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Synthesis and characterization of some azobenzene compounds and their derivatives exhibiting liquid crystalline properties

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UNIVERSITI SAINS MALAYSIA

2010

Synthesis and characterization of some azobenzene compounds and their derivatives exhibiting liquid crystalline properties

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TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENT	ii
TABLE OF CONTENTS	iii
LIST OF TABLES	vii
LIST OF FIGURES	ix
ABSTRAK	xii
ABSTRACT	xiv
Chapter 1 Introduction	1
1.1 Overview of azobenzene	1
1.1.1 Isomerization of azobenzene induced by photon	3
1.1.2 The application of an azobenzene	4
1.1.2.1 Photo induced azo containing compounds for organic light-emitting devices	5
1.1.2.2 Azo as non-linear optical material	6
1.1.2.3 Azobenzene-containing copolymer	7
1.2 States of matter	8
1.2.1 Classification and types of liquid crystals	9
1.2.1.1 Calamitic liquid crystals	10
1.2.1.2 Discotic liquid crystals	10
1.2.1.3 Banana-shaped liquid crystals	11
1.2.2.1 Nematic phase	11
1.2.2.2 Smectic phase	12

1.2.2.3 Chirality 13

1.2.3 The influence of molecular structure on mesophase formatian 14

1.2.3.1 The structure of calamitic liquid crystals 14

1.2.3.2 Linking groups 15

1.2.3.3 Terminal groups 16

1.3 Binary mixtures 16

1.4 Objectives of the project 17

Chapter 2 Experimental 19

2.1 Chemicals 19

2.2 Instruments 19

2.3 Synthesis and characterization 21

2.3.1 Synthesis and characterization of 2,2'-(4-alkoxy-1,3-phenylene)-bis(1-(4-chlorophenyl)diazene) 21

2.3.1.1 Synthesis of 2,2'-(4-hydroxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene), **ABClOH** 23

2.3.1.2 Synthesis of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene), **ABClOC$_n$** (n = 6, 8, 10, 12, 14 and 16) 23

2.3.1.3 Characterization of compounds **ABClOC$_n$** (n = 6, 8, 10, 12, 14 and 16) 24

2.3.2 Synthesis and characterization of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(substitutedphenyl)diazene) 25

2.3.2.1 Synthesis of 2,2'-(4-hydroxy-1,3-phenylene)bis(1-(4-bromophenyl)diazene), **ABBrOH** 27

2.3.2.2 Synthesis of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-bromophenyl)diazene), **ABBrOC$_n$** (n =6, 8, 10, 12 and 14) 27

2.3.2.3 Synthesis of 2,2'-(4-hydroxy-1,3-phenylene)bis(1-(substitutedphenyl)diazene), **ABOCH$_3$** and **ABC$_2$H$_5$** 27

2.3.2.4 Synthesis of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(substituted-phenyl)diazene), **ABOCH$_3$ C$_{10}$** and **ABC$_2$H$_5$C$_{10}$** 27

2.3.2.5 Characterization of compounds **ABBrOC$_n$** (n = 6, 8, 10, 12 and 14), **ABOCH$_3$C$_{10}$** and **ABC$_2$H$_5$C$_{10}$** 28

2.3.3 Synthesis of 4,4'-bis(1-(substitutedphenyl)-2-(4-alkoxyphenyl)-diazene)-4-(4-benzylideneamino)phenol 28

2.3.3.1 Synthesis of 4-hydroxyphenyl-2-(4-chlorophenyl)diazane, **ClABOH** 30

2.3.3.2 Synthesis of 4-hydroxyphenyl-2-(4-bromophenyl)diazane, **BrABOH** 30

2.3.3.3 Synthesis of n-bromoalkoxyphenyl-2-(4-chlorophenyl)-diazane, **ClABOC$_n$** (n = 4, 6, 8 and 10) 30

2.3.3.4 Synthesis of n-bromoalkoxyphenyl-2-(4-bromophenyl)-diazane, **BrABOC$_n$** (n = 4, 6, 8 and 10) 31

2.3.3.5 Synthesis of 4-(4-hydroxybenzylideneamino)phenol, **SBOH** 31

2.3.3.6 Synthesis of 4,4'-bis(1-(4-chlorophenyl)-2-(4-alkoxyphenyl)diazene)-4-(4-benzylideneamino)phenol, **BNABClOC$_n$** (n = 4, 6, 8 and 10) 31

2.3.3.7 Synthesis of 4,4'-bis(1-(4-bromophenyl)-2-(4-alkoxyphenyl)diazene)-4-(4-benzylideneamino)phenol, **BNABBrOC$_n$** (n = 4, 6, 8 and 10) 32

2.3.3.8 Characterization of compounds **BNABXOC$_n$** (X = Cl and Br), (n = 4, 6, 8 and 10) 32

Chapter 3 Results and discussion for 2,2'-(4-alkoxy-1,3-phenylene)bis(1- (4-chlorophenyl)diazene), ABClOC$_n$ 33

3.1 Fourier transform infrared spectroscopy (FT-IR) 34

3.2 Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR) 37

3.2.1 ^{1}H NMR spectral assignment 38

3.2.2 ^{13}C NMR spectral assignment 41

3.3 Crystal structure of 2,2'-(4-(octyloxy)-1,3-phenylene)bis(1-(4-chlorophenyl)diazene), **ABClOC$_8$** 45

Chapter 4 Results and discussion for 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(substitutedphenyl)diazene), $ABXOC_n$ 52

4.1 Fourier transform infrared spectroscopy (FT-IR) 54

4.2 Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR) 56

4.2.1 ^{1}H NMR spectral assignment 56

4.2.2 ^{13}C NMR spectral assignment 60

4.3 Thermal and optical behavior 65

4.3.1 Binary Mixture with 2-(4-octanoxy-1-phenylen)bis(1-(bromophenyl)-diazene), **$PAZOC_8$** 67

Chapter 5 Results and discussion for 4,4'-bis(1-(4-substitutedphenyl)-2-(4-alkoxyphenyl)diazene)-4-(4-benzylideneamino)phenol 70

5.1 Fourier transform infrared spectroscopy (FT-IR) 72

5.2 Fourier transform nuclear magnetic resonance spectroscopy (FT-NMR) 75

5.2.1 ^{1}H NMR spectral assignment 76

5.2.2 ^{13}C NMR spectral assignment 79

5.3 Thermal and optical behavior 84

5.3.1 Thermal behaviour and texture observation 85

Chapter 6 Conclusions 87

6.1 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene), **$ABClOC_n$** (n = 6, 8, 10, 12, 14 and 16) 87

6.2 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(substitutedphenyl)diazene), **$ABXOC_n$** (n =6, 8, 10, 12 and 14 and X = Br, OCH_3 and C_2H_5) 87

6.3 4,4'-bis(1-(4-substitutedphenyl)-2-(4-alkoxyphenyl)diazene)-4-(4-benzylideneamino)phenol , **$BNABXOC_n$** (X = Cl and Br and the spacer chain lengths of n = 4, 6, 8 and 10) 88

