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Synthesis and liquid crystalline studies of disc-shaped molecule on azo-bridged benzothiazole-phenyl ethers

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ABSTRACT

A new series of triphenylene core attached by six peripheral arms containing benzothiazoleazo with terminal ethoxy unit have successfully been synthesized and their liquid crystalline properties were characterized. The members in this series differ by the length of the methylene unit of $-(CH_2)_n$, where n, varied following ascending order from 5 to 10. The molecular structure was characterized by elemental (C, H and N) analysis and spectroscopic methods including Fourier Transform Infrared (FT-IR) and Proton Nuclear Magnetic Resonance (¹H NMR). The texture and the phase transition temperatures were investigated by using polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The disc-shape molecule with shorter spacer (n = 5) showed monotropic nematic phase. The higher homologues with n = 8-10 exhibited enantiotropic nematic phase and monotropic smectic C phase. The XRD diffraction studies further confirm the presence of smectic C without any discotic columnar phase.

Keywords: Triphenylene; discotic liquid crystal; nematic phase; smectic C phase; phase transition

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1. Introduction

Discotic liquid crystals have attracted much attention among chemists as well as physicists due to their unique structural features and unusual material characteristics [1]. Discotic liquid crystals show a number of potential applications in a variety of devices such as one-dimensional conductors, photo-conductors, field effect transistors and photovoltaic solar cells [1-3]. The most intensively studied discotic liquid crystals are triphenylene derivatives [4] since the triphenylene core is readily accessible through established synthetic routes, and is excellent at conferring liquid crystalline properties [5]. Triphenylene also can combine synthetic versatility with the molecular robustness required for device applications [6]. Hexa-esters and hexa-ethers of triphenylene are the most widely investigated discotic materials since they possess a large conjugated aromatic core [7] and have a strong tendency to form columnar mesophases [6-9], which are of interest for one-dimensional energy and electron transport. They are also useful in optical compensation films particularly in opto-electronic devices [5,10-11].

Current efforts have been directed towards designing novel molecules which in some ways combine the features of rod-shape and disc-like molecules having photoactive properties. However, the combination of calamitic moieties was incompatible with the molecular topology and induced the formation of smectic phase. Compatible combination of discotic and calamitic mesogens results in the formation of a nematic phase [8]. Recent studies by Shimizu *et al.* on a triphenylene mesogen with peripheral azobenzene units, was found to show kinetically controlled bimesomorphism with metastable smectic and stable hexagonal columnar phases created by the rod–disc alternation of the molecular shape on cooling. This molecule comprised a triphenylene core with six azobenzene units linked via short (C₃) alkyl chains [12]. Azobenzene-containing materials have potential technological applications such as in high density optical data storage, optical image processing, dynamic holography, optical computing and pattern recognition. In addition, the aromatic azo compounds undergo the *cis-trans* isomerization in response to light or heat and thus offer many opportunities in photonic liquid crystal applications [8,13,17].

In this report, we incorporate azo-bridged benzothiazole-phenyl ethers moieties into triphenylene molecule via respective alkyl chains giving triphenylene-based discotic liquid crystals with six peripheral rod-like azobenzene units. The spacers with odd and even-parity ranging from C_5H_{10} to $C_{10}H_{20}$ are introduced into this discotic system. The synthetic route used for the preparation of final compounds **5a-5f** is summarized in Scheme 1.



Scheme 1. Synthesis route toward formation of the compounds 5a-5f

2. Experimental

2.1 *Materials*

All solvents and reagents were purchased commercially and used without any further purification. 2-amino-6-ethoxybenzothiazole and 1,2-dimethoxybenzene were purchased from Acros Organics and TCI. Dibromoalkane ($C_nH_{2n}Br_2$, where n = 5, 6, 7, 8, 9, 10) was

obtained from TCI, Merck and Sigma-Aldrich. Sodium nitrite, phenol, anhydrous $FeCl_3$, boron tribromide were obtained from Sigma-Aldrich.

