



UNIVERSITI PUTRA MALAYSIA

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

ABDULSALAM ABUBAKAR SALISU

FS 2009 24

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

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**

May 2009



Abstract of the thesis presented to the senate of University Putra Malaysia in fulfillment of the requirement for the degree of Doctor of Philosophy

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

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 calorimetry (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 (C₃-C₆) while, compound AZO8 (C₈) 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-bromoalkyl-(4-phenylazo)acetophenone. Compound with C₅ polymethylene flexible alkyl spacer (AZOT5) exhibited enantiotropic nematic and smectic A liquid crystalline properties. While the compound with C₆ 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 bisazobenzene 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

May 2009

Pengerusi: Profesor Madya Mohamad Zaki Ab Rahman PhD

Fakulti: Sains

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 menggunakan 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 kejujuran 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 termal daripada mesofasa dan anisotropi bagi kebolehpolaran molekul tersebut. Eksperimen keisomeran foto menunjukkan suatu penurunan dalam keamatan jalur serapan bagi sebatian BA4 (siri BAn). Ini menunjukkan struktur 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 BAO_nO.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

ACKNOWLEDGEMENTS

In the name of Allah the Beneficent, the Merciful and all praises are due to Allah for all the favors bestowed upon mankind. I wish to express my sincere gratitude to my Supervisor, Associate Professor Dr Mohamad Zaki Ab Rahman of the Department of Chemistry, Faculty of Science for all the support and guidance. He initiated me to join the novel and interesting research area of liquid crystal. I am indeed very grateful to my research committee members in the names of Associate Professor Dr Sidik Silong, of Department of Chemistry, Faculty of Science who has been there all through to entertain all my problems in the cause of my lab work. Associate Professor Dr Mansor Bn Ahmad also of the Department of Chemistry, Faculty of Science and Dr Md Lutfor Rahman of School of Science and Technology, Universiti Malaysia Sabah whose guidance and support made this research feasible.

I would like also thank all the technical and administrative staff of the Department of Chemistry especially, Mr. Johadi Iskandar in-charge of NMR, Mrs. Rosnani Amirudeen in-charge of FT-IR, Mr. Zainal Abidin Kasim in-charge of GC-MS, Mr. Kamal Margona to mention but a few. I am also thankful to the entire fellow graduate students in Chemistry Department and especially, present and past members of the material chemistry research laboratory for being friendly and supportive during difficult times. I would like as well to extend my sincere appreciation to the department of Chemistry, Univesiti Putra Malaysia for supporting my research work by supplying chemicals and other consumables, the Ministry of Science, Technology and Innovation for providing facilities and the research grand No 04-01-04SF0144.

I would also like to extend my sincere appreciation to all fellow Nigerians in UPM especially, Mal. Nasir Umar Tsafe, Mal. Umar Ibrahim Gaya, Umar Yusuf, Dr Abdulkarim Sabo Mohammed, Dr Salisu Garba, Mal. Samaila Bawa, Mal. Mohammed Ajiya to mention but a few.

I wish to acknowledge my employers Bayero University Kano, Nigeria who awarded fellowship to me and MacArthur Grant No [82511]. Also the Kano State Government of Nigeria for financial assistance during the period of the study. Sincere thanks goes to the members of Muslim Education Association for Nigerian Students (MEANS) for their moral and financial support. A warm and sincere appreciation goes to all my colleagues at the Bayero University Kano, especially, the academic staff of chemistry department.

Lastly, I would like to thank my parents, brothers and sisters, my wife Wasila and my Children Mu`azu, Ahmad and Faridah for their support, prayers and care at all times.

This thesis submitted to the Senate of University Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee are as follows:

Main Supervisor,

Associate Prof. Dr. Mohamad Zaki Ab Rahman
Faculty of Science
Department of Chemistry
University Putra Malaysia
(Chairman)

Co-Supervisor

Associate Prof. Dr Sidik Bn Silong
Faculty of Science
Department of Chemistry
University Putra Malaysia
(Member)

Co-Supervisor

Associate Prof. Dr Mansor Bn Ahmad @ Ayob
Faculty of Science
Department of Chemistry
University Putra Malaysia
(Member)

Co-Supervisor

Dr. Md Lutfor Rahman
Lecturer
School of Science
University Malaysia Sabah
Malaysia
(Member)