REFERENCES 89

APPENDICES 94

LIST OF TABLES

		PAGE
Table 1.1	Linking groups and their common names	15
Table 2.1	Chemical list	19
Table 3.1	Colours, yields and melting points (^{o}C) of compounds **ABClOC$_n$**	33
Table 3.2	Empirical formula, molecular weight (M.W.) and CHN microanalytical data of compounds **ABClOC$_n$** (n = 6, 8, 10, 12, 14 and 16)	34
Table 3.3	Frequencies, ν (cm^{-1}) and relative intensities of the diagnostic bands in the FT-IR spectra of compounds **ABClOC$_n$** (n = 6, 8, 10, 12, 14 and 16)	39
Table 3.4	^{1}H NMR chemical shifts (ppm) of **ABClOC$_n$** in $CDCl_3$	38
Table 3.5	^{1}H-^{1}H COSY correlation data for compounds **ABClOC$_n$** in $CDCl_3$	39
Table 3.6	^{13}C NMR chemical shifts (ppm) of **ABClOC$_n$** in $CDCl_3$	42
Table 3.7	^{1}H-^{13}C HMQC and HMBC correlations for **ABClOC$_8$**	44
Table 3.8	Summary of crystal data, intensity data collection and structure refinement of compound **ABClOC$_8$** at 298 K	47
Table 3.9	Fractional atomic coordinates and isotropic temperature factors (Å^2), with standard deviations in the least significant digits in parentheses for compound **ABClOC$_8$**. For anisotropic atoms, the equivalent isotropic temperature factors are shown	48
Table 3.10	Bond lengths (Å), bond angles (^{o}) and torsion angles (^{o}) of compound **ABClOC$_8$**	49
Table 4.1	Colours, yields and melting points of compounds **ABBrOC$_n$** (n = 6, 8, 10,12 and 14), **ABOCH$_3$C$_{10}$** and **ABC$_2$H$_5$C$_{10}$**	52

Table 4.2	Empirical formula, molecular weight (M.W), CHN microanalytical data of compounds **ABBrOC$_n$** (n = 6, 8, 10, 12 and 14), **ABOCH$_3$C$_{10}$** and **ABC$_2$H$_5$C$_{10}$**	53
Table 4.3	Frequencies, ν (cm^{-1}) and relative intensities of the diagnostic bands in the FT-IR spectra of compounds **ABBrOC$_n$** (n = 6, 8, 12 and 14)	55
Table 4.4	^{1}H NMR chemical shifts (ppm) of **ABXOC$_n$** in $CDCl_3$	58
Table 4.5	^{1}H-^{1}H COSY correlation data for compounds **ABXOC$_n$** in $CDCl_3$	58
Table 4.6	^{13}C NMR chemical shifts (ppm) of **ABBrOC$_n$** in $CDCl_3$	62
Table 4.7	^{1}H-^{13}C HMQC and HMBC correlations for **ABBrOC$_8$**	62
Table 4.8	Transition temperatures of compounds **ABBrOC$_n$** (n = 6, 8, 10,12 and 14), **ABOCH$_3$C$_{10}$** and **ABC$_2$H$_5$C$_{10}$**	65
Table 4.9	Phase transition temperatures (^{o}C) of binary mixture of compounds **ABBrOC$_8$** and **PAZOC$_8$** with respective composition (%)	68
Table 5.1	Colours, yields and melting points (^{o}C) of compounds **BNABXOC$_n$**	71
Table 5.2	Empirical formula, molecular weight CHN microanalytical data of compounds **BNABXOC$_n$** X = Cl and Br and the alkyl chain lengths of n = 4, 6, 8 and 10	72
Table 5.3	Frequencies, ν(cm^{-1}) and relative intensities of the diagnostic bands in the FT-IR spectra of compounds **BNABXOC$_n$**	74
Table 5.4	^{1}H NMR chemical shifts (ppm) of **BNABXOC$_n$** in $CDCl_3$	77
Table 5.5	^{1}H-^{1}H COSY correlation data for compounds **BNABClOC$_4$** in $CDCl_3$	78
Table 5.6	^{13}C NMR chemical shifts (ppm) of **BNABClOC$_n$** in $CDCl_3$	81
Table 5.7	^{13}C NMR chemical shifts (ppm) of **BNABBrOC$_n$** in $CDCl_3$	82
Table 5.8	Transition temperatures of compounds **BNABXOC$_n$** (n =4, 6, 8 and 10, X = Cl and Br)	85

LIST OF FIGURES

		PAGE
Figure 1.1	Structure of azobenzene	1
Figure 1.2	Structure of the C.I. Acid Red 14	2
Figure 1.3	Structure of 4, 4'-cyanoamylbiphenyl	2
Figure 1.4	Structure of 4-(N-(2-hydroxyethyl)-N-ethylamino-4'nitroazobenzene	6
Figure 1.5	Structure of azobenzene polymethacrylate, PAzoMA	8
Figure 1.6	Structure of chlolesteryl benzoate	9
Figure 1.7	Calamitic liquid crystal	10
Figure 1.8	Structure of first discotic liquid crystal discovered in year 1977	11
Figure 1.9	Model structure of the nematic phase	12
Figure 1.10	Molecular alignment of SmA phase where molecules are oriented along the director	13
Figure 1.11	Molecular alignment of SmC phase with a tilt angle, θ	13
Figure 1.12	General structural template for calamitic liquid crystal	14
Figure 1.13	Possible associates in polar biphenyl analogues.	16
Figure 2.1	Synthetic scheme of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene)	22
Figure 2.2	Synthetic scheme of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-substitutedphenyl)diazene)	26
Figure 2.3	Synthetic scheme of 4,4'-bis(1-(4-chlorophenyl)-2-(4-alkoxyphenyl)diazene)-4-(4-benzylideneamino)phenol	29
Figure 3.1	Absorption frequency (cm^{-1}) and relative intensity associated with FT-IR bands for **ABClOC$_8$**	35

Figure 3.2	The atomic labeling scheme of compounds **ABClOC$_n$**	37
Figure 3.3	The COSY spectrum of compound **ABClOC$_8$**	39
Figure 3.4	The ^{13}C NMR chemical shifts (ppm) of **ABClOC$_8$**	41
Figure 3.5	The HMQC spectrum of compound **ABClOC$_8$**	43
Figure 3.6	The HMBC spectrum resulted from long-range ^{1}H-^{13}C connectivities for compound **ABClOC$_8$**.	44
Figure 3.7	Atom numbering scheme for crystal structure of **ABClOC$_8$**	45
Figure 3.8	Molecular packing diagram of compound **ABClOC$_8$**	46
Figure 4.1	Absorption frequency (cm^{-1}) and relative intensity associated with FT-IR bands for **ABBrOC$_8$**	54
Figure 4.2	The atomic labeling scheme for titled compounds **ABBrOC$_n$** (n = 6, 8, 10, 12 and 14)	56
Figure 4.3	The COSY spectrum of compounds **ABXOC$_8$**	57
Figure 4.4	The ^{13}C NMR spectrum of compounds **ABBrOC$_8$**	59
Figure 4.5	HMQC spectrum of compound **ABXOC$_8$**	63
Figure 4.6	The HMBC spectrum for compound **ABXOC$_8$**	64
Figure 4.7	Photomicrograph showing the crystal phase of compound **ABBrOC$_8$** at 56.3 ^{o}C.	66
Figure 4.8	Photomicrograph showing the nematic phase of compound **PAZOC$_8$** at 65.8 ^{o}C	66
Figure 4.9	Structure of 2-(4-octanoxy-1-phenylen)bis(1-(bromophenyl)diazene), **PAZOC$_8$**	67
Figure 4.10	Photomicrograph showing the nematic phase of compound **mixture 4** at 62.8 ^{o}C	69
Figure 5.1	The title compounds **BNABXOC$_n$** X = Cl and Br and the spacer chain lengths of n = 4, 6, 8 and 10	70
Figure 5.2	Absorption frequency (cm^{-1}) and relative intensity associated with FT-IR bands for **BNABClOC$_4$**	73

Figure 5.3	The atomic labeling scheme for compounds **BNABClOC$_4$**	75
Figure 5.4	The ^{1}H NMR spectrum of compound **BNABClOC$_4$**	76
Figure 5.5	The COSY spectrum of compounds **BNABClOC$_4$**	78
Figure 5.6	^{13}NMR for compound **BNABClOC$_4$**	80
Figure 5.7	Photomicrograph for **BNABClOC$_8$** which exhibits nematic phase at 75.2 ^{o}C during the I-N transition	84
Figure 5.8	Photomicrograph for **BNABBrOC$_8$** which exhibits nematic phase at 74 .9 ^{o}C during the I-N transition	84