2.2 Measurements

The infrared (IR) spectra for all intermediates and final compounds were recorded using the Perkin Elmer 2000 FT-IR spectrophotometer, in which the samples were prepared as KBr disks. ¹H- and ¹³C-NMR spectra were recorded in CDCl₃ and deuterated DMSO using a Bruker 500 MHz Ultrashield TMFT-NMR spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Elemental analyses were carried out on a Perkin Elmer 2400 LS Series CHNS/O analyser.

The phase transition temperature and associated enthalpy values were determined using a differential scanning calorimeter (DSC) (Seiko DSC6200R), in which the samples were heated and cooled at the rates of ± 5 °C min⁻¹. Texture observation of the mesophase was carried out by using polarizing optical microscopy (POM) (Carl Zeiss Axioskop 40 polarizing microscope) equipped with a hot stage (Linkam LTS350) and a temperature controller (TMS94).

Synchrotron powder X-ray diffraction (XRD) measurements were performed at beamline BL17A of the National Synchrotron Radiation Research Center, Taiwan, where the wavelength of X-ray was 1.33366 Å. The XRD data were collected using imaging plates (area = 20×40 cm² with a pixel resolution of 100) curved with a radius equivalent to a sample-toimage plate distance of 280 mm, and the diffraction signals were accumulated for 3 min. The powder samples were packed into capillary tubes heated by a heat gun, whose temperature controller was programmable by a computer with a proportional, integral and differential feedback system. The scattering angle θ was calibrated by a mixture of silver behenate and silicon.

2.3 Synthesis

2.3.1. Synthesis of 4-((5-ethoxybenzothiazol-2-yl)diazenyl)phenol (1)

Compound **1** was prepared according to the method described in earlier report [13]. A solution containing 20 ml diluted sulphuric acid (60 %) and 6-ethoxy-2-aminobenzothiazole (1 g, 5.1 mmol), which was earlier dissolved in 15 ml glacial acetic acid, was cooled down to 5°C. Sodium nitrite (0.35 g, 5.1 mmol) in 12.5 ml water was added dropwise to the cooled

mixture and stirred for 1h in an ice bath. Phenol (0.47 g, 5.1 mmol) dissolved in 15 ml ethanol was cooled to 5°C and the diazonium salt solution was added dropwise at a temperature below 5°C. The mixture was stirred for 1h. The pH was subsequently increased to 6-7 by the addition of 1 N NaOH and the mixture was stirred for 1h in an ice bath. Finally, water was added to the resulting mixture and the red crystals were collected by filtration. The product was recrystallized from ethanol. Yield: 75 %. IR (KBr) v/cm^{-1} : 3300–2600 (OH broad), 3042 (C–H aromatic), 1605, 1579 (C=C aromatic, C=N thiazole), 2943 (C–H aliphatic), 1057 (benzothiazole), 1135 (C–O). ¹H-NMR (DMSO-d₆) δ /ppm: 1.39 (t, 3H, – CH₃), 4.1 (q, 2H, –OCH₂), 7.01 (d, 2H, ArH), 7.1 (d, 1H, ArH), 7.6 (d, 1H, ArH), 7.8 (d, 2H, Ar), 8.0 (s, 1H, ArH).

2.3.2. Synthesis of 4-((6-ethoxybenzothiazole-2-yl)diazenyl)bromo-pentanoxyphenyl (2a)

The mixture consisting of compound **1** (1.0 g, 3.34 mmol) in 150 ml dry acetone, potassium carbonate (K₂CO₃) (4.61 g, 33.4 mmol), a catalytic amount of potassium iodide (100 mg), and a five-fold excess of 1,5-dibromopentane (3.82 g, 16.7 mmol) was refluxed for 24 h. K₂CO₃ was removed by filtration while it was still hot and the acetone was removed under reduced pressure. The product was recrystallized three times from ethanol whereupon the pure compound was isolated giving orange solid. Yield: 60 %. IR (KBr) v/cm⁻¹: 3071 (C-H aromatic), 2973, 2860 (C-H aliphatic), 1600 (C=C aromatic), 1579 (C=N thiazole), 1264 (Ar-O-R ether), 1052 (C-S-C thiazole). ¹H-NMR (CDCl₃) δ /ppm: 1.47 (t, 3H, CH₃–), 1.53–1.55 (m, 2H, –(CH₂)₂–), 1.8–1.9 (m, 4H, – (CH₂)₂–), 3.46 (t, 2H, –CH₂Br), 4.09–4.14 (m, 4H, (CH₂)O–), 7.01 (d, 2H, Ar–H), 7.08 (d-d, 1H, Ar–H), 7.26 (d, 1H, Ar–H), 7.9 (s, 1H, Ar–H), 8.0 (d, 2H, Ar–H).

