UNIVERSITI PUTRA MALAYSIA

# SYNTHESIS AND CHARACTERIZATION OF NEW SERIES OF LIQUID CRYSTALLINE COMPOUNDS CONTAINING AZOBENZENE AND BISAZOBENZENE MOIETIES

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**ABDULSALAM ABUBAKAR SALISU**

**Thesis Submitted to the School of Graduate studies, University Putra Malaysia, in Fulfilment of the Requirement for the Degree of Doctor of Philosophy**

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By

**ABDULSALAM ABUBAKAR SALISU**

**May 2009**

**Chairman:** **Associate Professor Mohamad Zaki Ab Rahman PhD**

**Faculty:** **Science**

New molecular structures based on azobenzene and bisazobenzene mesogenic units, which can support mesophase were prepared, in particular four different types of liquid crystalline materials have been synthesized and characterized, following the general criteria. All materials were characterized by spectroscopic methods (FT-IR, NMR, MS and CHNS analyses) and the liquid crystalline properties were investigated using differential scanning colorimetry (DSC), optical polarizing microscopy (OPM) and, X-ray diffraction. The presence of smectic A mesophase was confirmed by the textures and X-ray diffraction studies (XRD).

The calamitic liquid crystals (rod-shaped) compounds were generally synthesized via diazotization of primary aromatic amine, coupling with phenol and subsequent etherification of phenol with ten fold excess of an appropriate α,ω-dibromoalkane which

was further etherified in methanol to give the final compounds, giving rise to a typical features of calamitic liquid crystals (rod-shaped) compounds. Four of the liquid crystalline compounds containing azobenzene moiety denoted as AZOn series, exhibited enantiotropic smectic A phase AZO3-AZO6 ($C_3$-$C_6$) while, compound AZO8 ($C_8$) show monotropic smectic A phase.

The liquid crystalline trimer (AZOTn series) containing azobenzene with a short acetyl mesogenic group and a biphenyl as central mesogenic core were prepared by employing the procedures described for the calamitic mesogenic compounds above. The final compound was produced by etherification of the 4`4-hydroxybiphenyl with two-fold mole ratio of 1-bromoalky-(4-phenylazo)acetophenone. Compound with $C_5$ polymethylene flexible alkyl spacer (AZOT5**)** exhibited enantiotropic nematic and smectic A liquid crystalline properties. While the compound with $C_6$ polymethylene flexible alkyl spacer showed an enantiotropic nematic phase, the (AZOT6) exhibited the higher values of melting and clearing temperatures.

The calamitic bisazobenzene liquid crystal series (BAn series) were synthesized from 4-phenylazoaniline as mentioned above. All the compounds were found to show enantiotropic mesophase behavior and the presence of enantiotropic behavior throughout the series might be connected to the bisazobezene core and the terminal groups that extend the molecules along their molecular axes which, increase thermal stability of the mesophases and anisotropy of molecular polarizability. The photoisomerization experiment indicates a decrease in intensities of the absorption

bands for compound BA4 (BAn series**).** These show that the structure of the compounds does not have significant effect on the photoisomerization rate. This group of compounds have potential application in photonics more specifically, in reversible optical data storage, optical switching devices, optical computing and integrated optical devices for communication.

The final series of compound 4-propyloxy-[4-biphenyloxyalkyl]-4`-(4-phenylazo)azobenzene for the dimer containing bisazobenzene mesogenic moiety and alkoxybiphenyl linked by flexible spacers (BAOnO.3 series) was prepared by reacting the 4-propyloxy-4-hydroxybiphenyl with 1-bromoalkyloxy-4`-(4-phenylazo)azobenzene. The synthesized compounds exhibited enantiotropic phase with dimer containing propyl, butyl and octyl as flexible alkyl spacers showing SmA and those with pentyl and hexyl spacers exhibited SmA and SmC phases respectively. The stability of the smectic layer depends on the spacer length for the compounds studied.

Abstrak tesis yang dikemukakan kepada senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doctor Falsafah

**SINTESIS, DAN PENCIRIAN SIRI BAHARU SEBATIAN HABLUR PEPEJAL MENGANDUNGI MOETI AZOBENZENA DAN BISAZOBENZENA.**

Oleh

**ABDULSALAM ABUBAKAR SALISU**

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Struktur-struktur molekul baharu berasaskan unit mesogenik azobenzena dan bisazobenzena yang dapat menyokong satu mesofasa, empat jenis bahan-bahan mesogenik berbeza telah direkabentuk dan dikembangkan, mengikut ciri umum tertentu. Semua bahan dicirikan melalui kaedah-kaedah spektroskopi (FT-IR, NMR, MS dan analisis CHN) dan sifat-sifat mesomorfik dikaji menggunakan kalorimetri imbasan pembezaan (DSC), mikroskopi optik mempolar (OPM) dan, pembelauan sinar-X. Kehadiran mesofasa smektik A disahkan melalui rupacorak dan kajian pembelauan sinar-X (XRD).

Sebatian cecair hablur kalamatik (bentuk-batang) adalah disintesis menerusi pengdiazotan amina aromatik primer, pengkupelan dengan fenol dan diikuti dengan

pengeteran fenol dengan α,ω-dibromoalkana berlebihan 10 kali ganda, yang mana seterusnya dieterifikasikan dalam metanol bagi menghasilkan sebatian akhir, yang menghasilkan sebatian-sebatian cecair hablur kalamatik (bentuk-batang). Empat sebatian cecair hablur yang mengandungi moeti azobenzena (siri AZOn), menunjuk fasa enantropik smektik A AZO3-AZO6 ($C_3$-$C_6$) sedangkan sebatian AZO8 ($C_8$) menunjukkan fasa monotropik smektik A.