Sintesis dan pencirian beberapa sebatian azobenzena dan terbitan yang bersifat hablur cecair

Abstrak

Siri pertama sebatian yang dikategorikan sebagai halobenzena berkonjugat, seperti, 2,2'-(4-hidroksi-1,3-fenilen)bis(1-(4-klorofenil)diazena) dengan struktur [$ClC_6H_4N=NC_6H_3OHN=NC_6H_4Cl$] telah disintesis melalui tindak balas pengkupelan pada suhu dan juga kepekatan yang dikawal. Proses ini menyebabkan ion benzenediazonium menukarganti pada bahagian *orto* dan *para* sebatian fenol seperti yang terbukti secara spektroskopi and analisis struktur sinar-X. Tindak balas seterusnya antara haloazobenzena yang telah disintesis dengan pelbagai bromoalkana dalam nombor genap ($C_nH_{2n+1}Br$ dengan n = 6, 8, 10, 12, 14 dan 16) telah menghasilkan sebatian baru yang terdiri daripada dua kumpulan azo [$ClC_6H_4N=NC_6H_3OHN=NC_6H_4Cl$]. Bagi siri kedua, sebanyak tujuh sebatian yang dikelaskan sebagai 2,2'-(4-alkoxy-1,3-fenilena)bis(1-(tertukargantifenil)diazena) dengan zat penukarganti bromo (Br), metoksi (OCH_3) and etil (C_2H_5) telah disintesis dan dipencilkan. Kesan induktif daripada zat penukargantian sepanjang sistem konjugat dalam sebatian diazo juga dikaji. Sifat termal berkaitan dengan kemasukan pelbagai rantai karbon (C_nH_{2n+1}) dengan nombor genap n dari n = 6, 8, 10, 12 dan 14 telah dikaji dengan mikroskop cahaya berkutub pada suhu tertentu. Kajian korelasi berhubungan dengan fasa peralihan, Tg(°C) bagi campuran binari sebatian (1-(4-klorofenil)-2-(4-oktiloksifenil)diazena, **PAZOC$_8$** (*para* –N=N-) dan 2,2'-(4-oktiloksifenil-1,3-fenilen)bi(1-bromo)diazene), **ABBrOC$_8$** dalam komposisi yang berbeza (%) telah dilakukan. Kajian sekarang menunjukkan bahawa campuran keempat yang mengandungi

75% $PAZOC_8$ dalam 25% $ABBrOC_8$ menurunkan suhu daripada 65.8 °C ke 62.7 °C di mana suhu yang lebih tinggi dikaitkan dengan 100% $PAZOC_8$. Dalam siri ketiga, tujuh sebatian 4,4'-bi(1-(4-feniltertukarganti)-2-(4-alkoksifenil)diazena)-4-(4-benzillidenamino)fenol telah disintesis secara memasukkan bes Schiff [$XC_6H_4N=NC_6H_4OC_nH_{2n}OC_6H_4CH=NC_6H_4OC_6H_4X$] ke dalam sistem haloazobenzena dengan kumpulan alkil yang bernombor n genap bertindak sebagai penyambung antara dua kumpulan. Ciri mesomorfik yang unik bagi 4,4'-bis(1-(4-feniltertukarganti)-2-(4-alkoksifenil)diazena)-4-(4-benzilidenamino)fenol ditunjukkan oleh kehadiran tekstur schlieren nematik di bawah cahaya terkutub apabila sebatian ini disejukkan pada kadar -20 ^oC per min. Walau bagaimanapun, kesemua ahli didapati mempamerkan fasa nematik monotropik melalui penyejukan melampau pada julat suhu 73.4-77.1 ^oC, kecuali bagi n = 4.

Synthesis and characterization of some azobenzene compounds and their derivatives exhibiting liquid crystalline properties

Abstract

The first series of compounds categorized as conjugated haloazobenzene typically 2,2'-(4-hydroxyl-1,3-phenylene)bis(1-(4-chlorophenyl)diazene) [$ClC_6H_4N=NC_6H_3OHN=NC_6H_4Cl$] were synthesized by coupling reaction under controlled temperature and concentration. This particular process has led to the attack of benzenediazonium upon both *ortho* and *para* positions of phenol as evident by spectroscopic and X-ray structural analyses. The subsequent reactions between the earlier synthesized haloazobenzenes with various bromoalkanes in even-parity ($C_nH_{2n+1}Br$ where n = 6, 8, 10, 12, 14 and 16) have resulted in the formation of new compounds with dual-azo groups [$ClC_6H_4N=NC_6H_3OHN=NC_6H_4Cl$]. As for second series, a total of seven compounds classified as 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(substitutedphenyl) diazene) of which the substituents are bromo (Br), methoxy (OCH_3) and ethyl (C_2H_5) have been synthesized and isolated. The inductive effect from these substituents residing along the conjugated system in these dual-azo compounds was studied. The thermal properties associated with the incorporation of various carbon chains (C_nH_{2n+1}) of even-parity n ranging from n = 6, 8, 10, 12 and 14 have also been studied using thermally-controlled polarizing optical microscope. A correlation study in relation to phase transition, Tg (^oC) of binary mixture of compounds *para* –N=N-, 1-(4-chlorophenyl)-2-(4-octyloxyphenyl)diazene, **PAZOC$_8$** and 2,2'-(4-octyloxyphenyl-1,3-phenylene)bis(1-bromo)diazene), **ABBrOC$_8$** in varied composition (%) has been carried

out. Present study reveals that the first mixture containing 75% of **PAZOC$_8$** in 25% of **ABBrOC$_8$** decreases the temperature from 65.8 °C to 62.7 ^{o}C in which the higher temperature referred to 100% **PAZOC$_8$**. In the third series, seven compounds of 4, 4'-bis(1-(4-substitutedphenyl)-2-(4-alkoxyphenyl)diazene)-4-(4-benzylideneamino)phenol were synthesized by incorporating Schiff base [$XC_6H_4N{=}NC_6H_4OC_nH_{2n}OC_6H_4CH{=}NC_6H_4OC_6H_4X$] into the haloazobenzene system whereby the even n number of alkyl group acting as spacer between the two moieties. The unique feature with respect to the mesomorphic properties for 4, 4'-bis(1-(4-substitutedphenyl)-2-(4-alkoxy-phenyl)-diazene)-4-(4-benzylideneamino)phenol has been exemplified by the presence of nematic schlieren texture under polarized light when this compound was cooled down at the rate of -20 ^{o}C per min. However, all members were found to exhibit the monotropic nematic phase by super cooling at the range of 73.4-77.1 ^{o}C, except for n = 4.

Chapter 1 Introduction

1.1 Overview of azobenzene

Azobenzene is a chemical compound composed of two phenyl rings linked by a N=N double bond. The term 'azobenzene' or simply 'azo' is often used to refer to a class of molecules that share the core azobenzene structure with different substituted groups extending from the phenyl rings. These compounds should be formally referred as diazenes [Koppes 2008, Albertin 2003 and Ahmed 2004]. The molecular structure for azobenene can be shown as follow:

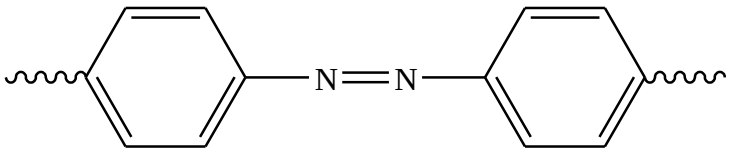


Figure 1.1 Structure of azobenzene

The diazene strongly absorbs light and was historically used as dyes in various industries. These azobenzene derivatives are commonly used as colouring dyes wherein the different degrees of conjugation and the substituents attached to the conjugated system led to different colours [Okada 2008, Pinheiro 2004 and Venkata Mohan 2007]. More than 50% of all commercial dyes are azo dyes [Aleboyeh 2008], such as C.I. Acid Red 14 (Figure 1.2).

