamatan atau kepentingan Malaysia seperti yang termaktub di dalam AKTA RAHSIA RASMI 1972)
☐	TERHAD	(Mengandungi maklumat TERHAD yang telah ditentukan oleh organisasi/badan di mana penyelidikan dijalankan)
☐	TIDAK TERHAD	

Disahkan oleh

(TANDATANGAN PENULIS)

(TANDATANGAN PUSTAKAWAN)

nat Tetap: PETI SURAT 1947, 722 SANDAKAN, SABAH.

DR. MD LUTFOR RAHMAN
Nama Penyelia

:h: 18-04-2007

Tarikh: 18-04-2007

ATAN: * Potong yang tidak berkenaan.
** Jika tesis ini SULIT atau TERHAD, sila lampirkan surat daripada pihak berkuasa/organisasi berkenaan dengan menyatakan sekali sebab dan tempoh tesis ini perlu dikelaskan sebagai SULIT dan TERHAD.
@ Tesis dimaksudkan sebagai tesis bagi Ijazah Doktor Falsafah dan Sarjana secara penyelidikan, atau disertasi bagi pengajian secara kerja kursus dan penyelidikan, atau Laporan Projek Sarjana Muda (LPSM).

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

APRIL, 2007

HUI KOK KENG
HS2004-3340

VERIFICATION

Name : Hui Kok Keng

Title : Preparation of chloro-substituted liquid crystals containing azobenzene moieties

DR. MD LUTFOR RAHMAN

DR. HOW SIEW ENG

MR. MOH PAK YAN

DEAN

SCHOOL OF SCIENCE AND TECHNOLOGY

APRIL, 2007

ACKNOWLEDGEMENT

Firstly, I would like to express my greatly gratitude to my supervisor, Dr. Md. Lutfor Rahman, a greatness individual who providing his guidance and his valuable knowledge to help me complete this research project smoothly. Without him, this research project will hardly to be completed. His patience and time are very much appreciated.

Secondly, I would like to thank our laboratory assistants Mr. Sani for his cooperation throughout the practical section of my project in the chemistry lab. Thank also goes out to the director of Institute for Tropical Biology and Conservation (IBTP) University Malaysia Sabah for providing the use of FT-IR and H-NMR analysis tools.

Lastly, I would like to thank my parents and family members for giving me support and encouragement throughout the period of this study.

ABSTRACT

Ethyl-4-aminobenzoate was used as the starting material, and undergone diazo coupling reaction with phenol to produced 4-(4-hydroxyphenylazo)-ethyl benzoate. Then, the product formed was reacted with bromohexane via Williamson ether synthesis to yield 4-(4-hexyloxyphenylazo)-ethyl benzoate. After that, the ester compound was proceeded to base-catalysed hydrolysis using potassium hydroxide to yield 4-(4-hexyloxyphenylazo)-benzoic acid. Finally, the benzoic acid was reacted with 4-chlororesorcinol, to this catalytic amount of 4-dimethylaminopyridine (DMAP) was added as catalyst and 1,3-dicyclohexylcarbodiimide (DCC) as a dehydrating agent. The expected final compound was 1-chloro-2,4-phenylene-bis-[4-(4-hexyloxyphenylazo)-benzoate], with the total yield of 0.227g (68.29% of percentage yield) and melting point at the range of 195 to 199°C. However FT-IR spectrum of the final compound showed that it was lacked of carbonyl group (C=O) of ester and complete assignment of the ^{1}H-NMR also could not be made due to the present of impurities. Therefore, the preparation of chloro-substituted liquid crystals containing azobenzene moieties was not successful, this might be due to the operative errors such as personal errors that occurred during the synthesis steps. The final compound possibly a mixture of benzoic acid and 4-chlororesorcinol. The thermal behaviour of the final compound was investigated using differential scanning calorimeter (DSC) and the DSC thermogram which showed that there was no existence of mesophase for the final compound.