Siri trimer cecair hablur bukan-simetri (siri AZOTn) mengandungi azobenzena dengan satu kumpulan mesogenik asitil pendek dan satu bifenil sebagai teras mesogenik sentral. Kumpulan mesogenik azobenzene disediakan dengan menggunapakai kaedah serupa seperti yang diterangkan untuk sebatian-sebatian mesogenik kalamatik di atas. Sebatian akhir dihasilkan melalui pengeteran 4'4-hidroksibifenil dengan dua kali ganda nisbah mol 1-bromoalkil-(4-fenilazo)asetofenon. Sebatian tulen (AZOT5) dengan spaser fleksibel polimetilena $C_5$ memperagakan sifat-sifat cecair hablur anantiotropik nematik dan smektik A. Sedangkan sebatian (AZOT6) dengan spaser fleksibel polimetilena $C_6$ mempamirkan satu fasa enantiotropik nematik dan menunjukkan nilai suhu lebur dan suhu penjernihan yang lebih tinggi.

Siri bahan cecair hablur bisazobenzena kalamatik (siri BAn) disediakan daripada 4-fenilazoanilina seperti yang diterangkan di atas. Semua sebatian didapati menunjukkan sifat mesofasa enantropik dan keujudan sifat enantropik pada keseluruhan siri yang boleh dikaitkan dengan pusat bisazobenzena dan kumpulan terminal yang memanjangkan molekul berkenaan pada sepanjang paksi molekulnya. Ini meningkatkan

kestabilan terma daripada mesofasa dan anisotropi bagi kebolehpolaran molekul tersebut. Eksperimen keisomeran foto menunjukkan suatu penurunan dalam keamatan jalur serapan bagi sebatian BA4 (siri BAn). Ini menunjukan strukrur sebatian tidak memberi kesan yang besar kepada kadar keisomeran foto. Kumpulan sebatian ini berpotensi mempunyai kegunaan di dalam fotonik yang lebih spesifiknya, di dalam penyimpanan data optik yang boleh balik, alatan suis optik, komputer optik dan integrasi alat optik untuk komunikasi.

Siri sebatian terakhir 4-propiloksi-[4-bifeniloksialkil]-4'-(4-fenilazo)azobenzena mengandungi moeti mesogenik bisazobenzena dan suatu alkoksibifenil dan dirangkaikan oleh spaser-spaser fleksibel (siri BAOnO.3) adalah disintesis melalui tindak balas 4-propiloksi-4-hidroksifenil dengan 1-bromoalkil-4'-(4-fenilazo). Semua sebatian yang disintesis menunjukkan fasa enantiotropik dengan dimer spaser fleksibel alkil, yang mengandungi propil, butil dan oktil mempamerkan SmA dan sebatian dengan pentil dan spaser fleksibel alkil heksil menunjukkan fasa SmA dan SmC masing-masing. Kestabilan lapisan smektik itu bergantung kepada panjang spaser sebatian yang dikaji.

## DEDICATION

The work in this thesis is dedicated to my late father Alhaji Muazu Muhammd Dan`almajir and the entire family of late Muhammad Dan`almajir

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## DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

**ABDULSALAM ABUBAKAR SALISU**
Date:

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## LIST OF ABBREVIATIONS

| | |
|---|---|
| LC | Liquid crystals |
| CB | Cyanobiphenyl |
| Sm | Smectic |
| SmA | Smectic A |
| SmC | Smectic C |
| SmC* | Chiral smectic C |
| N | Nematic |
| $CDCl_3$ | Deuterated –chloroform |
| SCLCPs | Side chain liquid crystal polymers |
| Tg | Glass transition temperature |
| LCDs | Liquid crystal displays |
| Cr | Crystal |
| I | Isotropic |
| **n** | Director |
| DLC | Discotic liquid crystal |
| $N_D$ | Nematic discotic |
| $N_D$* | Chiral nematic discotic |
| Ncol | Nematic coloumnar |
| $N_L$ | Nematic lateral |
| N* | Chiral nematic |
| TNDs | Twisted nematic displays |

| | |
|---|---|
| TN | Twisted nematic |
| STNDs | Super twisted nematic displays |
| IPS | In-plane switching |
| VAN | Vertically aligned nematic |
| FFS | Fringe-field switching |
| FLC | Ferroelectric liquid crystals |
| $B_2$ | Achiral Switchable ferroelectric mesophase |
| $P_s$ | Spontaneous polarization |
| TGBA | Twist grains boundry |
| CB.O*n*O.*m* | α-(4-cyanobiphenyl-4`-yloxy)-ω-(4-n-alkylaniline benzylidine-4`-oxy)alkanes, |
| PLC | Polymer liquid crystal |
| MC-PLCs | Main chain liquid crystal polymer |
| VDU | Video display unit |
| CRT | Cathode ray tube |
| PDP | Plasma display panel, |
| DLP | Digital light processing |
| LCoS | Liquid crystal on silicon projection |
| DLP | Digital light processing |
| ITO | Indium-Tinoxide |
| TFT | Thin film transistor |
| TNLCD | Twisted nematic liuiqd crystal display |
| $SiO_2$ | Silicon oxide |
| DSC | Differential scanning caolorimetry |