



Research Article

ISSN : 0975-7384  
CODEN(USA) : JCPRC5

## Symmetric liquid crystal trimer containing bisazobenzene moieties: Synthesis and Mesomorphic Properties.

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### ABSTRACT

*A new system of liquid crystal trimer containing bisazobenzene groups and biphenyl core has been synthesized by diazotization and coupling of primary aromatic amine and subsequent etherification with polymethylene spacer group and further etherification to react to the biphenyl core. The material was characterized using spectroscopic methods and X-ray diffraction. The spacer length was found to exert a profound influence on the clearing temperatures of these materials and a large odd-even effect was observed for the series. The smectic A phase stability was observed to increase with the increasing spacer length. X-ray diffraction has revealed the structure of the smectic A phase of the representative symmetric bisazobenzene trimers to be of the monolayer type and not intercalated.*

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### INTRODUCTION

A liquid crystal trimer consists of molecules containing three mesogenic units inter-connected via two flexible spacers [5]. These structural components may be assembled in a number of differing ways to give, for example: linear trimers [4]; trimers in which one or more mesogenic units are connected in a lateral position [2]; cyclic trimers [6]; star-shaped trimers and trimers containing rod-like and disc-like mesogenic moieties [5]. Trimers can be classed as being either symmetric or non-symmetric. The non-symmetry may be introduced in a number of ways including by having differing mesogenic units by using alkyl chains of differing lengths or by using differing terminal groups or indeed some combination of all these differences [3].

Liquid crystal trimers have been reported in which the two spacers are of differing lengths [9]. The trimers exhibit the chiral nematic phase but the clearing temperatures exhibit only a weak dependence on the parity of the spacers. This is apparently a consequence of molecular shape and specifically, reflects that the bonds connecting the spacers to the steroid nucleus are not co-parallel. Thus changing the parity of the spacers has a much reduced effect on the average molecular shape.

Liquid crystal trimers have been reported with both differing mesogenic units and differing spacer length by [10 & 11]. He described the properties of the homologues containing spacers of matched parity exhibit the undulated twist grain boundary phase (UTGBC\*) over a wide temperature range. The nature of the driving force responsible for the formation of this phase is at present unclear. Discotic trimers have been prepared in which three triphenylene-based units are attached to a central benzene ring [6]. This trimer exhibited a monotropic columnar phase but which did not crystallize even after 5 months storage at room temperature. Hybrid liquid crystal trimers have been reported [5] which contain both discotic and calamitic mesogenic units. These trimers exhibited a nematic columnar phase.

Azobenzene is well known to undergo reversible *trans-cis* (*E/Z*) isomerization upon irradiation with UV/VIS light [12, 13, 18 and 19]. A survey into the literature composed of molecules revealed that compounds with bisazo linkages have hardly been studied. Nevertheless, bisazobenzene chromophores are distinguished by high anisotropy of molecular polarizability that can lead to large photoinduced orders when compared to Monoazobenzene-based materials [1]. The level of photoinduced birefringence was shown to depend strongly on the type and size of azobenzene groups [1 & 17]. The photoinduced birefringence per azobenzene structure in bisazobenzene-based polymers was reported to be five times larger and more stable than that in monoazobenzene polymers [1].

In this contribution a bisazobenzene and alkoxybiphenyl mesogenic units has been combined through flexible alkyl spacer to produce a calamitic non-symmetric trimer with aims to study the liquid crystalline properties and probably obtained a new promising material that can be utilized for application such, as optical information storage technology.