PENYEDIAN BAHAN MESOGENIK GANTIAN KLORO YANG MENGANDUNGI AZOBENZINA

ABSTRAK

Etil-4-aminobenzoat digunakan sebagai bahan permulaan, dan melalui tindak balas penghubungan diazo dengan fenol untuk menghasilkan 4-(4-hidrosifenilazo)-etil benzoat. Selepas itu, produk yang dihasilkan telah ditindak balas dengan bromohesana melalui penghasilan eter Williamson dengan untuk menghasilkan 4-(4-heksilosifenilazo)-etil benzoat. Kemudian, bahan ester telah melalui hidrolisis pemangkinan bes dengan meggunakan kalium hidroksida untuk menghasilkan asid 4-(4-heksilosifenilazo)-benzoik. Akhirnya, asid benzoik ditindak balas dengan 4-klororesosinol, dalam ini, sedikit 4-dimetilpiridin (DMAP) ditambah sabagai mangkin dan 1,3-disikloheksikarbodiimide (DCC) sebagai agen pengondangan. Bahan akhir jangkaan ialah 1-kloro-2,4-fenilena-bis-[4-(4-heksilosifenilazo)-benzoat] dengan jumlah penghasilan 0.227g (68.29% peratusan penghasilan) dan takat lebur dalam lingkungan 195 sehingga 199°C. Walaubagaimanapun, pengimbasan infra merah (FT-IR) menunjukkan ia kekurangan kumpulan karbonil (C=O) daripada ester dan pemadanan yang lengkap bagi ^{1}H-NMR juga tidak dapat dilakukan disebabkan kehadiran ketidaktulenan. Oleh itu, penyedian bahan mesogenik gentian kloro yang mengandungi azobenzina adalan tidak berjaya, ini mungkin disebabkan oleh kesilapan yang berlaku seperti kesilapan perseorangan semasa langkah sintesis. Bahan akhir mungkin adalah campuran asid benzoik dan 4-klororesosinol. Sifat terma bagi bahan akhir diselidik dengan menggunakan DSC dan termagram DSC menunjukkan tiada kehadiran fasa meso bagi bahan akhir.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

Number of Scheme Page

LIST OF SYMBOLS

L	Linking group
R	Alipatic group or terminal
Z	Lateral substituent
d	Diameter
t	Thickness
S_A	Smectic A phase
S_C	Smectic C phase
SmC*	Ferroelectric chiral smectic C phase
$\mathbf{P}_s$	Spontaneous polarization
n^	Director
δ	Chemical shift (ppm)\
T	Temperature (°C)
ΔH	Enthalpy (Jg^{-1})
C	Carbon
H	Hydrogen
N	Nitrogen
O	Oxygen
–	Single bond
=	Double bond

CHAPTER 1

INTRODUCTION

1.1 Introduction to Liquid Crystals

Liquid crystalline state is an intermediate phase lies between the crystalline solid and the isotropic liquid phases (Demus *et al.*, 1998). The liquid crystals phase which is also known as mesophase shares properties of both the crystal and liquid phases, possessing an intermediate molecular order between the perfect three-dimensional long-range positional and orientational order found in crystals, and the absence of long-range order found in the isotropic liquids (and amorphous solids). The materials that able to sustain mesophases termed as mesogens.

The liquid crystals phase was first discovered in 1888 by an Austrian botanist F. Reinitzer. He observed a "double melting" behaviour of cholesteryl benzoate. The crystals of this sample melted at 145.5°C into a hazy liquid, which upon further heating to 178.5°C became clear and transparent liquid. This discovery represented the first recorded documentation of the liquid crystals phase.

Most liquid crystals have been designed to be either low molecular weight for display applications or high molecular weight for prototypical polymers (Demus *et al.*, 1998). Besides the conventional Liquid Crystals Display (LCD) used in watches and computer screen, liquid crystals material also used in various photonic applications, such as optical storage, optical switching, optical display, and optical computing (Demus *et al.*, 1998).

There are basically a few types of classification of liquid crystals according to the molecular structure, which are rod-like (calamitic) liquid crystalline compound, disc-like (discotic) liquid crystalline compound, and 'unconventional' liquid crystalline compounds. The 'unconventional' liquid crystals refers to a new class of liquid crystals in which the anisotropic shape of the molecules is distorted away from the classical rod or disc shapes (Demus, 1988). Some examples for 'unconventional' liquid crystals are oligomeric liquid crystals, bent-core molecules, polycatenars, and dendrimers.

The bent-core molecules can be broadly classified into two categories: (i) V-shaped, and (ii) banana-shaped. Bent-core V-shaped molecules formed when two mesogenic segments attaching covalently to a benzene ring in the 1,2-positions, whereas bent-core banana-shaped materials are formed when two mesogenic segments are covalently connected either to a benzene ring in the 1,3-positions or by an odd-numbered alkylene spacer (Pelzl *et al.*, 1999). Bent-core V-shaped molecules are known to exhibit mesophases similar to those shown by classical calamitic liquid crystals, whereas banana-shaped mesogens exhibit new smectic phases including two-dimensional phases, which are not comparable to or miscible with the phases formed by calamitics (Yelamaggad *et al.*, 2004).

