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Nematic Calamitic Bisazobenzene Liquid Crystal: Synthesis and Mesomorphic Properties of 1-Methoxybutyloxy-4'-(4-Phenylazo)Azobenzene

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Abstract: A new calamitic liquid crystal material with rod-shape bisazobenzene moieties as a core has been synthesized and characterized by spectroscopic methods. The mesomorphic properties were investigated by differential scanning calorimetry and polarizing optical microscopy. The rod-shaped molecule 1-methoxybutyloxy-4'-(4-phenylazo)azobenzene was prepared by diazotization of 4-phenylazoaniline, coupling with phenol and subsequent etherification of 1-Bromobutyloxy-4'-(4-phenylazo) azobenzene in methanol. The presence of nematic mesophase was confirmed by the textures.

Key words: Liquid crystal, calamitic, nematic phase, bisazobenzene, thermotropic

INTRODUCTION

Rod-like molecules containing rigid core have traditionally been regarded as the most suitable geometry to give rise to mesogenic behavior (Wan *et al.*, 1998). The nematic liquid crystal phase is technologically the most important mesophase. It is used in almost all commercially available LC displays (Kilic and Çinar, 2007; Kuo *et al.*, 2007; Hsieh, 2008; Kim *et al.*, 2004). Most of the known thermotropic LCs are calamitic structurally (Kilic and Çinar, 2007; Hsu *et al.*, 2005). A calamitic mesogen molecule consists of a core, terminal chains and lateral substituents. The core provides rigidity which is required for anisotropy, whereas the terminal chains provide flexibility to stabilize the molecular alignment within the mesophase. The core is usually a linearly linked aromatic ring system.

The rings can be directly linked or they may be joined by a linking group (Kilic and Çinar, 2007). The terminal chains are either straight alkyl or alkoxy chains and one terminal unit is often a polar substituent (Kiliç and Çinar, 2007; Gray, 1987).

However, in present molecular design hydrogen is the terminal group on the bisazobenzene core, no terminal polar substituent on the bisazobenzene unit. It is well known that photo-orientation of azobenzene units is easily induced through trans-cis-trans isomerisation cycles by irradiating liquid crystalline materials containing azo chromophores with linearly polarised light. Thus, azobenzene-containing materials have potential technological applications such as in high density optical data storage, optical image processing, dynamic holography and optical computing and, pattern recognition (Lutfor *et al.*, 2005; Yu and Ikeda, 2004; Cojocariu and Rochon, 2005).

Although, chromophores having only one azo group in their chemical structure (monoazobenzenes) have been primarily studied, systems with bisazobenzene moieties are also being prepared and investigated for optical storage applications (Zheng *et al.*, 2007; Cojocariu and Rochon, 2005). Bisazobenzene chromophores are distinguished by high anisotropy of molecular polarizability that can lead to large photoinduced orders when compared to Monoazobenzene-based materials.

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Birefringence per azo structural unit in a copolymer with 11 mol% bisazobenzene was reported to be five times larger than that corresponding to a monoazobenzene based copolymer having similar azo content (Zheng *et al.*, 2007; Cojocariu and Rochon, 2005).

In present study a new molecule containing two extended azobenzene chromophore (bisazobenzene) with a methoxy terminal group is reported. Giving nematic calamitic based liquid crystals having a rod-like bisazobenzene unit as a core.

This new material was designed and prepared with aim to study its' mesophase characteristics and to best of our knowledge no such material is reported in the literature. The synthetic routes (Scheme 1) and the mesomorphic properties are discussed.

MATERIALS AND METHODS

This study was conducted (between, July 2007-June 2008) at the Department of Chemistry, Faculty of Science, Universiti Putra Malaysia.