## EXPERIMENTAL SECTION

All materials are of analytical grade unless otherwise stated. 4-phenylazoaniline (Fluka), 4,4'-Dihydroxybiphenyl (Acros), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck),  $\alpha$ ,  $\omega$ -dibromoalkanes (Fluka), potassium carbonate (Fluka), potassium hydroxide (Hamburg), potassium carbonate (Fluka) (Acros) were used as received. Dry acetone, dry butanone and dry N,N-dimethylformamide (DMF) were obtained from distilling over phosphorous pentoxide (Merck). Other solvent and chemicals were used without further purification. Silica gel 60 (230-460nm) was used Column Chromatography, FT-IR spectra were measured on a BX spectrum II FT-IR spectrometer (Perkin Elmer).  $^1\text{H}$  NMR spectra (400 MHz) were recorded on a Jeol ECA 400 NMR spectrometer (Jeol, Japan). Phase transition temperatures and thermodynamic parameters were determined by using a DSC 7 (Perkin Elmer) and DSC 8 (diamond DSC. Perkin Elmer) equipped with a liquid nitrogen cooling system under nitrogen atmosphere. The heating and cooling rates were  $10^\circ\text{C min}^{-1}$ . Phase transition temperatures were collected during the second heating and the second cooling scans. An Olympus (Leica, Germany) polarizing optical microscope equipped with a Linkam THMSE-600 (Linkam, England) hot stage was used to observe phase transition temperatures and optical textures to analyze liquid crystal properties of the new material. The X-Ray measurement was performed using a nickel-filtered  $\text{Cu-K}_{\alpha 1}$  radiation with a Philips X-Ray diffractometer X'PERT PRO PW 3040 (PanAnalytical, Holland).

### Methodology

#### Synthesis

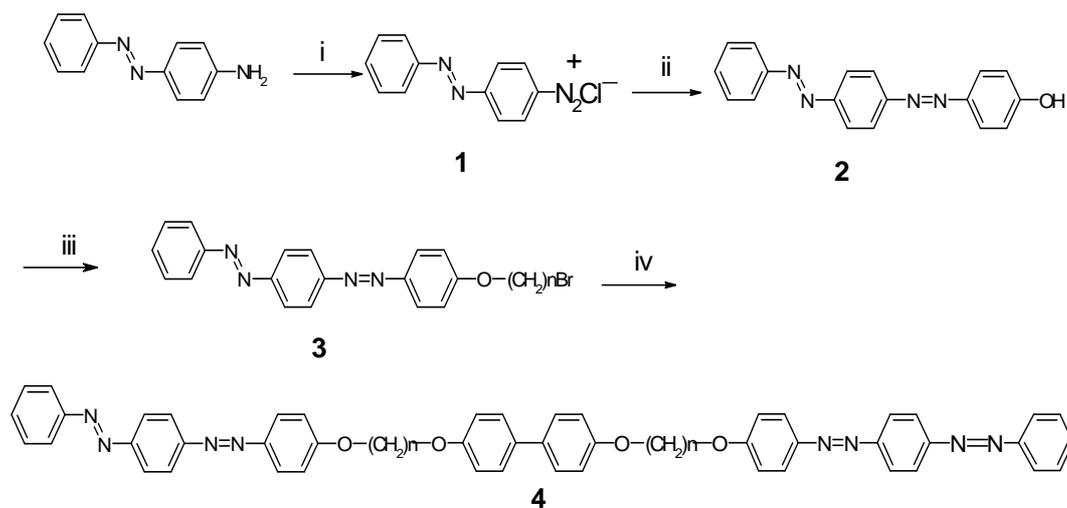
Scheme 1 illustrates the structures and the synthetic approach to the liquid crystal trimer molecule. The peripheral units of the mesogenic part were prepared by diazotization of a well known powerful dye, 4-phenylazoaniline and then coupling of the resulting diazonium salt **1**, with phenol yielding 4-hydroxy-4'-(4-phenylazo)azobenzene **2**.

The flexible spacers were introduced by alkylation of phenol side of compound **2**, with a 10-fold excess of the appropriate  $\alpha$ ,  $\omega$ -dibromoalkane in the presence of potassium carbonate as base to give 1-Bromohexyloxy-4'-(4-phenylazo)azobenzene **3** according to modified literature [13 & 16].

The final trimer compound **4** was produced by reacting 2 moles of compound **3** with 1mole equivalent of 4, 4'-Dihydroxybiphenyl in freshly distilled DMF. The detailed procedure for each compound was described below.