2.3.3. Synthesis 2,3,6,7,10,11-Hexamethoxytriphenylene (3)

A solution of 1,2-dimethoxybenzene (10 g, 72.4 mmol) in dichloromethane (50 ml) was added dropwise to a suspension of anhydrous $FeCl_3$ (35.22 g, 217.2 mmol) in dichloromethane (100 ml) and concentrated sulphuric acid (0.5 ml). After complete addition (15 min), the reaction mixture was further stirred for 3 h at room temperature. 200 ml of methanol were then slowly added under vigorous stirring. The obtained mixture was further stirred for additional 30 min. and the precipitate was filtered off, washed with methanol (5 x

100 ml) and dried under reduced pressure to give a purple solid. Yield: 80 %, ¹H-NMR (CDCl₃) δ /ppm: 4.10 (s, 18H, OCH₃), 7.80 (s, 6H, ArH)

2.3.4. Synthesis 2,3,6,7,10,11-Hexahydroxytriphenylene (4)

The preparation of compound **4** is similar to that reported in the literature [14]. Hexamethoxytriphenylene (7 g, 17.14 mmol) was dissolved in dichoromethane (50 ml) and the solution thus obtained was cooled in ice bath. A solution of boron tribromide (11.47 ml) was then added slowly to the reaction mixture over a period of 30 min. After complete addition, the reaction was left stirring overnight in room temperature. The reaction mixture was then slowly poured into crushed ice (100 g) and the obtained mixture was stirred vigorously until the ice melted. It was then extracted with ethyl acetate (6 x 150 ml), dried over anhydrous sodium sulphate and evaporated to dryness giving dark purple solid. The yield was quantitative and this compound was used without further purification.

2.3.5. Synthesis of compound **5a**

Similar procedure with equal amount of molar ratio of intermediate 4 was used to synthesize the derivatives 5a-5f. Derivative 5a is chosen as a representative compound for detailed description. In round bottom flask, compound 4 (0.038 g, 0.12 mmol) was dissolved in 50 ml of N-N-dimethylformamide. K₂CO₃ (0.15 g, 1.2 mmol) and a catalytic amount of potassium iodide (50 mg) was added to the solution and the reaction mixture was heated at refluxed for 2 h. Compound 2a (0.52 g, 1.2 mmol) was dissolved in minimal amount of N,Ndimethylformamide and was subsequently added to the reaction mixture and refluxed at 100°C for 120 h. The reaction was monitored by TLC. The resulting solution was poured into the water (100 ml) whereupon the precipitate will form. The precipitate was filtered out and was purified by silica gel column chromatography with chloroform as the mobile phase to afford orange solid. Yield: 68 %. Elemental analysis: Calculated for C₁₃₈H₁₃₈N₁₈O₁₈S₆: C 65.47, H 5.46, N 9.96%; found: C 65.72, H 5.58, N 10.09%. IR (KBr) v/cm⁻¹: 3065 (C-H aromatic), 2938, 2868 (C-H aliphatic), 1594 (C=C aromatic), 1578 (C=N thiazole), 1249 (Ar-O-R ether), 1055 (C-S-C thiazole). ¹H-NMR (CDCl₃) δ/ppm: 1.45 (t, 3H, CH₃-), 1.72-1.79 (m, 2H, -(CH₂)₂-),1.9-2.0 (m, 4H, -(CH₂)₂-), 3.94-4.0 (m, 4H, CH₂O-), 4.29 (t, 2H, CH₂O-Ar), 6.95 (d, 2H, Ar-H), 7.05 (d-d, 1H, Ar-H), 7.21 (d, 1H, Ar-H), 7.87 (s, 1H, Ar-H), 7.94 (d, 2H, Ar-H), 7.98 (s, 1H, Ar-H). ¹³C-NMR (CDCl₃) δ/ppm: 173.88 (C=N thiazole), 163.39-

104.96 (Ar-C), 69.43, 68.41 (O-CH₂-CH₂), 64.10 (O-CH₂-CH₃), 29.21-22.95 (-(CH₂)₃-), 14.77 (-CH₃).

