



## SYNTHESIS AND MESOMORPHIC PROPERTIES OF A TRIPHENYLENE-BASED DISCOTIC LIQUID CRYSTAL MOLECULE WITH BISAZOBENZENE AT THE PERIPHERY

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### ABSTRACT

*A new triphenylene liquid crystal material with six rod-shape bisazobenzene moieties as the peripheral units has been synthesized and characterized by spectroscopic methods. The mesomorphic properties were investigated by differential scanning calorimetry, polarizing optical microscopy and, X-ray diffraction. The mesogenic bisazobenzene was prepared by diazotization and coupling and subsequent etherification. The disc-shaped molecule, 2,3,6,7,10,11-hexakis[4'-(4-phenylazo)azobenzenehexyloxy]triphenylene was prepared by etherification of 1-bromohexyloxy-4'-(4-phenylazo)azobenzene on to the 2,3,6,7,10,11-hexahydroxytriphenylene nucleus. The presence of a nematic and smectic A mesophases was confirmed by optical textures and X-ray diffraction measurement.*

**Keywords:** Liquid crystal, Bisazobenzene, Triphenylene, Nematic phase, Smectic phase,

### INTRODUCTION

Discotic Liquid Crystals (DLCs) materials have recently attracted a great deal of attention because of their versatility and potential application to novel nanodevices for next-generation photonics and electronics [Kumar *et al.* 2004, Furumi *et al.* 2005 and Kumar 2005]. Most DLC materials display the columnar mesophases due to the strong self-organization of the  $\pi$ - $\pi$  interaction between their rigid central cores, whereas few compounds show the nematic discotic ( $N_D$ ) phases [Kumar *et al.* 2004, Furumi *et al.* 2005, Kouwer *et al.* 2005, Lutfor *et al.* 2005 and Liu *et al.* 2005]. However, some current effort in the field of DLCs have been towards designing novel molecules, which in some way combine the features of rod-shaped and disc-like molecules having photoactive properties [Bushby *et al.* 2004 and Lutfor *et al.* 2005]. The combination of two or three incompatible calamitic mesogens and a disc-shaped mesogen was reported to have molecular topology that induces the formation of smectic phases, with alternating layers of discs and rod shaped mesogens while, compatible combination of disc-shaped and calamitic mesogen results, in the formation of nematic phase [Shimizu *et al.* 2003, Buden *et al.* 1999, Kouwer *et al.* 2003 and Kouwer *et al.* 2004].

Shimizu *et al.* (2003) described a disc-shaped triphenylene linked with six alkoxy substituted rod-shaped azobenzene moieties via short ( $C_3$ ) alkyl chains using ester bonds. This compound shows kinetically controlled bimesomorphism with metastable smectic A and a stable hexagonal columnar phase due to a change of the average molecular shape from rod-like to disc-like. In addition, a novel molecule with six rod-shaped monoazobenzene moieties, each carrying a short electron withdrawing acetyl group at the terminus, attached to a disc-shaped triphenylene unit via alkylene spacers ( $C_6$ ) and ether linkages was reported [Lutfor *et al.* 2005] to show Smectic A and

Nematic mesophases which are formed due to assembly of the rod-shaped azobenzene parts.

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]. Bisazobenzene chromophores are distinguished by high anisotropy of molecular polarizability that can lead to large photoinduced orders when compared to monoazobenzene-based materials. 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 [Cojocariu and Rochon 2005].

To the best of our knowledge there is no report of triphenylene liquid crystal molecule incorporating six peripheral bisazobenzene units through ether linkages. In the work described here, a new molecule containing two extended azobenzene chromophore (bisazobenzene) is reported. We have successfully incorporated bisazobenzene moieties into a triphenylene molecule through an alkyl spacer ( $C_6$ ) using etherification, giving, triphenylene based discotic liquid crystals having six peripheral rod-like bisazobenzene units.

### EXPERIMENTAL

#### Materials

All materials are of analytical grade unless otherwise stated. 4-phenylazoaniline (Fluka), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck), 1,6-dibromohexane (Fluka), potassium carbonate (Fluka), potassium hydroxide (Fluka), methanol (Merck) were used as received. Dry acetone was obtained by distillation over phosphorous pentoxide (Merck). Other solvent and chemicals were used without further purification.