All materials are of analytical grade unless otherwise stated. 4-phenylazoaniline (Fluka), sodium nitrite (BDH), Urea (BDH), Phenol (Merck), 1,4-dibromobutane (Fluka), potassium carbonate (Fluka), potassium hydroxide (Fluka), methanol (Merck) were used as received. Dry acetone was obtained from distilling over phosphorous pentoxide (Merck). Other solvent and chemicals were used without further purification.

The structures of the intermediates and the final product were confirmed by spectroscopic methods: FT-IR spectra were measured on a Spectrum BXII FT-IR spectrophotometer (Perkin Elmer). ¹H NMR spectra (400 MHz) were recorded on a JEOL ECA 400 spectrometer (JOEL, Japan). Mass spectra was obtained on Shimadzu QP5050A (Shimadzu Japan). Phase transition temperatures and thermodynamic parameters were determined by using a DSC 7 (Perkin Elmer) equipped with a liquid nitrogen cooling system under nitrogen atmosphere and the heating and cooling rates were 10 °C min⁻¹. Phase transition temperatures were collected during the second heating and the second cooling scans using an Olympus BX50 (Japan) optical polarizing microscope (OPM) equipped with a Linkam THMSE-600 (Linkam, England) hot stage and a TMS 92 control unit to observe phase transition temperatures and optical textures to analyze liquid crystal properties.

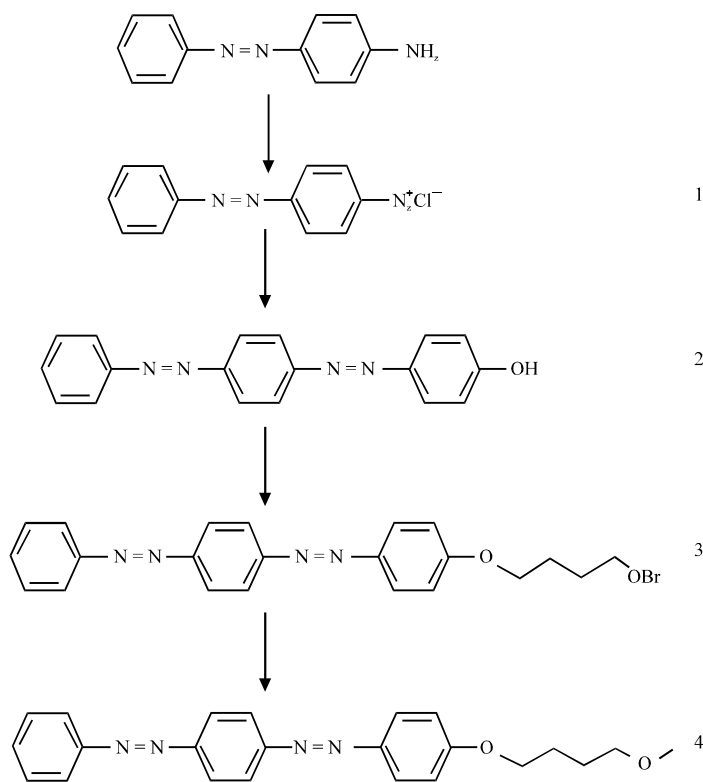
RESULTS AND DISCUSSION

Scheme 1 illustrates the structures and our synthetic approach to the calamitic bisazobenzene molecule. The mesogenic part was prepared by diazotization of a well known powerful dye, 4-phenylazoaniline and then coupling of the resulting diazonium salt, with phenol yielding 4-hydroxy-4'-(4-phenylazo)azobenzene 2.