The physical results, IR, ¹H- and ¹³C-NMR along with elemental analysis data for the compound **5b-5f** are shown in Sections 2.3.6-2.3.10.

2.3.6. Synthesis of compound 5b

Yield: 52 %. Elemental analysis: Calculated for $C_{144}H_{150}N_{18}O_{18}S_6$: C 66.12, H 5.74, N 9.64%; found: C 66.41, H 5.85, N 9.78%. IR (KBr) v/cm⁻¹: 3068 (C-H aromatic), 2935, 2865 (C-H aliphatic), 1595 (C=C aromatic), 1578 (C=N thiazole), 1253 (Ar-O-R ether), 1056 (C-S-C thiazole). ¹H-NMR (CDCl₃) δ /ppm: 1.45 (t, 3H, CH₃), 1.65-1.75 (m, 4H, -(CH₂)₂-),1.85-2.0 (m, 4H, -(CH₂)₂-), 4.04 (t, 2H, CH₂O-), 4.06-4.11 (m, 2H, CH₂O-), 4.26 (t, 2H, CH₂O-Ar), 6.95 (d, 2H, Ar-H), 7.06 (d-d, 1H, Ar-H), 7.22 (d, 1H, Ar-H), 7.86 (s, 1H, Ar-H), 7.95 (d, 2H, Ar-H), 7.98 (s, 1H, Ar-H). ¹³C-NMR (CDCl₃) δ /ppm: 173.89 (C=N thiazole), 163.45-104.97 (Ar-C), 69.50, 68.39 (O-CH₂-CH₂), 64.11 (O-CH₂-CH₃), 29.42-25.86 (-(CH₂)₄-), 14.77 (-CH₃).

2.3.7. Synthesis of compound 5c

Yield: 63 %. Elemental analysis: Calculated for $C_{150}H_{162}N_{18}O_{18}S_6$: C 66.73, H 6.01, N 9.34%; found: C 67.04, H 6.12, N 9.45%. IR (KBr) ν/cm^{-1} : 3066 (C-H aromatic), 2931, 2863 (C-H aliphatic), 1595 (C=C aromatic), 1577 (C=N thiazole), 1252 (Ar-O-R ether), 1056 (C-S-C thiazole). ¹H-NMR (CDCl₃) δ /ppm: 1.48 (t, 3H, CH₃), 1.40-1.46 (m, 6H, -(CH₂)₂-),1.82-1.96 (m, 4H, -(CH₂)₂-), 4.07 (t, 2H, CH₂O-), 4.10-4.16 (m, 2H, CH₂O-), 4.25 (t, 2H, CH₂O-Ar), 6.95 (d, 2H, Ar-H), 7.09 (d-d, 1H, Ar-H), 7.23 (d, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.96 (d, 2H, Ar-H), 7.98 (s, 1H, Ar-H). ¹³C-NMR (CDCl₃) δ /ppm: 173.90 (C=N thiazole), 163.49-104.99 (Ar-C), 69.50, 68.43 (O-CH₂-CH₂), 64.11 (O-CH₂-CH₃), 29.51-25.65 (-(CH₂)₅-), 14.78 (-CH₃).

2.3.8. Synthesis of compound 5d

Yield: 58 %. Elemental analysis: Calculated for C₁₅₆H₁₇₄N₁₈O₁₈S₆: C 67.31, H 6.26, N 9.06%; found: C 67.55, H 6.41, N 9.15%. IR (KBr) v/cm⁻¹: 3070 (C-H aromatic), 2933, 2857 (C-H aliphatic), 1594 (C=C aromatic), 1578 (C=N thiazole), 1252 (Ar-O-R ether), 1055 (C-