There are many researches shown that, the introducing of different substituents and linkages has greatly affected the mesomorphic properties of the liquid crystals. So in this project, a liquid crystals containing chloro substituent and azobenzene linkage will be synthesized, and its mesomorphic properties will be determined by several analysis techniques.

1.2 Research Objectives

1. To prepare a chloro-substituted liquid crystals containing azobenzene moieties.
2. To determine the functional groups of the material using Fourier Transform Infrared Spectroscopy (FT-IR) and Nuclear Magnetic Resonance (NMR) Spectroscopy.
3. To determine the phase transition of synthesized compounds using Differential Scanning Calorimetry (DSC).

1.3 Research Scope

The project focused on the organic synthesis of the liquid crystals and the determination of liquid crystals properties. The procedures involved in the process were refluxes, hydrolysis, recrystallization and esterification using specific chemicals (ethyl-4-aminobenzoate, DCC, DMAP, 4-chlororesorcinol etc) and basic chemicals in lab (acetone, dichloromethane, methanol etc). Instrument used are that available in industrial chemistry lab (DSC etc) and Institute of Borneo Tropical Research lab (FT-IR and ^{1}H NMR) for molecular determination.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Liquid Crystals

The molecules in a crystal are ordered whereas in a liquid they are not. The existing order in a crystal is usually both positional and orientational, i.e., the molecules are constrained both to occupy specific sites in a lattice and to point their molecular axes in specific directions. However, the molecules in liquids diffuse randomly throughout the sample container with the molecular axes tumbling wildly (Singh, 2002).

When crystalline substances are heated, they normally transform straightly to isotropic liquid. However for some compound, they show different intermediate states between the crystalline and the liquid state. These intermediate states include liquid crystals, plastic crystals and condis crystals. But in this project, only liquid crystals state is emphasized.

In the molecule level of liquid crystals state, the positional order either fully or partially disappears while some degree of orientational order is maintained. The liquid crystals phase is one of the mesophase that occurs over a definite range of temperature, pressure or concentration of a substance (Barón and Stepto, 2002). In this phase the unique axes of the molecules remain, on average, parallel to each other, leading to a preferred direction in space.

2.2 Types of Mesophase

Transitions to the mesophases may be brought about in two different ways; one by purely thermal processes and the other by the influence of solvents. The liquid crystals obtained by the first method are called "thermotropics" whereas those obtained by the second one are "lyotropics". Amphotropic materials are able to form both thermotropic and lyotropic mesophases (Singh, 2002).

2.2.1 Thermotropic Mesophase

A thermotropic phase develops as a result of a change in temperature. A substances is considered to have thermotropic mesophase when a mesophase is formed by heating a solid or cooling an isotropic liquid, or by heating or cooling a thermodynamically stable mesophase (Barón and Stepto, 2002). 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 (Silberberg, 2003). Thermotropic liquid crystals are the most widely used and extensively studied for their linear as well as nonliniear optical properties. This is because thermotropic liquid crystals exhibit various liquid crystalline phases as a function of temperature (Whinnery *et al.*, 1977).

2.3 Typical Molecular Structures of Mesogens

There are basically a few types of classification of liquid crystals according to the molecular structure, which are rod-like (calamitic), disc-like (discotic), and 'unconventional' types. The 'unconventional' liquid crystals refer to a new class of liquid crystals in which the anisotropic shape of the molecules is distorted away from the classical rod or disc shapes (Demus *et al.*, 1998). Bent-shaped liquid crystal is one type of the 'unconventional' liquid crystals.

2.3.1 Rod-like (Calamitic) Liquid Crystalline Compound

Most of the rod-like liquid crystalline compound consists of two or more rings, which are bonded directly to one another or connected by linking groups (L), and may have terminal (R) and lateral (Z) substituents. The chemical structure of many mesogens can be represented by the general formula shown in Figure 2.1.