**Techniques**

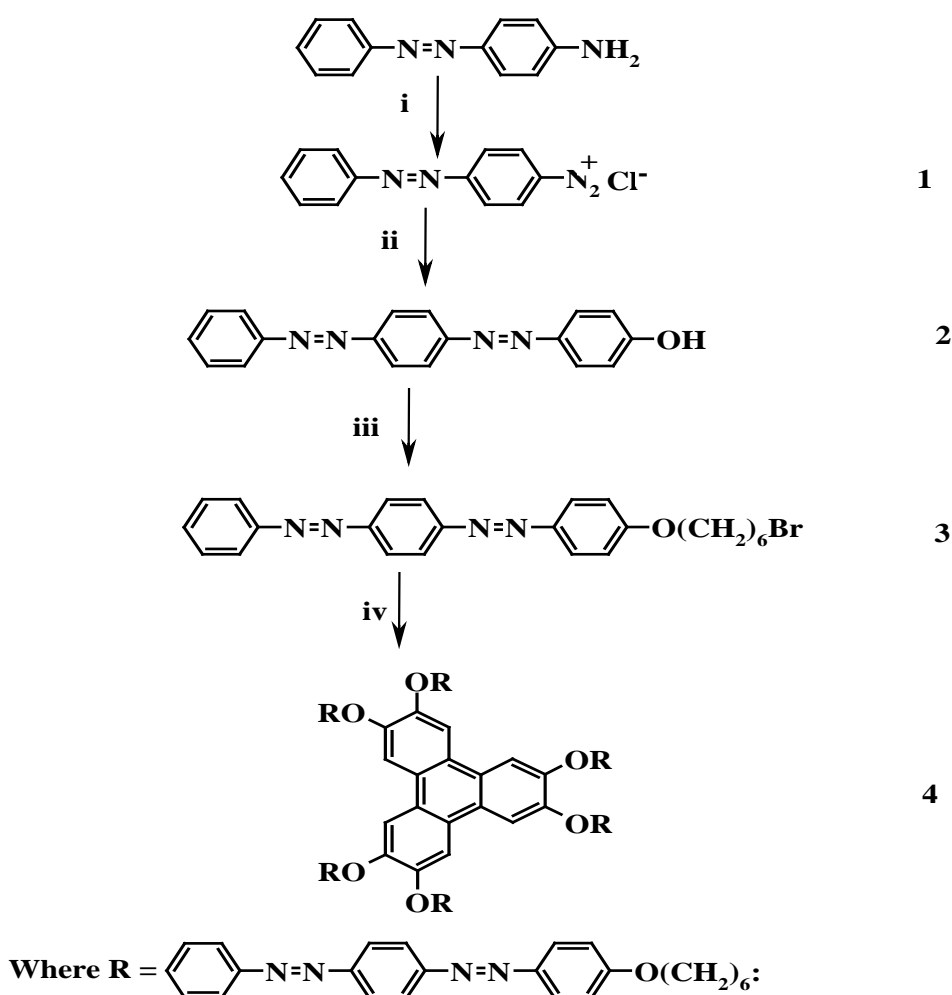
FT-IR spectra were measured on a BX spectrum II FT-IR spectrometer (Perkin Elmer). <sup>1</sup>H NMR spectra (400 MHz) were recorded on a Jeol ECA 400 NMR spectrometer (Jeol, USA). Phase transition temperatures and thermodynamic parameters were determined by using a DSC 7 (Perkin Elmer) equipped with a liquid nitrogen cooling system under nitrogen atmosphere. The heating and cooling rates were 10 °C min<sup>-1</sup>. Phase transition temperatures were recorded 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 Cu-K<sub>α1</sub> radiation with a Philips X-Ray diffractometer X'PERT PRO PW 3040 (PanAnalytical, Holland).

**Synthesis**

Scheme 1 illustrates the structures and the synthetic approach to the disc-shaped, 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, 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 1,6- dibromohexane in the presence of potassium carbonate as base to give 1-Bromohexyloxy-4'-(4-phenylazo)azobenzene **3** according to modified literature [Lutfor *et al.* 2005].



**Scheme 1:** Reaction and conditions (i) HCl, NaNO<sub>2</sub>, 0°C; (ii) phenol ;(iii) K<sub>2</sub>CO<sub>3</sub>, KI, Br(CH<sub>2</sub>)<sub>6</sub>Br, acetone; (IV) K<sub>2</sub>CO<sub>3</sub>, C<sub>18</sub>H<sub>12</sub>O<sub>6</sub>, DMF.