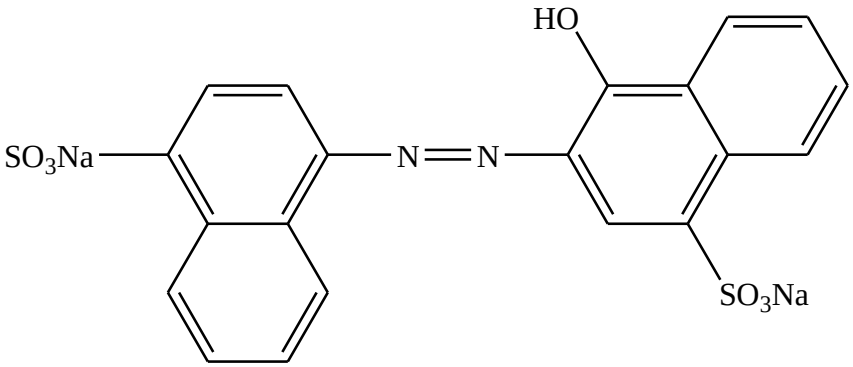


Figure 1.2 Structure of the C.I. Acid Red 14

In addition, the thermo- and photoisomerization of azobenzene derivatives are also important for the development in information recording systems such as high-density optical data stroge, optical switching, displays and nonlinear optics [Gayathri 2008, Yazdanbakhsh 2009 and Xu 2008]. The unique properties of azobenzene in relation to its photoisomerization behaviour can be ascribed to the existence of *cis* and *trans* conformations which are switchable and the intensity in switching is dominated by the particular wavelength of light. The *cis* isomer is genarally found to be less stable than the *trans*. This can be ascribed to the fact that *cis* isomer has distorted configuration and is less delocalized than the *trans* configuration. Thus, *cis*-azobenzene is thermally relaxed and change the conformation from *cis* to *trans* via *cis*-to-*trans* isomerization [Jursic 1996]. Another interesting feature of azobenzene compounds lies on its potential to form rod-like molecules leading to the materials exhibiting liquid crystalline properties [Saad 1998], example of azo type rod-like liquid crystal is shown in Figure 1.3.

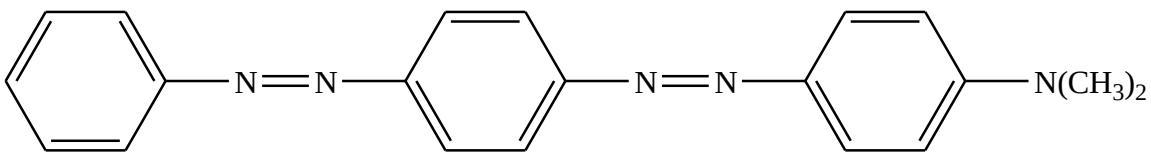


Figure 1.3 Structure of 4, 4’-cyanoamylbiphenyl

1.1.1 Isomerization of azobenzene induced by photon

Photoisomerization can be referred as molecular behaviour in which structural change between isomers is caused by photoexcitation. The aforementioned structural change is referred to the conformational transition from *cis* (close-ring) to *trans* (open-ring) or vice versa. Additionally, both reversible and irreversible pathways exist for photoisomerization reactions [Pu 2005].

Thus, photoisomerization of azobenzene can start from either the *cis* or the *trans* isomer since both isomers have well defined absorption bands in the UV–visible region. The photoisomerization process proceeds differently on two different electronically excited states. The first state involved the inversion path for $n \rightarrow \pi^*$ (S_1 state) excitation [Simonov 2001] and the second state involved the rotation path about the N-N bond, with disruption of the double bond, or via an inversion, with a semi-linear and hybridized transition state. It has been suggested that the *trans*-to-*cis* conversion occurs via rotation of $\pi \rightarrow \pi^*$ (S_2 state) excitation [Angeli 1996 and Martin 1997].

Theoretical investigations on the mechanism of the photoisomerization of azobenzene typically use static approaches to search for minimum energy paths by connecting some singular points. [Badawi 2005 and Demaison 1997].

1.1.2 The application of azobenzene

It is an undeniable fact that the investigation upon the azo dyes and the findings reported so far has served as impetus toward encouraging the researchers to look into its usage, namely optical data storage, optical switching, polarization holography, optical modulation, nonlinear optics and photolabile surfactants. There are many recent reports on the research of photoinduced motions [Okutan 2009, Lutfor 2009, Yu 2008, Chen 2008 and Xu 2008]. In particular, photoinduced motion is referred to the process in which the azo moieties are connected to the side chain of the polymer or doped into the polymer matrix [Jafari 2008, Teyssedre 2007 and Raghu 2007].

It is well known that the substituents of the azo chromophores [Xie 2001] play an important role in molecular motion during photoisomerization. Ikeda *et. al*., 1995 reported that the azobenzene liquid crystal films showed a nematic phase in trans isomer but no liquid crystal phase in cis isomers. By using a laser pulse, a nematic to isotropic phase transition we're observed without the changing temperature or solvent. Many other efforts have been made to investigate the motion of the azobenzene derivatives by introducing substituents which were attached to the azobenzene, such as the aminoazobenzene group which possessed longer *cis* lifetimes than pseudostilbene group. Consequently, aminoazobenzenes are also treated as good candidates for photoinduced birefringence materials when a blue or green laser is used as a pump source. Moreover, potential hydrogen bondings in azobenzenes also contributed to the photoinduced effect. Intramolecular hydrogen bonding, formed by introducing *o*-hydroxyl phenyl moiety into azobenzene has significant effect on liquid crystalline properties [Ya 2008, Altomare 2005 and Shembekar 2006] .

1.1.2.1 Photoinduced azo containing compounds for organic light-emitting devices

Organic light-emitting devices (OLEDs) have attracted much attention owing to their advantages of low-power consumption, high brightness, high contrast and potential applications to full color flat panel displays. Luminescent materials for OLED devices are generally classified into two groups: fluorescence and phosphorescence [Rajeswaran 2009]. The OLED based on phosphorescent materials can significantly improve electroluminescence performance because both singlet and triplet excitons can be harvested for light emission. Theoretically, the internal quantum efficiency of phosphorescent emitters can approach 100%.

The irradiation with an interference pattern of polarized laser beams was observed due to reversible induction of azo-dye polymer, for example 4-(N-(2-hydroxyethyl)-N-ethyl)amino-4-nitroazobenzene (Figure 1.4)[Rocha 2002]. In detail, the chromophores inside azo-dye polymer work as molecular trucks, pushing or pulling the whole polymer chains to which they are grafted. Those processes will lead to a quantitative photo driven mass transport. Finally, the photo-patternable azo-dye polymer is formed and its absorption will shift down to the blue region. While great success has been achieved in the development of green phosphorescent materials, the design and synthesis of efficient red phosphorescent materials are basically more difficult because their luminescence quantum yields tend to decrease as the emission wavelength increases in accordance with low energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) [Zhao 2000, Simonov 2001 and Rocha 2002].