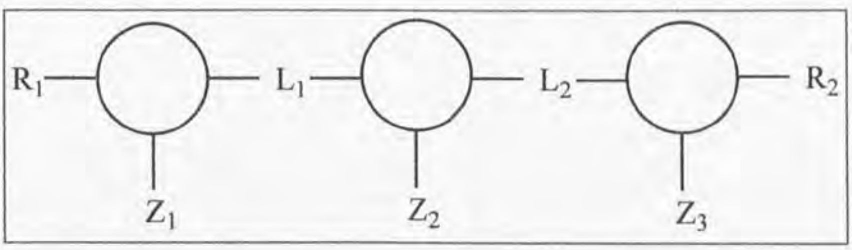


Figure 2.1 A chemical structure for general rod-like liquid crystalline compound.

The rings are represented by circles, and the linking group L form the core of the compound. The core is usually a relatively stiff unit, compared to the terminal substituents, which in most cases are flexible moieties such as alkyl groups. The lateral substituents Z are usually small units such as halogens, methyl groups and —CN groups (Demus *et al.*, 1998).

2.3.2 Disc-like (Discotic) Liquid Crystalline Compound

Similarly to the calamitic liquid crystals, discotic liquid crystals posses a general structure comprising a planar (usually aromatic) central rigid core surrounded by a flexible periphery, represented mostly by pendant chains, usually four, six, or eight. The general chemical structure for discotic liquid crystalline compound is shown in Figure 2.2.

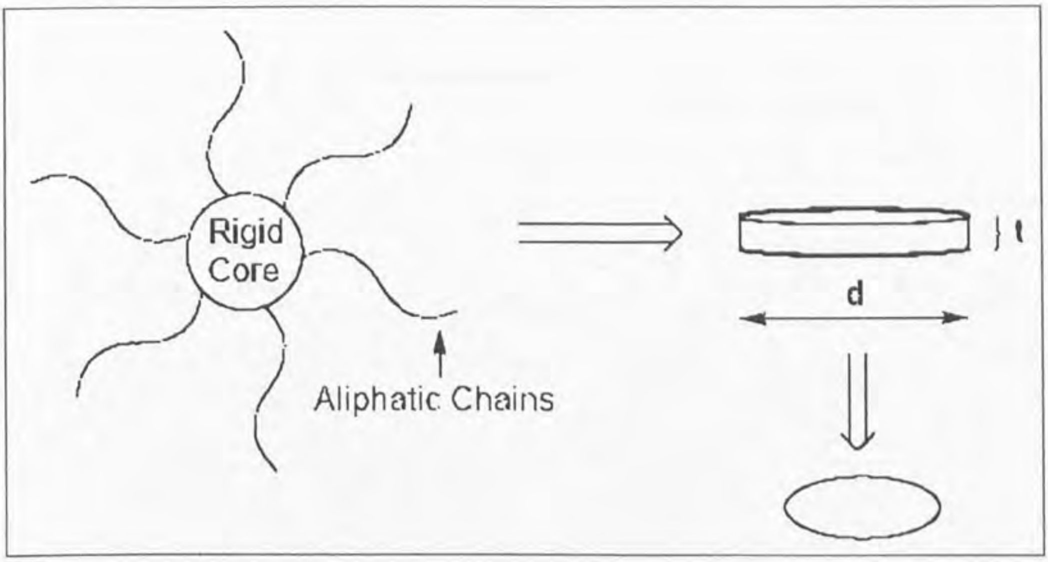
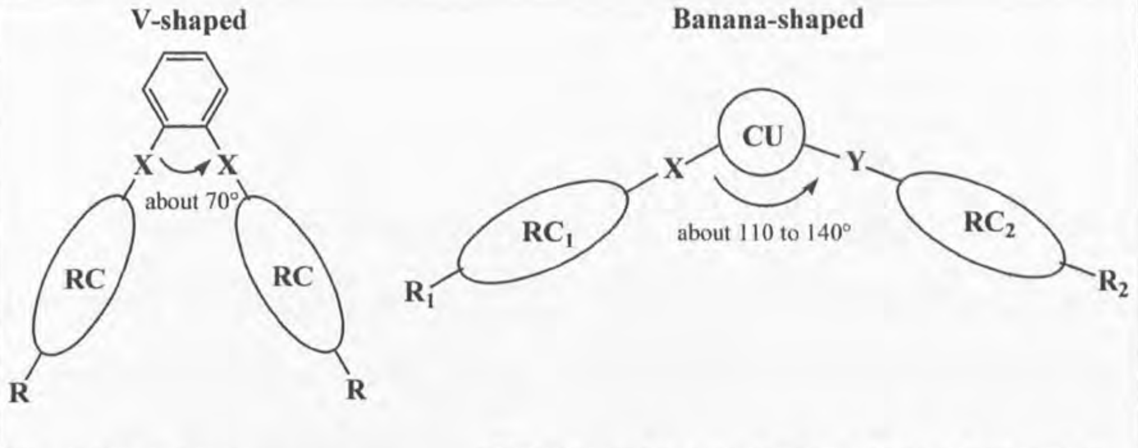


Figure 2.2 General shaped of discotic liquid crystals, where $\mathbf{d} \geq \mathbf{t}$.