I certify that an Examination Committee met on date of viva to conduct the final examination of Abdulsalam Abubakar Salisu on his Doctor of Philosophy thesis entitled ``Synthesis and characterization of new series of liquid crystalline compounds containing azobenzene and bisazobenzene moieties`` in accordance with Universiti Pertanian Malaysia (Higher Degree) act 1980 and Universiti Pertanian (Higher Degree) Regulations 1981. The committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Examination Committee were as follows:

Md Jelas Haron, PhD

Professor

Faculty of Science

University Putra Malaysia

(Chairman)

Mohd Aspollah Hj. Sukari, PhD

Professor

Faculty of Science

University Putra Malaysia

(Internal Examiner)

Rauziah Hashim, PhD

Professor

Faculty of Science

University Malaya

(External Examiner)

Dr. Norazah, PhD

Lecturer

Faculty of Science

University Putra Malaysia

(Internal Examiner)

BUJANG KIM HUAT

Professor and Deputy Dean

School of Graduate Studies

University Putra Malaysia

Date:

This thesis was submitted to the Senate of University Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Dr. Mohamad Zaki Ab Rahman, PhD

Associate Professor
Faculty of Science
Department of Chemistry
University Putra Malaysia
(Chairman)

Sidik Bn Silong PhD

Associate Professor
Faculty of Science
Department of Chemistry
University Putra Malaysia
(Member)

Mansor Bn Ahmad @ Ayob PhD

Associate Professor
Faculty of Science
Department of Chemistry
University Putra Malaysia
(Member)

Md Lutfor Rahman PhD

Lecturer
School of Science
University Malaysia Sabah
Malaysia
(Member)

HASANA MOHD. GHAZALI, PhD

Professor and Dean
School of Graduate Studies,
Universiti Putra Malaysia
Date:

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:

LIST OF TABLES

Table		Page
4.1	Physical and analytical data of the azobenzene calamitic liquid crystal series	109
4.2	Phase transition temperatures and enthalpies obtained from DSC scans for AZOn Series	120
4.3	Physical and analytical data of the unsymmetrical liquid crystal trimers containing azobenzene moiety (AZOTn Series)	124
4.4	Phase transition temperatures and enthalpies obtained from DSC second heating scans for liquid crystalline unsymmetrical trimer (AZOTn Series).	131
4.5	Physical and analytical data for the bisazobenzene calamitic liquid crystal (BAn series)	136
4.6	Phase transition temperatures and enthalpies obtained from DSC second heating scans of BA1-BA4 and BA5.	144
4.7	Physical and analytical data for the unsymmetrical liquid crystal dimer containing bisazobenzene moiety (BAOnO.3 Series).	154
4.8	Phase transition temperatures and enthalpies obtained from DSC second heating scans for (BAOnO.3) Series	163

LIST OF FIGURES

Figure	Page
1.1 Chiral calamitic azobezene (2) Calamitic azobenzene (3) Tollen calamitic (4) Schiff's base calamitic liquid cryastals	3
1.2 Molecular structure of 4-pentyl-4'-cyanobiphenyl (5CB) 1 (The transition temperatures are expressed in $^{\circ}\text{C}$).	6
1.3 Schematic mechanistic routes to azobenzene synthesis	9
1.4 Schematic mechanistic routes to bisazobenzene synthesis	9
1.5 Optical isomerization of azobenzene	10
1.6 <i>trans-cis</i> photoisomerization of azobenzene; N, nematic; I, isotropic	12
1.7 Orientation of azobenzene in side-chain polymer on the surface	13
1.8 Optical polarizing microscope (a) in our Lab (b) OPM configuration (Abramowitz et al. 2009)	15
1.9 Polarization of light Waves by a polarizer	16
1.10 Schematic structure of optical polarizing microscope configuration	18
1.11 Typical DSC curve demonstrating the appearance of several common Features	21
1.12 Reflection of X-rays from two planes of atoms in a solid	22
1.13 Scattering of X-ray powder diffraction	24
1.14 A typical example of X-ray spectra (Katoh <i>et al.</i> 2007)	25
1.15 Photograph of X-ray diffractometer (Dutrow and Clark 2009)	26
2.1 Classes of liquid crystals defined by molecular shape, the structures of their Condensed phases and their applications	33
2.2 (a) Schematic representations of Lyotropic LCs (b) sodium dodecylsulfate (soap) forming micelles, (c) a phospholipid (lecitine) present in cell membranes, in a bilayer lyotropic liquid crystal	