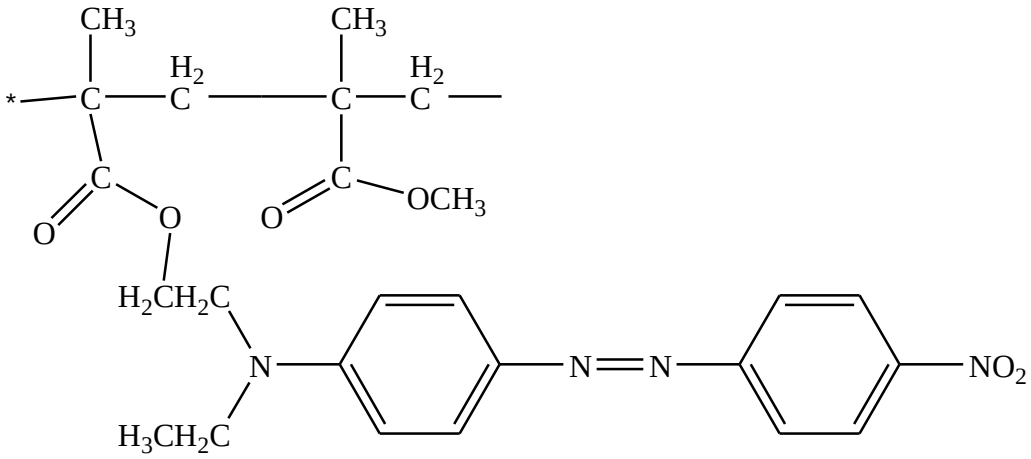


Figure 1.4 Structure of 4-(N-(2-hydroxyethyl)-N-ethyl)amino-4-nitroazobenzene

1.1.2.2 Azo as non-linear optical material

Azobenzenes are well-known compounds used primarily as synthetic colourants for dye industry. In addition to its application in dye industry, azobenzenes possess interesting properties such as the reversible *cis–trans* photoisomerization [Li 2006] about the –N=N- bond and non-linear optical (NLO) effect related to the donor–acceptor azobenzenes. NLO effects require either non-centrosymmetric or polar packing (space group) of the NLO active material. It has been claimed that controlling the packing of an achiral NLO molecule is a very difficult task. Hence, it is easier to make the NLO candidate chiral and use its inherent chirality to prevent centrosymmetric packing.

In designing new materials to fulfill the needs of advanced technology, chiral azobenzene systems have proven to be useful candidates. In addition to attributes mentioned above, they also display optical activity which can be observed by circular dichroism (CD) measurement. Recently, several studies of azobenzene systems with chiral functionality have been studied since they provide properties useful in various

research topics including molecular switches, optically active polymers, liquid crystals, and non-linear optics [Walba 1999 and Martin 2002].

1.1.2.3 Azobenzene-containing copolymers

Azobenzene amphiphilic copolymers showed photoinduced reversible changes [Li 2004] in morphology of micellar aggregates. Amphiphilic block copolymer scan self-assemble to form micellar aggregates of various morphologies including star micelles, crew-cut micelles, rods, and vesicles [Wang 2004 and Raposo 2005].

The azobenzene polymethacrylate, PAzoMA (Figure 1.5) is copolymers contain a hydrophobic side-chain which have liquid crystalline properties. With the presence of water, the aggregation of the hydrophobic block would be induced and the insoluble PAzoMA would form the compact core of the micelle or the bilayer membrane of vesicles.

As a result, the LC order formed by azobenzene mesogens may persist inside the compact regions under UV light irradiation, azobenzene in the elongated *trans* form is converted to the contracted *cis* form which is known to destabilize the liquid cystal phase and induce a photochemical LC to isotropic phase transition. If this happens, a strong disruption effect should be expected because it arises not only from the conformational change of azobenzene but also from the phase transformation in the core or membrane regions. Since the azobenzene polymer in the isotropic state is more fluid than in the LC state, therefore such optically plasticized compact regions of PAzoMA under UV light may be deformed more easily due to, among others, a lower mechanical stability [Wang 2004]

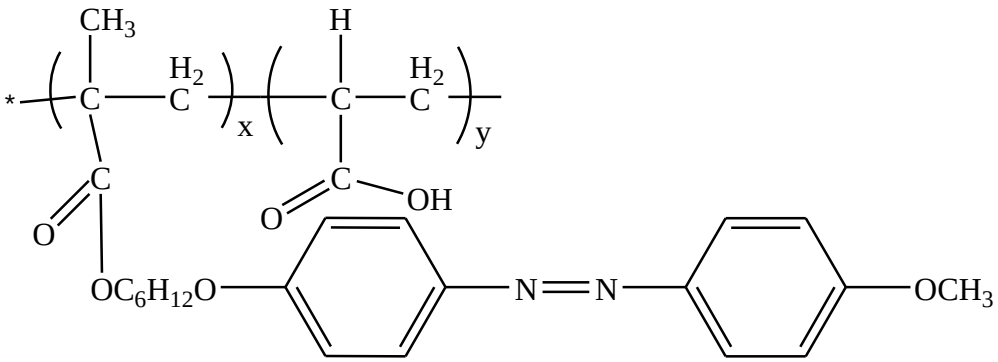


Figure 1.5 Structure of azobenzene polymethacrylate, PAzoMA

1.2 States of matter

The liquid crystal phase is a partially ordered, anisotropic fluid, which lies between the solid and isotropic liquid phases [Sudhakar 2000]. In the crystal phase the molecules have a high degree of order, occupying fixed positions in the lattice, which is characterized by translation of the unit cell. Therefore, the molecules are positioned in fixed orientations with no translational freedom.

In the isotropic liquid phase only a short-range order dominates. The molecules are mobile and have no orientation with respect to each other as the molecular axes are able to tumble freely. The liquid crystal phase shares both crystal and liquid properties, 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 found in the isotropic liquids. Specifically, we can quantitatively classify the amount of orientational order between a liquid and solid state by using the scalar order parameter, S, which gives 0 and 1, respectively [Petrov 2000 and Ribeiro 2001].

The first liquid crystal extracted from carrots (shown in Figure 1.6) has been reported by an Austrian botanist, Friedrich Reinitzeran, in 1888. The reported structure possesses “double” instead of one melting point properties, which it melted

at 145.5 ^{o}C into a cloudy fluid, prior to turn into a clear solution at 178.5 ^{o}C [Ribeiro 2001 and Hird 2001].

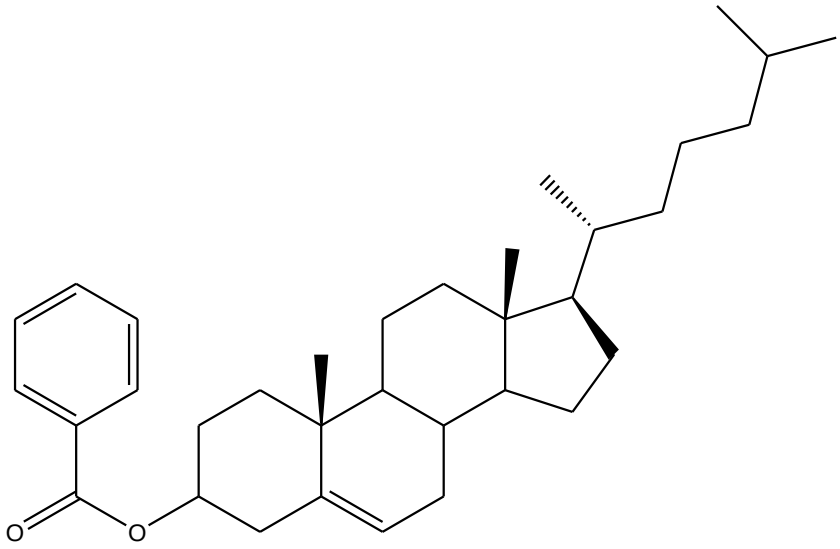


Figure 1.6: Structure of chlolesteryl benzoate

1.2.1 Classification and types of liquid crystal phases

Liquid crystalline materials can generally be divided into two categories:

i) The thermotropic

ii) The lyotropic

The presence of mesophase in thermotropic liquid crystal is temperature dependent. It can be further distinguished into calamitic for rod-like, discotic for disk-like, and sanidic for brick- or lath-like molecules, respectively, based on the diverse molecular shape of the constituent molecules [Attard 1997 and Mckenna 2004].