#### 4-hydroxy-4'-(4-phenylazo)azobenzene **2**:

4-Phenylazoaniline (5.0g, 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  $2^\circ\text{C}$ . Sodium nitrite (1.75g, 25.38 mmol), dissolved in water (20 ml) was added drop wise to the cooled mixture and stirred for 1h. Then, phenol (2.39g, 25.38 mmol), dissolved in an acetone/water mixture (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 (pH <5) with dilute hydrochloric acid (ca. 80 ml, 10%) and added 300ml of water for precipitation of the product and the precipitate was collected by filtration. The product was crystallized twice from methanol and ethanol. Yield 5.85 g (66%) as dark red crystal, mp. 223-225  $^\circ\text{C}$ . IR (KBr,  $\text{cm}^{-1}$ ): 3274 (OH,  $\nu$ ), 1642 (C=C,  $\nu$ ), 1592, 1500, 1424 (aromatic,  $\nu$ ), 1358 (C-H,  $\delta$ ), 1274, 1138 (C-O,  $\nu$ ), 850 (aromatic  $\delta$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.25 (H, s, ArOH), 8.16 (4H, d, J = 8.6 Hz, ArH) 7.95 (2H, d, J = 8.6Hz, d, J = 5.8 Hz, ArH), 7.93 (2H, d, J = 8.8 Hz, ArH), 7.92 (2H, d,  $\text{CH}_2$ ), 7.53(1H, s, j = 7.3Hz, Ar ).



Where,  $n=3, 4, 5, 6$  and  $8$

BAT1  $n=3$ , BAT2  $n=4$ , BAT3  $n=5$ , BAT4  $n=6$ , BAT5  $n=8$

**Scheme 1: Reagents and conditions: i)  $\text{NaNO}_2$ ,  $\text{HCl}$ ,  $0-5^\circ\text{C}$ ; ii)  $\text{NaOH}$ , Phenol,  $0-5^\circ\text{C}$ ; iii)  $\text{K}_2\text{CO}_3$ , Acetone, Dibromoalkane; iv)  $\text{K}_2\text{CO}_3$ , THF, 4-4' dihydroxybiphenyl;**

#### **1-Bromohexyloxy-4'-(4-phenylazo)azobenzene 3:**

A mixture of Compound **2** (1.00g, 3.31mmol) in dry acetone (80ml), potassium carbonate (0.50g, 91.3mmol), a catalytic amount of potassium iodide (50mg) and ten-fold excess of 1,6-dibromohexane (8.0g, 33.1mmol) was refluxed for 24 h under  $\text{N}_2$  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 1.4g (59%) and m.p.  $185-189^\circ\text{C}$ . IR, (KBr,  $\text{cm}^{-1}$ ): 2938, 2862 (C-H,  $\nu$ ), 1602, 1584, 1498, 1474 (aromatic,  $\nu$ ), 1394 (C-H,  $\delta$ ), 1250, 1148 (C-H,  $\delta$ ), 856 (aromatic,  $\delta$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.05 (2H, d,  $J = 8.2$  Hz, ArH), 7.93 (4H, d,  $J = 8.7$ Hz, d,  $J = 5.8$  Hz, ArH), 7.53 (2H, d,  $J = 8.9$  Hz, ArH), 7.05 (1H, t,  $j = 6.8$ Hz, ArH), 4.06 (2H, t,  $J = 6.4$  Hz,  $\text{OCH}_2$ ), 3.44 (2H, t,  $J = 5.2$  Hz,  $\text{CH}_2\text{Br}$ ), 2.66 (2H, d,  $j = 4.8$ Hz,  $\text{CH}_2$ ), 1.93-1.84 (4H, m,  $j = 7.4$ Hz,  $\text{CH}_2$ ).

#### **Bis-[4'-(4-phenylazo)azobenzenebutyloxy]biphenyl:4**

A mixture of compound **3** (1.0g, 0.002M), 4,4'-Dihydroxybiphenyl(0.0023g, 0.001M) and potassium carbonate (0.00164g, 0.001M) was heated to reflux with stirring in dried and freshly distilled  $\text{N,N}$ -dimethylformamide (80 ml) for 24 hrs 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 (c. 300ml) and stirring to coagulate the resulting precipitate which was collected by filtration and purified by column chromatography on silica gel with chloroform/methanol (9:1); as eluant. The solid was crystallized from Chloroform/THF twice respectively. Yield 68%, (1.2g), m.p.  $247-259^\circ\text{C}$ . IR, (KBr,  $\text{cm}^{-1}$ ): 2938, 2862 (C-H,  $\nu$ ), 1602, 1584, 1498, 1474 (aromatic,  $\nu$ ), 1394 (C-H,  $\delta$ ), 1250, 1148 (C-H,  $\delta$ ), 856 (aromatic,  $\delta$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.05 (2H, d,  $J = 8.2$  Hz, ArH), 7.93 (4H, d,  $J = 8.7$ Hz, d,  $J = 5.8$  Hz, ArH), 7.53 (2H, d,  $J = 8.9$  Hz, ArH), 7.05 (1H, t,  $j = 6.8$ Hz, ArH), 4.06 (2H, t,  $J = 6.4$  Hz,  $\text{OCH}_2$ ), 3.44 (2H, t,  $J = 5.2$  Hz,  $\text{CH}_2\text{Br}$ ), 2.66 (2H, d,  $j = 4.8$ Hz,  $\text{CH}_2$ ), 1.93-1.84 (4H, m,  $j = 7.4$ Hz,  $\text{CH}_2$ ).