	arrangement.	34
2.3	Schematic representations of thermotropic liquid crystals (Calamitics)	35
2.4	General structure of calamitic LCs	36
2.5	Schematic representation of Crystal, Nematic and Isotropic LCs	37
2.6	Comparison of the structures of the uniaxial nematic phase (a), and the biaxial nematic phase (b). Representation (c) shows the local structure of the biaxial nematic phase made up of bent-core molecules.	38
2.7	Diphenyloxadiazole moiety with oxadiazole motif that exhibits biaxial N phase	39
2.8	Schematic representations of molecular arrangements in crystal and smectic LC phases	40
2.9	Schematic representations of SmA, SmC and N LC phases.	40
2.10	Molecular structure of the first series of discotic LCs discovered: the benzene hexa-n-alkanoate derivatives.	41
2.11	Representation of the general shape of discotic LCs	42
2.12	Schematic illustration of common mesophases observed for disc-shaped liquid crystals: N_D nematic discotic and Col_{hd} columnar hexagonal disordered. The molecules (in the N_D phase) or assemblies of molecules (Col_{hd} phase) align to the director n (adopted Kouwer 2003)	43
2.13	Molecular structure of some discotic mesogens: 2,3,6,7,10,11-hexakisethoxytriphenylene 3 and 3,10-dipentylperylene discogen derivative 4.	44
2.15	Structure of cholesteryl benzoate	45
2.16	Definitions of helical twist direction in chiral nematic phases	45
2.17	Phases of liquid crystals (a) Ordinary Nematic (b) Chiral Nematic and Helical macrostructure of the chiral smectic C (SmC^*) phase	47
2.18	The Chiral Smectic C; Ferroelectrics LC has a dipole moment perpendicular to its long axis and is chiral. (Crawford 2006)	47

2.19	witching ``ON`` and ``OFF`` of Ferroelectric Liquid Crystal between cross polarizer (Zhang <i>et al.</i> 2004.).	48
2.20	Photochromic molecules simultaneously change their molecular shape and dipole moment upon photoirradiation	49
2.21	Example of bent shaped (Banana shaped) liquid crystal	50
2.22	Example of banana-shaped mesogenes that exhibits the B ₂ phase	52
2.23	The dependence of the transition temperatures on the number of methylene units, n, in the flexible alkyl spacer for the CB.OnO.10 series	62
2.24	The dependence of the transition temperatures on the number of methylene units, n, in the flexible alkyl spacer for the azobenzene homologous series trimers	66
2.25	Molecular shapes of the all-trans conformation of trimers containing (a) odd- (n = 3) and (b) even- (n = 4) membered flexible spacers.	66
2.26	Schematic representations of various kinds of side chain liquid crystal polymers	70
2.27	Schematic representation (a) Rigid and flexible main chain calamitic liquid crystal polymer (b) side chain calamitic liquid crystal polymer(c) main chain and (d) side chain discotic liquid crystalline polymers	72
2.28	(a) Side chain discotic liquid crystal Polymer (b and c) rod-shape Liquid Crystal co-polymers	73
2.29	The possible photoisomerization mechanism and reorientation process of side-on bisazobenzene chromophore under the irradiation of 488 nm Ar ⁺ laser.	75
2.30	(a) Schematic representation of a typical LC cell (b) fabrication process for LCD with a single glass substrate	82
2.31	The geometry of a twisted nematic liquid crystal display (TNLCD) the device is shown with only one twist domain present at zero voltage	82
3.1	Reactions and conditions for the synthesis of azobenzene calamitic LCs (AZOn series): (i) NaNO ₃ /HCl/0 °C ; (ii) Phenol, °C; (iii) K ₂ CO ₃ /KI, Br(CH ₂) _n Br, Acetone; (iv) KOH/MeOH	87