Lytropic liquid crystal are two-component systems where an amphiphilic is dissolved in a solvent. Thus, lyotropic mesophases are concentration and solvent dependent. The amphiphilic compounds are characterized by two distinct moieties, a hydrophilic polar and a hydrophobic region. These structures are formed by the

micro-phase segregation of two incompatible components on a nanometer scale [Bissell 1995].

1.2.1.1 Calamitic liquid crystals

Calamitic or rodlike liquid crystals are those mesomorphic compounds that possess an elongated shape. The rigid core is essential for the formation of liquid crystal by interacting with other molecules. However, the rigid core alone is not sufficient to generate liquid crystal. Hence, the phases should have certain flexibility to ensure the stabilization of the molecular alignment within the phase structure. As a result, rod-like molecular length (L) is significantly greater than the molecular breadth (H), as depicted in Figure 1.7 [Sakurai 1984].

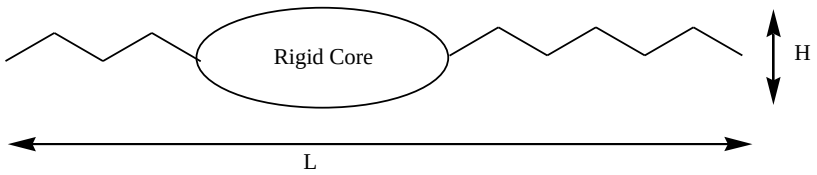
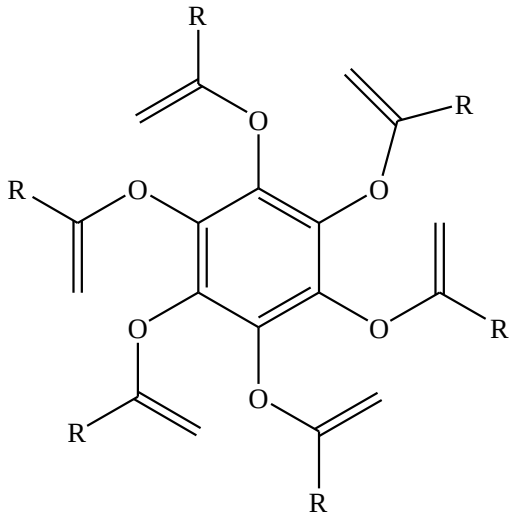


Figure 1.7 Calamitic liquid crystal.

1.2.1.2 Discotic liquid crystal

The first series of discotic compounds were discovered in year 1977 (Figure 1.8). The mesophase is as analogous as the hexa-substituted benzene derivatives. Disk-shaped mesogens can orient themselves in a layer-like discotic nematic phase. If the disks pack into stacks, the phase is called discotic columnar [Chandrasekhar 1997].



$R = C_4H_9$ to C_9H_{19}

Figure 1.8: Structure of first discotic liquid crystals discovered in year 1977

1.2.1.3 Banana-shaped liquid crystals

Banana-shaped liquid crystals formed by bent-core mesogens. Banana-shaped liquid crystal molecules have the ability to induce liquid crystalline mesophase that exhibit spontaneous polarization in the absence of chiral groups in their molecular structure. The special ability of band-shaped molecules made them distinctly different from those calamitic materials, with some unusual properties. The most striking phenomenon of banana phases is the occurrence of polar order and chiral properties from achiral molecules. This behaviour is attributed to steric packing effects of the bow-shaped molecules [Prasad 2004].

1.2.2.1 Nematic phase

Nematic phase is the one with the least order and the highest symmetry. It exhibits solely orientational order of the long molecular axis. In Figure 1.9, the spatial and temporal average of the long molecular axis is called the director n. The

angle θ denotes the deviation of the long molecular axis of an individual mesogen from the director [Rahman 2007].

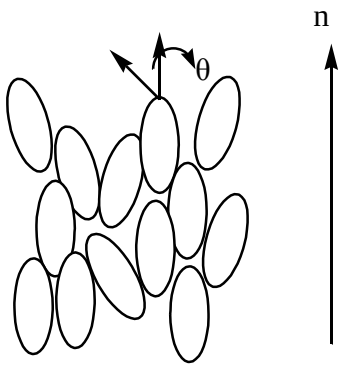


Figure 1.9 Model structure of the nematic phase

1.2.2.2 Smectic phase

When the crystalline order is lost in two dimensions, it will form a two-dimensional liquid crystal called smectic. The smectic liquid crystals have layered structures, with a well defined interlayer spacing which can be measured by X-ray diffraction. The smectic molecules exhibit some correlations in their positions in addition to the orientational ordering. In most smectic phases, the molecules are mobile in two directions and can rotate about one axis. The interlayer attractions are weak in comparison to the lateral forces between the molecules and the layers are able to slide over one another relatively. The molecular centers of mass are isotropically oriented with no positional correlation being observed within or across the layer planes. On the topic of SmA phase, the director *n* from optic axis are perpendicular to the smectic layer plane, as shown schematically in Figure 1.10. Another smectic phase with one dimensional positional order is the SmC phase, which looks similar to SmA, only with the director being tilted by an angle, θ as shown in Figure 1.11 [Jeon 1999 and Skarabot 1999].

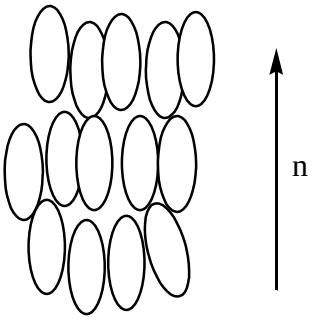


Figure 1.10 Molecular alignment of SmA phase where molecules are oriented along the director

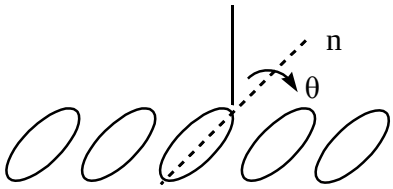


Figure 1.11 Molecular alignment of SmC phase with a tilt angle, θ

1.2.2.3 Chirality

Chirality is an inherent property of many systems, ranging from the well known molecular asymmetry, helical biomolecules, shells, snails, and plants growing in a one-handed fashion. In liquid crystal, chirality can be introduced in several different ways. Chirality can directly be introduced within the molecule by incorporation of chiral elements or chiral centers. Another way is the addition of a small amount of a chiral dopant molecule to an achiral host phase. The introduction of chirality into mesogenic systems has a tremendous impact on the respective liquid crystalline behaviour [Rokunohe 2004].

1.2.3 The influence of molecular structure on mesophase formation

The correlations between the chemical constitution and the liquid crystalline properties were largely developed by Vorländer in 1906. The most frequently found building block of mesogens consists of various types of 1, 4-disubstituted aromatic rings. Generally, the molecules with a rod-like geometrical shape are favourable to form liquid crystal molecules [Zienkiewicz 1997].

1.2.3.1 The structure of calamitic liquid crystals

Liquid crystals derived from rod-like molecules have been the most comprehensively studied. The general templates that can be used to describe the structure of calamitic mesogens are illustrated in Figure 1.12.