S-C thiazole). ¹H-NMR (CDCl₃) δ /ppm: 1.39 (t, 3H, CH₃), 1.42-1.50 (m, 8H, -(CH₂)₂-), 1.80-1.98 (m, 4H, -(CH₂)₂-), 4.02 (t, 2H, CH₂O-), 4.06-4.12 (m, 2H, CH₂O-), 4.24 (t, 2H, CH₂O-Ar), 6.96 (d, 2H, Ar-H), 7.06 (d-d, 1H, Ar-H), 7.24 (d, 1H, Ar-H), 7.84 (s, 1H, Ar-H), 7.97 (d, 2H, Ar-H), 7.99 (s, 1H, Ar-H). ¹³C-NMR (CDCl₃) δ /ppm: 173.92 (C=N thiazole), 163.55-105.01 (Ar-C), 69.52, 68.43 (O-CH₂-CH₂), 64.12 (O-CH₂-CH₃), 29.81-25.35 (-(CH₂)₆-), 14.79 (-CH₃).

2.3.9. Synthesis of compound 5e

Yield: 51 %. Elemental analysis: Calculated for $C_{162}H_{186}N_{18}O_{18}S_6$: C 67.84, H 6.49, N 8.79%; found: C 68.12, H 6.62, N 8.89%. IR (KBr) v/cm⁻¹: 3071 (C-H aromatic), 2933, 2856 (C-H aliphatic), 1595 (C=C aromatic), 1577 (C=N thiazole), 1253 (Ar-O-R ether), 1056 (C-S-C thiazole). ¹H-NMR (CDCl₃) δ /ppm: 1.47 (t, 3H, CH₃), 1.32-1.41 (q, 10H, -(CH₂)₂-), 1.78-1.96 (m, 4H, -(CH₂)₂-), 4.03 (t, 2H, CH₂O-), 4.05-4.14 (m, 2H, CH₂O-), 4.23 (t, 2H, CH₂O-Ar), 6.95 (d, 2H, Ar-H), 7.05 (d-d, 1H, Ar-H), 7.22 (d, 1H, Ar-H), 7.88 (s, 1H, Ar-H), 7.96 (d, 2H, Ar-H), 7.99 (s, 1H, Ar-H). ¹³C-NMR (CDCl₃) δ /ppm: 173.92 (C=N thiazole), 163.64-105.03 (Ar-C), 69.54, 68.45 (O-CH₂-CH₂), 64.14 (O-CH₂-CH₃), 29.89-24.95 (-(CH₂)₇-), 14.79 (-CH₃).

2.3.10. Synthesis of compound 5f

Yield: 69 %. Elemental analysis: Calculated for $C_{168}H_{198}N_{18}O_{18}S_6$: C 68.36, H 6.71, N 8.54%; found: C 68.64, H 6.67, N 8.42%. IR (KBr) v/cm⁻¹: 3070 (C-H aromatic), 2923, 2852 (C-H aliphatic), 1595 (C=C aromatic), 1578 (C=N thiazole), 1252 (Ar-O-R ether), 1055 (C-S-C thiazole). ¹H-NMR (CDCl₃) δ /ppm: 1.48 (t, 3H, CH₃), 1.30-1.42 (q, 12H, -(CH₂)₂-), 1.78-1.98 (m, 4H,-(CH₂)₂-), 4.02 (t, 2H, CH₂O-), 4.07-4.14 (m, 2H, CH₂O-), 4.24 (t, 2H, CH₂O-Ar), 6.97 (d, 2H, Ar-H), 7.07 (d-d, 1H, Ar-H), 7.25 (d, 1H, Ar-H), 7.83 (s, 1H, Ar-H), 7.97 (d, 2H, Ar-H), 7.99 (s, 1H, Ar-H). ¹³C-NMR (CDCl₃) δ /ppm: 173.92 (C=N thiazole), 163.69-105.05 (Ar-C), 69.55, 68.47 (O-CH₂-CH₂), 64.15 (O-CH₂-CH₃), 29.95-24.85 (-(CH₂)₈-), 14.79 (-CH₃).