The flexible spacer was introduced by alkylation of phenol 2, with a 10-fold excess of 1,4- dibromobutane in the presence of potassium carbonate as base and catalytic amount of potassium iodide to give 1-Bromobutyloxy-4'-(4-phenylazo)azobenzene 3 according to the method reported by Lutfar *et al.* (2005). The final compound 4, 1-methoxybutyloxy-4'-(4-phenylazo)azobenzene was produced by further reaction with methanol in presence of potassium hydroxide and a typical procedure for the compounds were as follows:

4-Hydroxy-4'-(4-Phenylazo)Azobenzene 2

4-Phenylazoaniline (5.0 g, 25.38 mmol) was dissolved in acetone (100 mL). Dilute hydrochloric acid [water (50 mL), conc. hydrochloric acid (6.36 mL)] was added and the mixture was cool to 2°C. Sodium nitrite (1.75 g, 25.38 mmol), dissolved in water (20 mL) was added drop wise to the cooled mixture and stirred for 1 h. Then, phenol (2.39 g, 25.38 mmol), dissolved in an acetone/water mixture



Scheme 1: Reactions and conditions (1) NaNO_2/HCl , (2) Phenol, 2°C , (3) $\text{Br}(\text{CH}_2)_4\text{Br}$, K_2CO_3 and (4) MeOH , KOH

(100 mL/50 mL) was added to the diazotized mixture and the reaction mixture was maintained at pH 8-9 by adding sodium hydroxide solution, stirring was continued for 2 h. The resulting mixture was made slightly acidic ($\text{pH} < 5$) with dilute hydrochloric acid (ca. 80 mL, 10%) and added 300 mL of water for precipitation of the product and the precipitate was collected by filtration. The product was crystallized twice from methanol and ethanol. Yield = 66% as dark red crystal, mp. $223\text{--}225^\circ\text{C}$. Elemental analysis found C 71.62, H 4.72, N 18.57; Calculated for $(\text{C}_{18}\text{H}_{14}\text{N}_4\text{O})$ C 71.51, H 4.67, N 18.53. MS m/z : 302 (M^+). IR (KBr, cm^{-1}): 3274 (OH, ν), 1642 (C = C, ν), 1592, 1500, 1424 (aromatic, ν), 1358 (C-H, δ), 1274, 1138 (C-O, ν), 850 (aromatic δ). ^1H NMR (400 MHz, CDCl_3) δ : 9.25 (H, s, ArOH), 8.16 (4H, d, ArH), 7.95 (2H, dd, ArH), 7.93 (2H, d, ArH), 7.53 (2H, d, ArH), 7.25 (1H, s, ArH).

1-Bromobutyl 4'-(4-Phenylazo)azobenzene 3

A mixture of Compound 2 (1.00 g, 3.31 mmol) in dry acetone (80 mL), potassium carbonate (0.50 g, 91.3 mmol), a catalytic amount of potassium iodide (50 mg) and ten-fold excess of 1, 4-dibromobutane (8.0 g, 33.1 mmol) was refluxed for 24 h under N_2 atmosphere. The reaction mixture was filtered hot and acetone was removed under reduced pressure. Hexane was added (sufficient amount) to the product to remove un-reacted 1,6-dibromohexane. The resulting precipitate insoluble in hexane was collected by filtration and the product was dissolved in dichloromethane and water. The organic phase was washed with dilute hydrochloric acid, sodium carbonate solution and

water successively. It was then dried over sodium sulfate and solvent was removed under reduced pressure. The product was crystallized from ethanol with hot filtration. Yield 80% and m.p. 146-149°C. Elemental analysis: Found C 60.53, H 4.92, N 12.86; Calculated ($C_{22}H_{21}BrN_4O$) C 60.42, H 4.84, N 12.81; MS m/z (M^+). IR, (KBr, cm^{-1}): 2938, 2862 (C-H, ν), 1602, 1584, 1498, 1474 (aromatic, ν), 1394 (C-H, δ), 1250, 1148 (C-H, δ), 856 (aromatic, δ). 1H NMR (400 MHz, $CDCl_3$) δ : 8.05 (2H, d, ArH), 7.93 (4H, dd, ArH), 7.02 (2H, d, ArH), 7.53 (2H, d, ArH), 7.25 (1H, s, ArH), 4.06 (2H, t, OCH_2), 3.44 (2H, t, CH_2Br), 1.55 (2H, m, CH_2), 1.25 (2H, m, CH_2).