Finally, compound **3** was used to hexa-alkylated 2,3,6,7,10,11-hexahydroxytriphenylene which, was prepared according to standard literature procedure [Cojocariu and Rochon 2005, Lutfor *et al.* 2005] to produced a disc-liked molecule 2,3,6,7,10,11-hexakis-[4'-(4-phenylazo)-azobenzenehexyloxy]triphenylene **4**. The detailed procedure for the synthesis of compound **4** is given 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 cooled to 2 °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 and stirring was continued for 2 h. The resulting mixture was made slightly acidic (pH <5) with dilute hydrochloric acid (ca. 80 ml, 10%). To it was added to 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 °C. IR (KBr, cm<sup>-1</sup>): 3274 (OH, u), 1642 (C=C, u), 1592, 1500, 1424 (aromatic, u), 1358 (C-H, δ), 1274, 1138 (C-O, u), 850 (aromatic δ). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 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), 7.53(1H, s, j = 7.3Hz, Ar ).

#### 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 N<sub>2</sub> atmosphere. The reaction mixture was filtered while 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 (45.6%) and mp 146-149°C. IR, (KBr, cm<sup>-1</sup>): 2938, 2862 (C-H, u), 1602, 1584, 1498, 1474 (aromatic, u), 1394 (C-H, δ), 1250, 1148 (C-H, δ), 856 (aromatic, δ). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.05 (2H, d, J = 8.2 Hz, ArH), 7.93 (4H, d, J = 8.7Hz, d, J = 5.8 Hz, ArH), 7.53 (2H, d, J = 8.9 Hz, ArH), 7.05 (1H, t, j = 6.8Hz, ArH), 4.06 (2H, t, j

= 6.4 Hz, OCH<sub>2</sub>), 3.44 (2H, t, J = 5.2 Hz, CH<sub>2</sub>Br), 2.66 (2H, d, j = 4.8Hz, CH<sub>2</sub>), 1.93-1.84 (4H, m, j = 7.4Hz, CH<sub>2</sub>).

#### 2,3,6,7,10,11-hexakis[4'-(4-phenylazo)azobenzenehexyloxy]triphenylene 4:

A mixture of compound 3 (0.5g, 1.07mmol), 2,3,6,7,10,11-hexahydroxytriphenylene (0.05793g, 0.178mmol), potassium carbonate (0.148g, 1.07mmol) and catalytic amount of potassium iodide were reflux in dry THF (50ml) for 24h under N<sub>2</sub> atmosphere. The reaction mixture was poured into ice-cold water and acidified with dilute hydrochloric acid (10%). The resulting precipitate was collected by filtration and the product was purified by column chromatography on silica gel with chloroform/methanol as eluant. The solid was crystallized from ethanol: chloroform (10:1); Yield 0.215g (39.82%) and mp= 117-121 °C. FT-IR, (KBr, cm<sup>-1</sup>), 2942, 2868 (C-H, u), 1600, 1496, 1468 (aromatic, u), 1394 (C-H, δ), 1248, 1144 (C-H, δ), 848 (aromatic, δ); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.05 (2H, d, J = 8.2 Hz, ArH), 7.93 (4H, d, J = 8.7Hz, d, J = 5.8 Hz, ArH), 7.02 (2H, d, J = 8.9 Hz, ArH), (7.05 (1H, t, j = 6.8Hz, ArH), 4.06 (2H, t, J = 6.4Hz, OCH<sub>2</sub>), (2H, t, J = 5.2Hz, ), 2.66 (H, , CH), 1.96-1.87 (4H, m, CH<sub>2</sub>); <sup>13</sup>C NMR (400 MHz CDCl<sub>3</sub>) δ: 25.63, 28.43, 29.05, 29.69, 32.63, 63.87, 68.11, 114.76, 122.99, 123.42, 123.75, 125.06, 129.13, 131.27, 147.05, 152.73, 153.27, 153.94, 161.16, 161.97. Elemental analysis; Calculated for C<sub>162</sub>H<sub>156</sub>N<sub>24</sub>O<sub>12</sub> (2631.20): C, 73.95%; H, 5.98%; N, 12.78%. Found C, 73.52%; H, 5.75% N, 12.82%

## RESULTS AND DISCUSSION

### Phase transitions by DSC

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 summarized in table 1. The material is very stable crystal at room temperature and exhibit enantiotropic phase behavior.