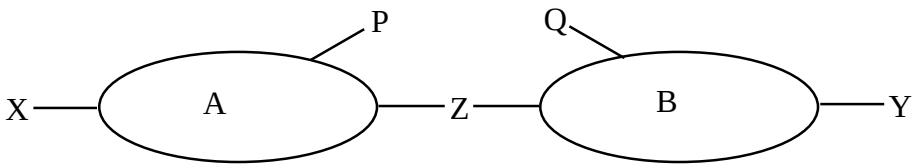


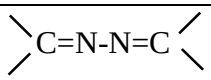
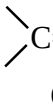
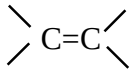
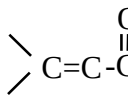
Figure 1.12 General structural templates for calamitic liquid crystal

Certain rigidity is required to provide the anisotropic molecular structure. This is achieved by linearly and directly linked aromatic rings (A and B), by a linking group (Z) which maintains the linearity of the central core. The terminal groups (X and Y), usually alkyl or alkoxy chains, are joined directly to the central core [Belmar 1999] to provide a certain degree of flexibility. However, one side of the terminal group can be just a small polar substituent, such as NO_2, CN, alkyl or halogen atoms. The lateral substituents (P and Q), generally detrimental to the formation of liquid crystal phases used to modify the mesophase morphology and the physical properties of liquid crystal to enhance properties for applications such as resolution of display properties [Dixit 2009 and Achten 2004].

1.2.3.2 Linking groups

Linking groups are normally those structural units, other than direct bond or bridging groups, which connect one part of a core to another. Linking group must maintain the linearity of the core. The common linking groups are shown in Table 1.1 [Petrov 2001, Belmar 1999, Yoshizawa 2004, Takemoto 2002 and Attard 1997].

Table 1.1 Linking groups and their common names

Compound	Common name	
-N=N-	Azo	A urinary tract analgesic
	Azoxy	N-oxides of azo compounds.
	Amide	An acyl group linked to a nitrogen atom.
-NH-NH-	Hydrazine	An inorganic chemical compound with the formula N_2H_4.
	Azine	Contains one or more atoms of nitrogen with a ring structure resembling that of benzene.
	Schiff bases	Contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group.
	Nitrone	N-oxide of an imine and a functional group in organic chemistry.
	Thioester	The bonding of sulfur with an acyl group.
	Ester	An inorganic or organic acid in which at least one -OH (hydroxyl) group is replaced by an -O-alkyl (alkoxy) group.
$-CH_2-O-$	Ether	An oxygen atom connected to two (substituted) alkyl or aryl groups.
-C≡C-	Alkyne	At least one triple bond between two carbon atoms.
	Trans alkene	An unsaturated chemical compound containing at least one carbon-to-carbon double bond with isomer trans position.
	Trans cinnamate	The ester of cinnamic acid and alcohol

1.2.3.3 Terminal groups

The terminal substituents are used to fine-tune mesomorphic properties. For example, the terminal alkyl groups have been used to raise or lower transition temperatures. The odd-even numbers of carbon atoms in the alkyl groups give pronounced odd-even effect in the N-I and SmA-N transitions which attenuate with the increasing spacer length. The terminal polar group show tendency to form dimer, for example biphenyl analogous compounds with CN as the terminal substitutent. The sketches of the possible dimers to illustrate the different effective length to breadth are shown in Figure 1.13 [Achten 2004].

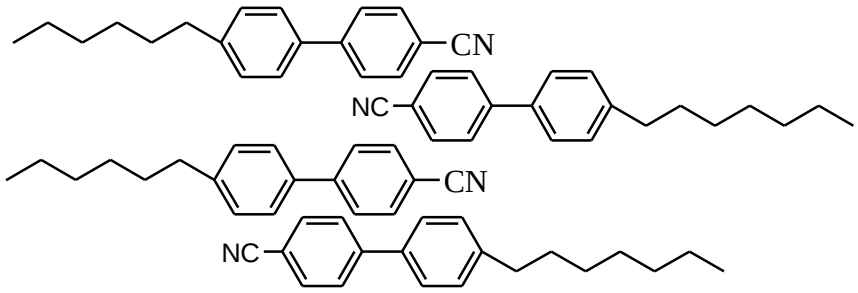


Figure 1.13 Possible associates in polar biphenyl analogues.

1.3 Binary mixtures

Liquid crystalline compounds and their mixture offer a unique opportunity to examine structure-property relationships in their condensed phase. In general, binary mixture of liquid crystalline materials exhibit eutectic behaviour in their crystalline-anisotropic transition temperatures, whereas their mesophase-isotropic transition temperature vary linearly with composition [Ha 2009 and Hird 2001].

1.4 Objectives of the project

Azo dye have attracted much attention for potential use in optical storage applications because of the reasonable photo-fatigue resistance and the transformation of molecular shape between *cis* (close-ring) and *trans* (open-ring) photoisomerization. Azo dye liquid crystals have reasonable dichroic ratio reflective liquid crystal device which are of considerable interest owing to their remarkably lower power consumption. Azobenzene liquid crystal films showed a nematic phase in *trans* isomer but no liquid crystal phase in *cis* isomers. It undergoes a transition from nematic to isotropic phase without changing temperature or solvent. Regarding the present study, three series of novel haloazobenzene have been synthesized. In view of the general objectives for these three series are listed as follows:

1. To synthesize and characterize novel azobenzene containing three aromatic rings with variable length of the flexible tails ranging from C_4H_9Br to $C_{18}H_{37}Br$.
2. To characterize all intermediate and title compounds with analytical techniques:
    - CHN microanalysis
    - Fourier transform infrared (FTIR)
    - Nucleus magnetic resonance (NMR)

        1D: ^{1}H NMR, ^{13}C NMR, DEPT 90, DEPT 135,

        2D: ^{1}H-^{1}H COSY, ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC.

3. To investigate the correlation between the length of the flexible tail and substituted group with the change in liquid crystalline behaviour.
4. To study the thermal and optical behaviour of azobenzene derivatives over the different temperatures.

Chapter 2 Experimental

2.1 Chemicals

List below are chemicals which were used for syntheses of all intermediates and final compounds.

Table 2.1 Chemicals list

Chemical	Purity	Company
1-Bromobutane	98%	Merck
1-Bromooctane	98%	Merck
1-Bromodecane	98%	Merck
1-Bromododecane	97%	Merck
1-Bromotetradecane	97%	Merck
1,6-Dibromohexane	97%	Merck
1,8-Dibromooctane	97%	Merck
1,10-Dibromodecane	97%	Merck
4-Bromoaniline	98%	Merck
4-Chloroaniline	99%	Merck
Sodium nitrite	98%	R & M Chemical
Sodium hydroxide	99%	R & M Chemical
4-Hydroxybenzaldehyde	95%	Acros
1-Bromohexane	98%	Acros
Phenol	99%	Sigma-Aldrich
Potassium carbonate	99%	Fisher Scientific

2.2 Instruments

i. The melting points of the intermediary and title compounds were measured by Gallenkamp melting point apparatus.

ii. The thin layer chromatography (TLC) analyses were performed by using aluminum-backed silica gel plates (Merck 60 F254). Silica gel 60 (0.040-0.063 mm, 230-400 mesh ASTM) in a 40 cm column is used as stationary phase.

iii. The Fourier transform infrared (FT-IR) analyses were conducted on a Perkin Elmer 2000-FT-IR spectrophotometer. The measurement was carried out with the samples mixed with KBr and the ultimate mixture was pressed into disc

form under 7 ton pressure. The KBr discs were prepared from mixture of samples with dry KBr in homologenous ratio of 1:10.

iv. The CHN microanalyses were carried out on a 2400 LS Series CHNS/O microanalyzer.

v. Both 1D ^{1}H and ^{13}C Fourier transform nuclear magnetic resonance (FT-NMR) and 2D ^{1}H-^{1}H correlation spectroscopy (COSY), ^{1}H-^{13}C heteronuclear multiple quantum correlation (HMQC) and ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC) analyses were recorded using Bruker 300 MHz and 400 MHz Ultrashield spectrometers.

vi. The X-ray crystal structure analytical data were collected using a Rigaku AFC10 coupled with Saturn CCD Detector at the Tokyo Institute of Technology, Japan.

vii. The optical properties of the compounds were determined using a Carl Zeiss Axioskop 40 polarizing microscope equipped with Mettler FP52 hot-stage.