## RESULTS AND DISCUSSION

### 3.1. Thermal behavior and texture observation

The phase transition temperatures as well as the phase transition enthalpies were determined using differential scanning calorimetry (DSC) and the result of the second heating and second cooling scans are summarized in table 1. The phase structures were determined by optical polarizing microscope. All materials are very stable crystals at

room temperature and compound **BAT1** with C<sub>3</sub> alkyl spacers exhibited enantiotropic nematic (N) phase behavior with a high clearing temperature. The nematic phase was characterized by the formation of Schlieren texture as observed under polarized light. On increasing the length of the polymethylene alkyl spacers to C<sub>4</sub> as in compound **BAT2**, two transitions were observed during both heating and cooling circles. Texture observation carried out on this compound shows that it exist as an enantiotropic nematogen (Figure 2), of which the formation of a schlieren texture, as typical for nematic phase, were observed on heating (165.3 °C) to the isotropic phase and on cooling (160.2 °C) process from the isotropic liquid phase, respectively

This nematic is of low fluidity containing a four-point brush disclination and flashed upon shearing, which appeared optically isotropic (figure 2a). There is no further phase transition on further cooling however, the material supercooled at 21 °C before it crystallized at 121.7 °C.

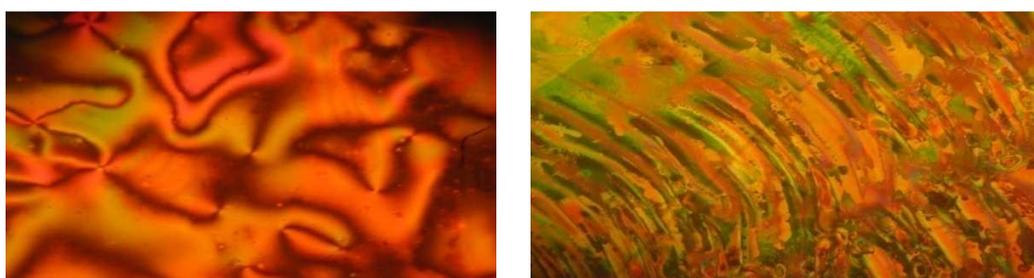
**Table I: Phase transition temperatures ( $T^{\circ}\text{C}$ ) and enthalpies ( $\Delta H/\text{Jg}^{-1}$ ) obtained from DSC scans of BAT1- BAT5.**

Compound	N	Heating cycle		Cooling cycle	
<b>BAT1</b>	3	Cr 99.75 (37.5)	SmA 122.34 (5.4)	I 117.34 (6.5)	N 97.99 (1.5)
<b>BAT2</b>	4	Cr 128.54 (29.36)	N 163.65 (0.57)	I 159.53(3.15)	N 119.39 (27.63)
<b>BAT3</b>	5	Cr 134.86 (39.6)	N245.86 (0.7)	I 126.42 (33.5)	Cr
<b>BAT4</b>	6	Cr106.99 (54.6)	SmA 131.19 (3.1)	N 164.5 (0.6)	I 161.14 (1.3)
<b>BAT5</b>	8	Cr 99.34 (59.5)	SmA 133.19 (2.89)	N 152.20 (1.4)	I 149.31 (1.2)

Abbreviations Cr = crystal, SmA = smectic A, N = nematic, I = isotropic phase

When the length of the polyalkylene chain was increased to C5 in compound **BAT3**, an enantiotropic smectic phase behavior was observed showing SmA in heating and cooling cycle with almost equal low thermal transition values ( $\Delta H = 0.92\text{J/g}$ ). The peaks were observed in the thermogram during heating and cooling cycle as confirmed by the texture under polarized light as shown in table 1