1-Methoxybutyloxy-4'-(4-Phenylazo)Azobenzene 4

Compound 3 1-Bromohexyloxy-4'-(4-phenylazo)azobenzene (0.5 g, 0.001 M) and potassium hydroxide (0.207 g, 0.004 M) was heated to reflux in methanol (80 mL) for 8 h under nitrogen atmosphere. The reaction mixture was filtered hot and allowed to cool to room temperature, then poured into acidified (10% HCl) ice-cold water. The resulting precipitate was collected by filtration and purified by column chromatography on silica gel with chloroform/methanol (10:1); as eluant. The solid was crystallized from methanol and ethanol respectively. Yield 49.82%, m.p. 129-132°C. Elemental analysis: Found C 71.24, H 6.33, N 14.51; Calculated for ($C_{23}H_{24}N_4O_2$), C 71.11 H 6.23, N 14.42; MS m/z 388 (M^+); IR, (KBr, cm^{-1}): 2938, 2862 (C-H, ν), 1602, 1584, 1498, 1474 (aromatic, ν), 1394 (C-H, δ), 1250, 1148 (C-H, δ), 856 (aromatic, δ). 1H NMR (400 MHz, $CDCl_3$) δ : 8.05 (2H, d, ArH), 8.05 (4H, dd, ArH), 7.96 (2H, t, ArH) 7.53 (2H, d, ArH), 7.25 (1H, s, ArH), 7.02 (2H, d, ArH), 7.00 (2H, d, ArH) 4.10 (2H, t, OCH_2), 3.45 (2H, OCH_2) 3.36 (3H, s, OCH_3) 1.55 (2H, s, CH_2) 1.25 (2H, m, CH_2). ^{13}C NMR (400 MHz $CDCl_3$) δ : 26.04, 26.20 (2C), 58.58, 68.06, 72.29 (3C), 114.78, 123.00, 123.41, 123.75 (10C), 125.06, 129.12, 131.25 (3C), 152.78, 153.30, 153.98, 162.00 (5).

Phase Transitions

The phase transition temperatures as well as the phase transition enthalpy changes were determined using differential scanning calorimetry (DSC) and the result of the second heating and second cooling scans are shown in Table 1. The material is very stable crystal at room temperature and exhibit enantiotropic nematogenic liquid crystalline behavior.

The DSC thermogram of compound 4 is shown in Fig. 1. Two exothermic peaks were found on cooling from the isotropic liquid.

On heating to the isotropic liquid, a sharp melting peak appeared at 128.54°C which was followed by a schlieren texture, as typical for nematic phase, centered at 164.8°C. On cooling from the isotropic liquid a Schlieren texture also appeared centered at 159.53°C. There was no any other peak appeared until the sharp crystallization peak centered at 119.39°C as shown in the DSC reheat trace above (Fig. 1). This material therefore, exhibits an enantiotropic nematogenic property.

Phase Structures

The phase structures were determined by Polarizing Optical Microscope (POM). The polarized optical micrograph of 4, observed for the nematic mesophases in the liquid crystalline phase during the second heating and cooling cycle, is shown in Fig. 2.

On heating to the isotropic phase a schlieren texture, as typical for nematic phase was observed at 165.3°C.

Table 1: Phase transition temperatures and enthalpies obtained from DSC scans of 4^a

Transition temperature ($T/^\circ C$)	Associated transition enthalpy values ($\Delta H/Jg^{-1}$)
2nd heating	Cr 128.54 (29.36) N 163.65 (0.57) I 165.50
2nd cooling	I 164.5 N 159.53(3.15) Cr 119.39 (27.63)