As can be seen, the molecular diameter (d) is much greater than the disc thickness (t), imparting the form anisotropy to the molecular structure.

2.3.3 Bent-core (Banana-shaped) Liquid Crystalline Compound

Recall from chapter one, the bent-core banana-shaped liquid crystalline compound are formed when two mesogenic segments are covalently connected either to a benzene ring in 1,3-positions or by odd-numbered alkylene spacer (Pelzl *et al.*, 1999). Based on this, the different between V-shaped and banana-shaped are distinguished. However, it is now well established that the mesomorphic behaviour of these two classes of bent-core molecules are different and this may be attributed to the angle between the mesogenic segments (arms) attached to the central benzene nucleus (Yelamaggad *et al.*, 2004). Figure 2.3 shows the general molecular structure for V-shaped and banana-shaped molecules.



X : Linking groups
RC: Linear mesogenic rigid cores
R : Terminal chains

CU: An angular central unit = 1,3-phenylene nuclues
OR
odd-parity alkylene spacer

X & Y : Linking groups
RC_1 & RC_2 : Linear mesogenic rigid cores
R_1 & R_2 : Terminal chains

Figure 2.3 A general template for the molecular structures of bent-core V-shaped and banana-shaped molecules (Yelamaggad *et al.*, 2004).

REFERENCES

Achten, R., Cuypers, R., Giesbers, A. K., Marcells, A. T. M., and Sudhölter, E. J. R., 2004. Asymmetric banana-shaped liquid crystals with two different terminal alkoxy chains. *Liquid Crystals* **31** (8), 1167-1174.

Amaranatha Reddy, R. and Sadashiva, B. K., 2002. Ferroelectric properties exhibited by mesophase of compounds composed of achiral banana-shaped molecules. *Journal of Materials Chemistry* **12**, 2627-2632.

Amaranatha Reddy, R. and Sadashiva, B. K., 2003. Influence of fluorine substituent on the mesomorphic properties of five-ring ester banana-shaped molecules. *Liquid Crystals* **30** (9), 1031-1050.

Amaranatha Reddy, R. and Sadashiva, B. K., 2004. New phase sequences in banana-shaped mesogens: influence of fluorine substituent in compounds derived from 2,7-dihydroxynapthalene. *Journal of Materials Chemistry* **14**, 1936-1947.

Barón, M. and Stepto, R. F. T., 2002. Definitions of basic terms relating to polymer liquid crystals. *Pure Applied Chemistry* **74** (3), 493-509.

Bedel, J. P., Rouillon, J. C., Marcerou, J. P., Laguerre, M., Nguyen, H. T., and Achard, M. F., 2000. Novel mesophases in fluorine substituted banana-shaped mesogens. *Liquid Crystals* **27** (11), 1411-1421.

Demus, D., Goodby, J., Gray, G. w., Spiess, H., W., and V. Vill, 1998. *Handbook of Liquid Crystals*. Wiley-VCH, New York.

Dong, S., 2000. Syntheses and Mesophase Characterizations of Novel Bent-Core Molecules. Science Doctorate Dissetation, Martin-Luther-University Halle-Wittenberg, Germany (unpublished).

Clayden, J., Geeves, N., and Warren, S., 2000. *Organic Chemistry*. Oxford University Press, Oxford.

Jiří Svoboda, Vladimíra Novotná, Václav Kozmíka, Milada Glogarová, Wolfgang Weissflog, Siegmar Diele, and Gerhard Pelzl. A novel type of banana liquid crystals based on 1-substituted naphthalene-2,7-diol cores. *Journal of Material Chemistry* **13**, 2104-2110.

Laue, T. and Plagens, A., 2005. *Named Organic Reactions* 2nd Ed. John Wiley & Sons Ltd. West Sussex.