A further lengthening of the polyalkylene group from compound **BAT3** to compounds **BAT4** (C<sub>6</sub>) and **BAT5** (C<sub>8</sub>) resulted in these compounds to exhibits a monotropic nematic phase behavior. Two peaks were observed in their thermograms during heating as well as during cooling cycles. Although the Cr–N, and N–I phase transitions were observed at a respective temperatures 106.99 °C and 164.5 °C for compound **BAT4** when it was heated up, the reverse process occurred at 161.4 °C (I–N) and 59.53 °C (N–Cr) respectively. Also for compound **BAT5** the Cr–N and N–I phase were observed at a respective temperatures 99.34 °C, and 152.20 °C when heated up, the reverse process occurred at 149.31 °C and 61.19 °C respectively. Texture observation for these compounds under polarized light showed that, nematic and phase appeared during heating and cooling circle. Typical examples in regards to texture observation under polarized light for compounds **BAT3**, **BAT4** and **BAT5** is shown by compound **BAT4**. The focal-conic fan shaped, in the isotropic matrix were observed during heating and the cooling process (Figure 4).



**Figure 1: Optical photomicrograph of (a) Nematic phase at 105.6 °C and (b) Supercool texture) of compound BAT4 at 94.8 °C with a polarizing microscope**

The enantiotropic behavior throughout the series of these compounds might be due to the extended azobenzene core length (bisazobenzene) that extend the molecules along their molecular axes which, increases thermal stability of the mesophases and anisotropy of molecular polarizability. The absence of terminal groups such as alkyl or polar groups (-CN, -NO<sub>2</sub>, -COCH<sub>3</sub>) might be responsible for higher clearing temperatures exhibited by these compounds. This observation indicates that molecules with longer alkyl chains are much more linear and, the increase in linearity gave rise to an efficient packing that led to higher clearing temperatures and thermal stability as observed for these compounds and similar compounds in the literature [14].

The absence of any substituted lateral group improved the lateral interaction between the molecules, which is an important factor for the conformational changes of the bisazobenzene chromophore. It has been demonstrated that the higher the length/diameter ratio of bisazobenzene chromophore the higher the order parameter (as well as birefringence) as a results materials with three rings mesogens are more favored in liquid crystal environment [13]. The interaction between bisazobenzene groups, are stronger than, those of monoazobenzene groups. Moreover, bisazobenzene mesogens are tend to exhibit higher ordered phases [1].

To complement DSC and OPM observations and gain more information on the molecular arrangements, modes of packing, and types of order in mesophases, a high temperature X-ray diffraction analysis was carried out on a representative sample, compound **BAT4**. Powdered sample was placed on the Pt heating strip and then thermally processed. The heating/cooling rate was 10 0C., followed by collection of data for 4 mins at, 120 0C according to the method described in the literature [13]. The diffraction patterns display one sharp and intense reflection at low angle 47.34 Å ( $2\theta = 20$ ) which indicates a lamellar structure corresponding to smectic layers. In the wide-angle region, a broad halo centered at about  $2\theta = 19.79^\circ$ , which corresponds to an average intermolecular distance of approximately 4.48 Å. These suggested that the lateral packing of the molecules within the smectic layer is disordered, i.e., a liquid-like arrangement of the mesogenic groups in the layers. Such arrangement is in consistent with a disordered mesophase of the smectic A, as observed under OPM the homoetropic regions, bâtonnets and fan-shaped textures.

### CONCLUSION

A series of five symmetric liquid crystals trimers based on bisazobenzene and biphenyl (**BAT1-BAT5**) with different alkyl terminal unit and bulky methoxy group at the terminal end has been synthesized and characterized. All compounds were found to be enantiotropic mesogens with compounds **BAT3** exhibiting smectic A and nematic, **BAT2** nematic, while **BAT3** smectic A phase in both heating and cooling cycles respectively. Compounds **BAT4** and **BAT5** showed nematic and smectic A mesophases in both circles. The core length (bisazobenzene), increase in length of terminal units, absence of lateral groups on the bisazobenzene and the presence of methoxy group at terminal end were thought to improve the enantiotropic behavior, thermal and mesophase stability throughout the series of these compounds. The photoisomerization of the chromophore does not happened significantly on irradiation with 364nm UV-Visible light. A higher energy light source (such as lesser) may be useful for the excitation of the molecule.

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