**Table 1: Phase transition temperatures and enthalpies obtained from DSC scans of compound 4<sup>a</sup>.**

	Transition temperature (T <sup>p</sup> /°C) and associated	
	Transition enthalpies values (ΔH/Jg <sup>-1</sup> )	
2 <sup>nd</sup> Heating	Cr 99.34 (59.5) SmA 133.19 (2.9) N152.20 (1.4) I	
2 <sup>nd</sup> Cooling	I 149.31 (1.23) N129.15 (2.7) SmA 61.19 (43.1) Cr	

<sup>a</sup>Abbreviations : Cr = crystal, SmA = smectic A, I = isotropic phase

The DSC thermogram of compound 4 is shown in Figure 2. Three exothermic peaks were found on cooling from the isotropic liquid. The enthalpy change

at the SmA-Nematic transition is higher than at the Nematic-Iso transition which is usually observed for this type of phase transition [Kouwer *et al.* 2003].

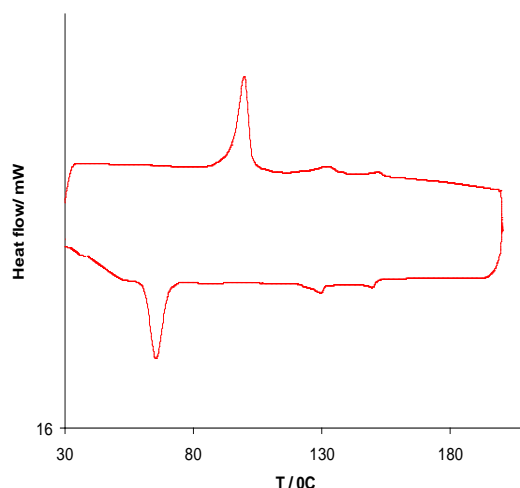


Figure 2: DSC heating and cooling traces of compound 4 ( $10\text{ }^{\circ}\text{C min}^{-1}$ )

#### Phase structures:

The phase structures were determined by polarizing optical microscope (POM). The polarized optical micrograph of **4**, observed for the two mesophases in the liquid crystalline phase during the second heating

and cooling cycle, is shown in Figure 2a and 2b. On heating to the isotropic phase, a smectic A texture was observed under the polarizing optical microscope at  $134.2\text{ }^{\circ}\text{C}$ . On further heating a schlieren texture, as typical for nematic phase was observed at  $152.8\text{ }^{\circ}\text{C}$ .

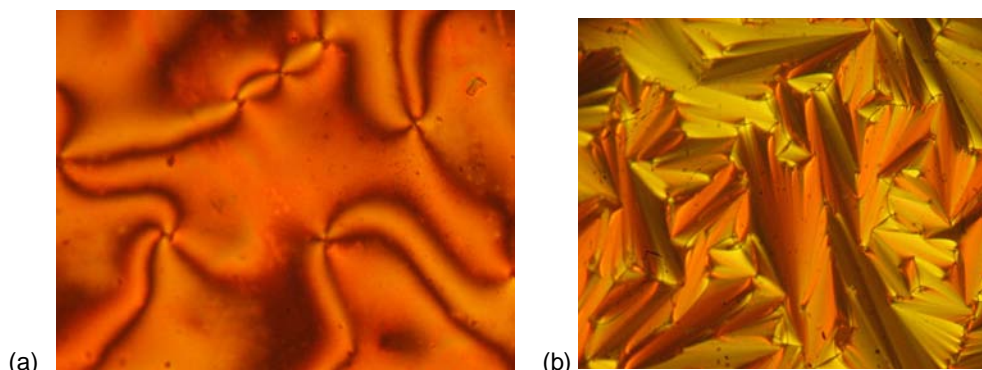


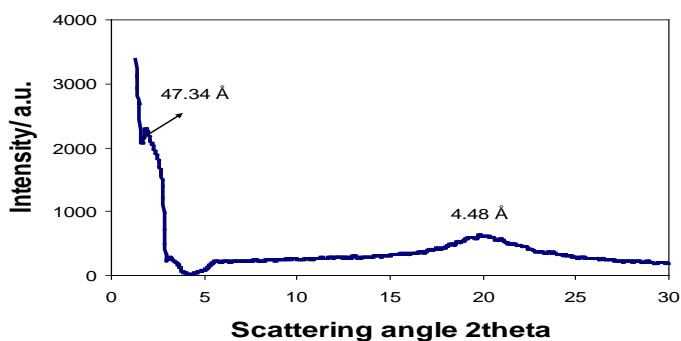
Figure 3: Optical photomicrograph of **4** obtained with a polarizing microscope (a) on cooling from the isotropic liquid at  $149.6\text{ }^{\circ}\text{C}$  (b) on cooling from the nematic phase  $130.2\text{ }^{\circ}\text{C}$  (Cross polarizer magnification  $\times 200$ ).