Lutfor, M. R., Tschierske, C., Yusoff, M., and Silong, S., 2005. Synthesis and liquid crystalline properties of a disc-shaped molecule with azobenzene at the periphery. *Tetrahedron Letters* **46**, 2303-2306.

Nadasi, H., Weissflog, W., Eremin, A., Delzl, G., Diele, S., Das, B., and Grande, S., 2002. Ferroelectric and antiferroelectric banana phases of new fluorinated five-ring bent-core mesogens. *Journal of Material Chemistry* **12** (5) 1316-1324.

Paula Yurkanis Bruice, 2004. *Organic Chemistry* 4th Ed. Pearson Education, Inc. USA

Pelzl, G., Diele, S., and Weissflog, W., 1999. Banana-shaped compounds – A new field of liquid crystals. *Advanced Materials* **11** (9), 707-724

Phillip Crews, Jaime Rodriguez, and Marcel Jaspars, 1998. *Organic Structure Analysis. Oxford University Press*, Inc. New York.

Prasad, V., 2001. Liquid crystalline compounds with V-shaped molecular structures: synthesis and characterization of new azo compounds. *Liquid Crystals* **28** (1), 145-150.

Prasad, V., Kang, S.-W., and Kumar, S., 2003. Novel examples of achiral bent-core azo compounds exhibiting B_1 and anticlinic–antiferroelectric B_2 mesophases. *Journal of Materials Chemistry* **13** (9), 1259-1264.

Rauch, S., Bault, P., Sawade, H., Heppke, G., Nair, G. G., and Jákli, A., 2002. Ferroelectric-chiral–antiferroelectric-racemic liquid crystal phase transition of bent-shape molecules. *Physical Review* **66**, 21709.

Satyendra Kumar, 2001. *Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions*. Cambridge University Press, Cambridge.

Shen, D., Pegenau, A., Diele, S., Wirth, I., and Tschierske, C., 2000. Molecular Design of Nonchiral Bent-Core Liquid Crystals with Antiferroelectric Properties. *Journal of American Chemical Society* **122** (8), 1593-1601.

Shreenivasa Murthy, H. N. and Sadashiva, B. K., 2004. Fluorine-substituted unsymmetrical bent-core mesogens derived from resorcinol. *Liquid Crystals* **31** (10), 1337-1346.

Silverstein, R. M. and Webster, F. X., 1997. *Spectrometric Identification of Organic Compounds* 6th Ed. John Wiley & Sons. New York.

Silberberg, M. S., 2003. *Chemistry: The Molecular Nature of Matter and Change*. 3rd Ed. McGraw-Hill, New York.

Singh. S., 2002. *Liqud Crystals: Fundamentals.* World Scientific Publishing Co. Pte. Ltd. Singapore.

Solomons, T. W. G. and Fryhle, C. B., 2004. *Organic Chemistry.* 8th Ed. John Wiley & Sons, Inc., New York.

Svoboda, J., Novotna, V., Kozmik, V., Glogarova, M., Weissflog, W., Diele, S., and Pelzl, G., 2003. A novel type of banana liquid crystals based on 1-substituted naphthalene-2,7-diol cores. *Journal of Materials Chemistry* **13** (9), 2104-2110.

Watanabe, J., Izumi, T., Niori, T., Zennyoji, M., Takanishi, Y., and Takezoe, H., 2000. Smectic mesophase properties of dimeric compounds. 2. Distinct formation of smectic structures with antiferroelectric ordering and frustration. *Molecular Crystals and Liquid Crystals* **346** (12), 77-86.

Weissflog, W., Nadasi, H., Dunemann, U., Pelzl, G., Diele, S., Eremin, A., and Kresse, H., 2001. Influence of lateral substituents on the mesophase behaviour of banana-shaped mesogens. *Journal of Materials Chemistry* **11** (11), 2748-2758.

Whinnery, J. r., Hu, C. ad Kwon, Y. S., 1977. Liquid Crystals waveguides for integrated optics, In: Khoo, I. C. (**eds**), *Liquid Crystals: physical Properties and Nonlinear Optical Phenomena*. John Wiley & Sons, Canada.

Yelamaggad, C. V., I Shashikala, Shankar Rao, D. S., and Krishna Prasad, S., 2004. Bent-core V-shaped mesogens consisting of salicylaldimine mesogenic segments: synthesis and characterization of mesomorphic behaviour. *Liquid Crystals* **31** (7), 1027-1036.