3.2	Reactions and conditions for the synthesis of unsymmetric azobenzene trimer LCs (AZOTn series): (i) $\text{NaNO}_2/\text{HCl}/0^\circ\text{C}$; (ii) Phenol, 0°C ; (iii) $\text{K}_2\text{CO}_3/\text{KI}$, $\text{Br}(\text{CH}_2)_n\text{Br}$, Acetone; (iv) $\text{C}_{12}\text{H}_{10}\text{O}_2/\text{K}_2\text{CO}_3/\text{DMF}$	92
3.3	Reactions and conditions for the synthesis of bisazobenzene calamitic LCs (BAn series): (i) $\text{NaNO}_2/\text{HCl}/0^\circ\text{C}$; (ii) Phenol, 2°C ; (iii) $\text{Br}(\text{CH}_2)_n\text{Br}$, $\text{K}_2\text{CO}_3/\text{KI}$ (iv) MeOH , KOH	95
3.4	Reactions and conditions for the synthesis of non-symmetric bisazobenzene dimer calamitic LCs (BAOnO.3 series): (i) $\text{NaNO}_2/\text{HCl}/0^\circ\text{C}$; (ii) Phenol, 2°C K_2CO_3 (iii) $\text{Br}(\text{CH}_2)_n\text{Br}$; (ib) $\text{Zn}/\text{THF}/\text{Br}(\text{CH}_2)_2\text{CH}_3/\text{KI}$; (iv) $\text{K}_2\text{CO}_3/\text{KI}/\text{DMF}$	101
4.1	Representative Mass Spectrum of compound AZO4 for azobenzne calamitic (AZOn) series of liquid crystalline compounds	109
4.2	FT-IR Spectrum for azobenzne calamitic (AZOn) series of liquid crystalline compounds	112
4.3	Representative ^1H NMR Spectrum of compound AZO4 for azobenzne calamitic (AZOn) series of liquid crystalline compounds	113
4.4	Representative ^{13}C NMR Spectrum of compound AZO4 for azobenzne calamitic (AZOn) series of liquid crystalline compounds	114
4.5	DSC second heating and cooling traces of compound AZO3 ($10^\circ\text{C min}^{-1}$)	118
4.6	DSC second heating and cooling traces of compound AZO4 ($10^\circ\text{C min}^{-1}$)	118
4.7	DSC second heating and cooling traces of compound AZO5 ($10^\circ\text{C min}^{-1}$)	119
4.8	DSC second heating and cooling traces of compound AZO8 ($10^\circ\text{C min}^{-1}$)	119
4.9	Optical photomicrograph of AZO3 (a) Bâtnnotes on cooling at 102.5°C (b) Smectic A on heating to the isotropic liquid at 103.6°C (c) Smectic A on cooling from the isotropic liquid at 94.2°C (Cross polarizer magnification $\times 200$)	121
4.10	Optical photomicrograph of AZO8 obtained with a polarizing microscope (a) Bâtnnotes appearing on cooling from isotropic liquid at 98.5°C (b) Smectic A on heating to the isotropic liquid 109.5°C (c) Smectic A on cooling from the isotropic liquid 101.6°C (Cross polarizer magnification $\times 200$).	121

4.11	Representative X-ray pattern of smectic A for compound AZO5 at the liquid crystal state for AZOn series	123
4.12	3D optimized structures of compound AZO5 representing AZOn Series	123
4.13	FT-IR Spectrum for AZOTn series of liquid crystalline compounds	125
4.14	Representative ^1H NMR Spectrum of compound AZOT5 for AZOTn Series	126
4.15	Representative ^{13}C NMR Spectrum of compound AZOT5 for Un-symmetrical trimer azobenzene series of liquid crystalline compounds	127
4.16	DSC second heating and cooling traces of compound AZOT5 ($10\text{ }^{\circ}\text{C min}^{-1}$)	130
4.17	DSC second heating and cooling traces of compound AZOT6 ($10\text{ }^{\circ}\text{C min}^{-1}$)	130
4.18	Optical photomicrograph of AZOT5 obtained with a polarizing microscope (a) Nematic phase appearing on cooling from isotropic liquid at $209\text{ }^{\circ}\text{C}$ (b) Smectic A on heating to the isotropic liquid $109.5\text{ }^{\circ}\text{C}$ (c) Smectic A on cooling from the isotropic liquid $132.2\text{ }^{\circ}\text{C}$ (Cross polarizer magnification $\times 200$)	132
4.19	3D optimized structure of compound AZOT5 representing AZOTn series	133
4.20	Representative X-ray pattern of smectic A for compound AZOT5 at the liquid crystal state	133
4.21	Representative Mass Spectrum of compound BA4 for BAn Series	137
4.22	FT-IR Spectrum for precursor compounds and BAn series of liquid crystalline compounds	138
4.23	Representative ^1H NMR Spectrum of compound BA4 for BAn Series	139
4.24	Representative ^{13}C NMR Spectrum of compound BA4 for BAn Series	140
4.25	DSC heating and cooling traces ($10\text{ }^{\circ}\text{C / min}$) of compounds BA3 and BA4	143
4.26	DSC second heating and cooling traces of compound BA5 and BA6 ($10\text{ }^{\circ}\text{C min}^{-1}$)	143