On cooling from the isotropic phase a schlieren texture, as typical for nematic phases, also appeared at  $149.6$  (figure 2a). This nematic is highly fluid and upon further cooling a well-defined texture, Fan-shaped conic texture appeared at  $130.2\text{ }^{\circ}\text{C}$  (figure 2b). This texture is a characteristic for Smectic A phases and remained stable up to  $78.5\text{ }^{\circ}\text{C}$ . Shearing leads to a homoeotropic alignment, which appeared optically isotropic. There is no further phase transition on further cooling until it crystallized at  $61.7\text{ }^{\circ}\text{C}$ . 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 (2004) 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.

#### X-ray diffraction

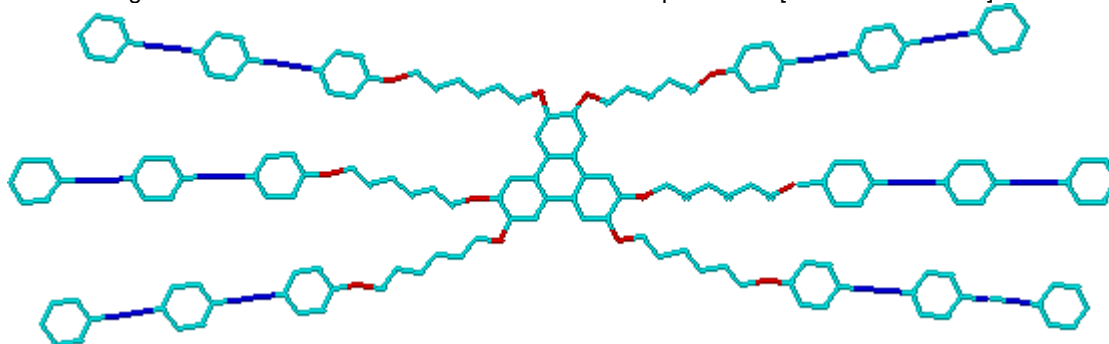
The Smectic structure of the liquid crystal phase was confirmed by XRD studies. The X-ray pattern of the Smectic A recorded at  $120\text{ }^{\circ}\text{C}$  contains a diffused band at  $4.48\text{ \AA}$  (wide angle), which shows that the alkyl chains have a liquid-like structure and are segregated from the aromatic core.



**Figure 4: Powder X-ray diffraction pattern of compound 4 in the liquid crystal state ( $T = 120\text{ }^{\circ}\text{C}$ ).**

There was no additional reflection that can be seen at the small angle region. The layer distance is less than one half of the molecular length in a conformation as shown in figure 4 above. It is obvious that a smectic

layer structure exists; no mixed reflections were found at the low angle region ( $47.34\text{ }\text{\AA}$ ,  $2\theta = 2\text{ }^{\circ}$ ). The layer structure is characterized by only small longitudinal displacement [Kouwer *et al.* 2004]



**Figure 5: Molecular model of compound 4 where triphenylene central core is linked to six bisazobenzene moieties as the peripheral units**

In the wide angle region, a broad halo centered at about  $2\theta = 19.56^{\circ}$ , which corresponds to an average intermolecular distance of approximately  $4.67\text{ }\text{\AA}$  as in Figure 4. It implies that the rod-like bisazobenzene units determine the mesophase structure, and thus, the smectic layers should be formed by the rod like units and the triphenylene acts only as linking unit interconnecting the rods figure 5. The spacer units are located between these aromatic sublayers and form sublayers with a reduced concentration of the bisazobenzene segments.

In addition the absence of terminal groups, do not have any effect on the segregation. Since the layer formation is only based on partial segregation of the hexamethylene spacers from the aromatic parts, a nematic phase is the alternative organization at higher temperature.

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## CONCLUSION

A new disc shaped liquid crystal molecule was prepared based on triphenylene central core, and six rod-like bisazobenzenes as the peripheral arm units connected through alkyl spacer by ether linkages. The material is a hybrid molecule exhibiting smectic A and nematic phase which are formed due to the congregation of the rod-shaped bisazobenzene mesogenic units. The triphenylene core, act only as a linking unit, interconnecting the rod-like (oligomer effect) rather than a disc-like unit, which might have lead to columnar organization.

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