^aCr = crystal, N = Nematic, I = isotropic phase

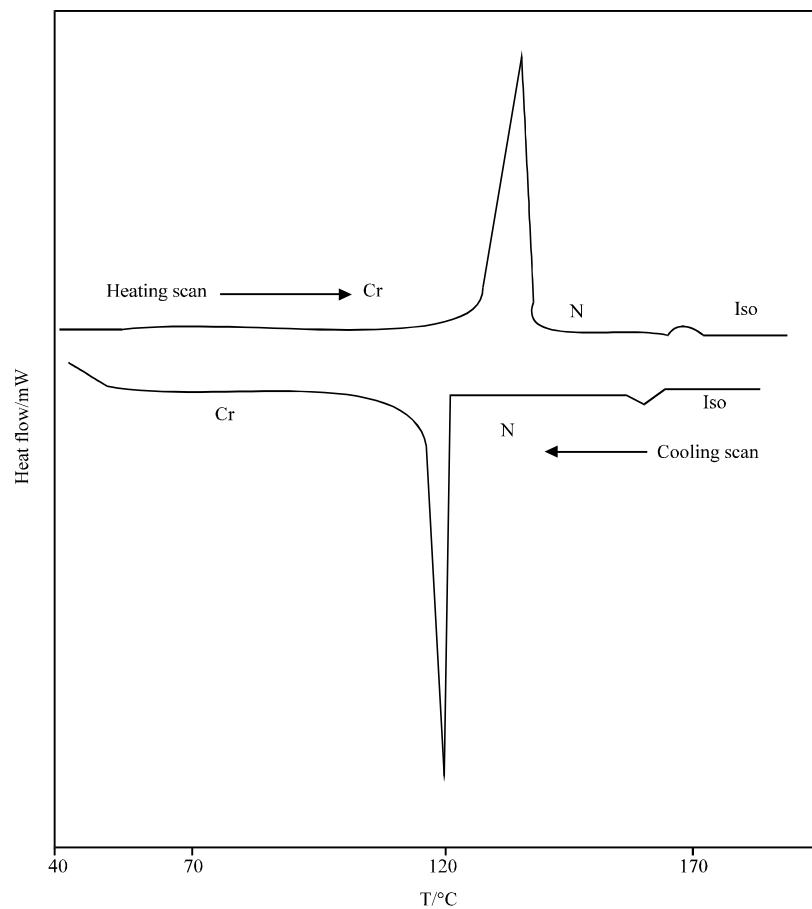


Fig. 1: DSC heating and cooling traces of compound 4 ($10^{\circ}\text{C min}^{-1}$)



Fig. 2: Optical photomicrograph of compound 4 at 160.2°C on cooling from the isotropic liquid

On cooling from the isotropic phase a schlieren texture, as typical for nematic phase, also appeared at 160.2 (Fig. 2). This nematic is highly fluid containing a four-point brush disclination and flashed upon shearing, which appeared optically isotropic. There is no further phase transition on further cooling however, the material supercooled at 21°C before it crystallized at 121.7°C. The higher clearing temperature T_{N-I} exhibited by this material may be ascribed to the greater conjugation provided by the lone pairs of electrons on the oxygen atom of the alkoxy group as reported for in the literature (Gray, 1987). This mesophase behavior shows that the two azobenzene chromophores have the same conformational (trans) direction in the liquid crystal state since, according to Yu and Ikeda azobenzene liquid crystals show a liquid crystal phase only when the azobenzene moieties are in the trans- form and they never show a liquid crystal phase at any temperature when all of the azobenzene moieties are in the cis- form (Yu and Ikeda, 2004).

CONCLUSION

A new calamitic liquid crystal molecule based on bisazobenzene core connected to a four alkylene units with methoxy group at the terminal end has been designed and synthesized. The material is an enantiotropic nematogen exhibiting nematic phase in both heating and cooling circles. The nematogenic characteristic of this molecule can be attributed to the presence of methoxy terminal group and the extended bisazobenzene core. Further studies such as Photoalignment behavior, Photoisomerization and photoinduced birefringence may lead to the actualization of possible utilization of this type of material for photonic application.

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