4.27	DSC second heating and cooling traces of compound BA8 (10^0C min^{-1})	143
4.28	Photomicrograph of (a) Nematic (Scheiloren texture) of compound BA2 on cooling from isotropic liquid at 160.2^0C (b) Smectic A (Focal-conic texture) of compound BA4 on cooling from isotropic liquid at 125^0C (Cross polarizer magnification $\times 200$)..	146
4.29	Optical photomicrograph of BA5 obtained with a polarizing microscope (a) Smectic A on heating to the isotropic liquid at 149.2^0C (b) Scheiloren texture on cooling from isotropic liquid	146
4.30	Representative X-ray diffraction pattern of smectic A for compound BA6 at the liquid crystal state	147
4.31	3D optimized structure of compound BA6 representing BAn series	148
4.32	UV/Vis absorption spectra of bisazobenzene BA4 compound in Chloroform after irradiation (a) 365 nm (b) 253 nm (Sample was irradiated before at 365 nm)	150
4.33	UV/Vis absorption spectra of the thermal back reaction <i>cis-trans</i> Of bisazobenzene compound in chloroform	150
4.34	Plot of $\ln(E_{\infty} - E_t)$ as a function of time of bisazobenzene compound BA4 in chloroform, thermal back reaction	152
4.35	Representative Mass Spectrum of compound $\text{BAO}_8\text{O.3}$ at the liquid crystal state for BAOnO.3 Series	155
4.36	FT-IR Spectrum for BAOnO.3 series of liquid crystalline compounds	156
4.37	Representative ^1H NMR Spectrum of compound $\text{BAO}_8\text{O.3}$ for BAOnO.3 Series	157
4.38	Representative ^{13}C NMR Spectrum of compound $\text{BAO}_8\text{O.3}$ for BAOnO.3 Series	158
4.39	Second heating DSC thermograph for compound $\text{BAO}_3\text{O.3}$	162
4.40	Second heating DSC thermograph for compounds $\text{BAO}_4\text{O.3}$	162
4.41	Second heating DSC thermograph for compound $\text{BAO}_5\text{O.3}$	162

4.42	Second heating DSC thermograph for compounds $\text{BAO}_6\text{O.3}$ and $\text{BAO}_8\text{O.3}$	162
4.43	Photomicrograph of (a) Smectic A (Focal-conic texture) of compound $\text{BAO}_3\text{O.3}$ on cooling from isotropic liquid at $125\text{ }^{\circ}\text{C}$ (b) Smectic C texture of compound $\text{BAO}_5\text{O.3}$ on cooling from isotropic liquid at $160.2\text{ }^{\circ}\text{C}$ after mechanical stress (Cross polarizer magnification $\times 200$)	164
4.44	Optical photomicrograph of (c) Bâtonates forming SmA at $105.6\text{ }^{\circ}\text{C}$ and (d) SmA (Focal-conic texture) of compound $\text{BAO}_6\text{O.3}$ at $94.8\text{ }^{\circ}\text{C}$ (e) SmA of compound $\text{BAO}_8\text{O.3}$ obtained on cooling from isotropic liquid at $90.4\text{ }^{\circ}\text{C}$ with a polarizing microscope	164
4.45	Representative X-ray diffraction pattern of smectic A for compound $\text{BAO}_6\text{O.3}$ at the liquid crystal state for BAOnO.3 Series	166
4.46	3D optimized structure of compound $\text{BAO}_4\text{O.3}$ representing BAOnO.3 series	166
4.47	The dependence of the transition temperatures on the number of carbon atoms in the alkyl spacer for BAOnO.3 series	167

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
T _g	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
N _{col}	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.OnO.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-Tin oxide
TFT	Thin film transistor
TN LCD	Twisted nematic liuiqd crystal display
SiO ₂	Silicon oxide
DSC	Differential scanning caolorimetry