2.3 Synthesis and characterization

All compounds were synthesized, purified, recrystallized and analyzed at ambient temperature by conventional method of which the details of synthesis and characterization can be described as follows:

2.3.1 Synthesis and characterization of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene)

The intermediary 2,2'-(4-hydroxy-1,3-phenylene)bis(1-(4-chlorophenyl)-diazene) and title compounds 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene) were synthesized based on the synthetic scheme as shown in Figure 2.1.

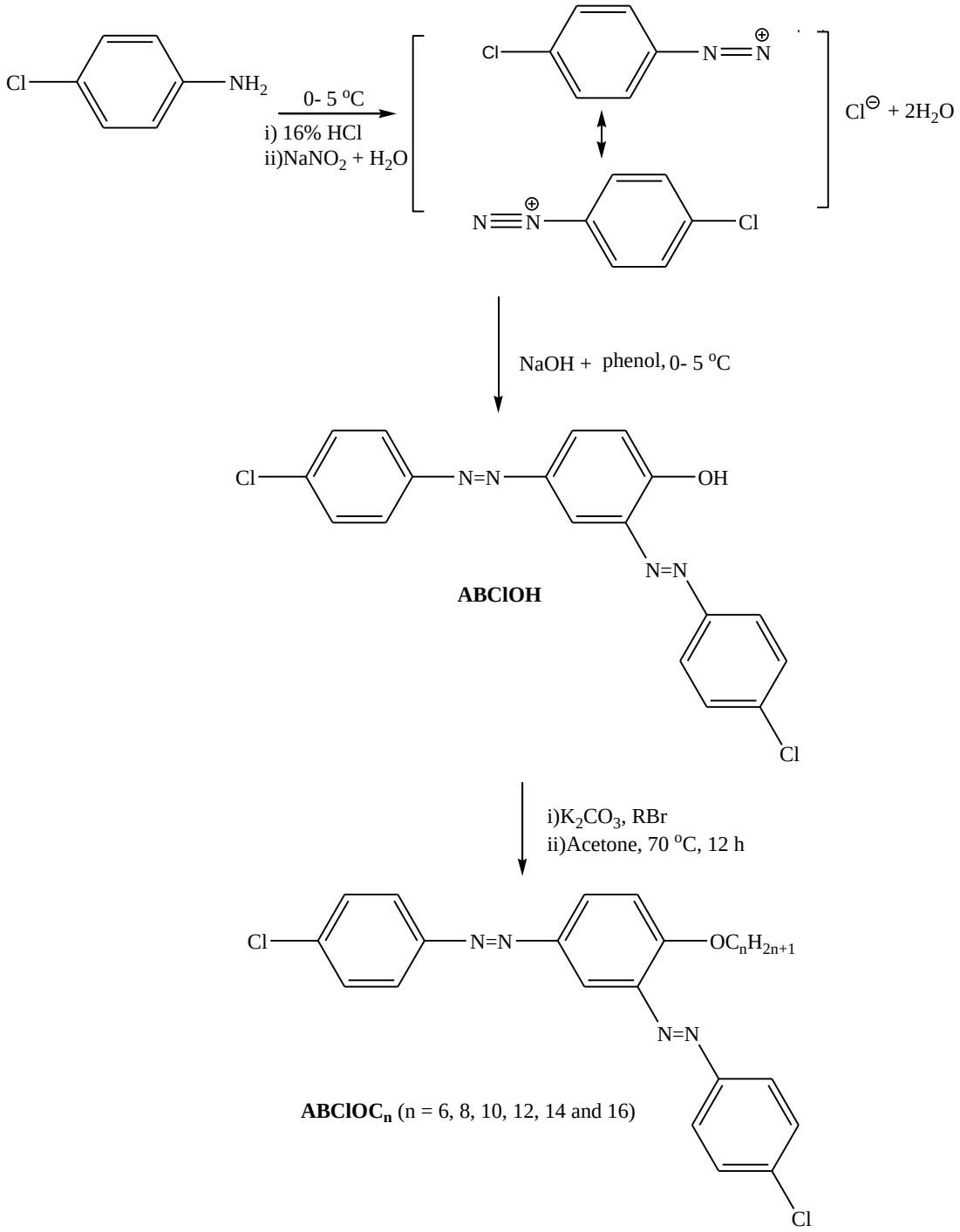


Figure 2.1: Synthetic scheme of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene)

2.3.1.1 Synthesis of 2,2'-(4-hydroxy-1,3-phenylene)bis(1-(4-chlorophenyl)-diazene), ABClOH

Compound **ABClOH** was synthesized by adding an aqueous solution of sodium nitrate (III), $NaNO_2$ to a mixture of 4-chloroaniline in the concentrated hydrochloric acid, HCl wherein the temperature of the mixture was kept within 0-5 ^oC. The cold mixture was subsequently added dropwise to a cold mixture of phenol, sodium hydroxide, NaOH and water. Acidification with aqueous HCl resulted in the yellow precipitate. It was filtered and dried before being recrystallized from acetone.

2.3.1.2 Synthesis of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-chlorophenyl)diazene), $ABClOC_n$ (n = 6, 8, 10, 12, 14 and 16)

The compound **ABClOH** was added to a mixture containing 1-bromooctane and K_2CO_3 anhydrous in acetone. The reaction mixture was then refluxed for 24 hours. The crude precipitate thus obtained was recrystallized from the mixture of chloroform and hexane whereupon the red crystal of $\mathbf{ABClOC_8}$ was collected.

The compounds $\mathbf{ABClOC_6}$, $\mathbf{ABClOC_8}$, $\mathbf{ABOClC_{10}}$, $\mathbf{ABClOC_{12}}$, $\mathbf{ABClOC_{14}}$ and $\mathbf{ABClOC_{16}}$ were carried out following the synthetic scheme presented in Figure 2.1.

2.3.1.3 Characterization of compounds $ABClOC_n$ (n = 6, 8, 10, 12, 14 and 16)

All title compounds were characterized using various methods as listed below:

- Determination of melting points by using capillary tube.
- Perkin Elmer 2000-FT-IR spectroscopy. One portion of samples mixed with ten portion of dry and homologenous KBr and then pressed into a pellet form. The samples were analyzed in the frequency range of 400- 4000 cm^{-1}.
- 1D and 2D NMR spectroscopy. $CDCl_3$ was used to dissolve the sample with tetramethlysilane (TMS) as internal reference. The ^1H and ^{13}C NMR assignments of representative compounds were obtained and substantiated by ^1H-^1H COSY, ^1H-^{13}C HMQC and ^1H- ^{13}C HMBC.
- CHN microanalyses. The percentages of carbon, hydrogen and nitrogen for compounds **$ABClOC_n$** were determined using CHN microanalyser.
- X-ray data collection. All intensity data for samples were collected using a Rigaku AFC10 (graphite monochromated MoKα radiation, λ= 0.71070 Å) coupled with Saturn CCD Detecter. The indexing was carried out from 0 images that were exposed for 0 s. The data were collected at a temperature of $-160^o \pm 1^oC$ to a maximum 2θ value of 55.0 ^{o}. A total of 720 oscillation images were collected. A sweep of data was completed using ω scans from -110.0 to 70.0 ^{o} in 0.5 ^{o} step. Out of the 11617 reflections that were collected, 4339 were unique (R_{int}= 0.072). Data were collected and processed using Crystal Clear (Rigaku).

2.3.2 Synthesis and characterization of 2,2'-(4-alkoxy-1,3-phenylene)bis(1-(4-substitutedphenyl)diazene)

The intermediary 2,2'-(4-hydroxy-1,3-phenylene)bis(1-(4-substitutedphenyl)--diazene) and title compounds 2,2'-(4-(alkoxy)-1,3-phenylene)bis(1-(4-substitutedphenyl)diazene) were synthesized based on the synthetic scheme as shown in Figure 2.2.