3. **Result and Discussion**

3.1 Mesomorphic behaviour

The transition temperatures and associated enthalpy changes determined by differential scanning calorimetry (DSC) for compounds **5a-5f** are listed in Table 1. On cooling the homologue **5a** with n = 5 showed monotropic nematic phase. Compounds **5b** and **5c** displayed enantiotropic nematic phase. However, the homologues with the spacer length n = 8-10 exhibit enantiotropic nematic phase and on cooling monotropic smectic C (SmC) phase was observed. Observation on **5e** under the polarized microscope upon cooling from its isotropic liquid phase showed the presence of two mesophases. Upon cooling the isotropic liquid of **5e**, Schlieren texture (Figure 1(a)) of nematic phase appeared at 142°C. Upon further cooling, the emergence of the smectic C phase (Figure 1(b)) was observed at 112°C.

Table 1. Phase transition temperature (°C) and associated enthalpy (in kJ mol⁻¹) (in brackets) for compounds **5a-5f** upon heating and cooling.

PP				
Compound	Cr	SmC	Ν	Ι
5a	• 215.3 (31.2)			•
	• 147.4 (38.9)		o 210.4 (0.50)	•
5b	• 128.2 (18.6)		• 184.7 (0.69)	•
	• 56.8 (23.6)		• 180.3 (1.14)	•
5c	• 133.6 (40.6)		• 189.7 (0.66)	•
	• 71.3 (25.8)		• 172.6 (0.94)	•
5d	• 136.2 (31.8)		• 178.4 (0.88)	•
	• 90.8 (30.6)	o 135.8 (1.12)	• 166.7 (1.32)	•
5e	• 139.2 (28.9)		• 173.8 (1.12)	•
	• 65.5 (26.3)	o 122.2 (0.64)	• 156.2 (0.98)	•
5f	• 127.7 (22.3)		• 166.4 (0.81)	•
	• 51.3 (18.8)	o 122.1 (0.49)	• 159.5 (0.25)	٠

Cr = crystalline phase; SmC = smectic C phase; N = nematic phase; I = isotropic; • = enantiotropic phase; o = monotropic phase





Figure 1. Optical photomicrographs of **5e** during cooling cycle. On cooling from the isotropic liquid, Schlieren texture (a) of nematic phase appeared at 142°C. On further cooling, broken fan-shaped texture of smectic C (b) observed at 112°C.

The DSC heating-cooling traces for representative compound **5f** are given in Figure 2. Upon heating, two endothermic peaks were observed at 127.7°C and 166.4°C with enthalpies $\Delta H = 22.3 \text{ kJ mol}^{-1}$ and 0.81 kJ mol⁻¹, which represent the crystal-nematic and nematic-isotropic transitions, respectively. However, on cooling three exothermic peaks are observed at 159.5°C, 122.1°C and 51.3°C, with respective enthalpies values of 0.25 kJ mol⁻¹, 0.49 kJ mol⁻¹ and 18.8 kJ mol⁻¹ assignable to the isotropic-nematic, nematic-smectic C and smectic C-crystal transitions.



The dependence of the transition temperatures on spacer length (*n*) for compounds **5a-5f** is shown in Figure 3. The melting point dropped from **5a** to **5b** and then gradually increased from **5b** to **5e**. As the length of spacer increased, the melting point continued to decrease from **5e** (n = 9) to **5f** (n = 10). However, the clearing temperature increased from **5b** to **5c** and then descended when the length of carbon chain is increased. This observation could be due to the dilution of the mesogenic core resulted from the flexibility of the spacer [15].



Figure 3. Dependence of the transition temperatures on the number of carbon atoms linking with the 2,3,6,7,10,11-hexahydroxytriphenylene comprising benzothiazole moieties with azo linkage, *n*, in the compounds **5a-5f** upon heating.

3.2 XRD analysis

XRD study has been carried out on a representative compound **5f** (n=10) in order to provide more detailed information on the liquid-crystalline phase structures of the rod-disc shape mesogen. Based on XRD data of **5f**, the presence of N phase is confirmed from the XRD pattern at 140°C (Figure 4) whereby no peak is recorded at small angle but a broad peak is recorded in wide-angle region wherein 2θ =13.53°, thus indicating a liquid-like order of N phase. Figure 5 demonstrate a typical XRD pattern of the SmC phase exhibited by **5f**. At 100°C, an obvious sharp peak is shown in the low angle 2θ =0.763° (with the d-spacing value of 7.703 nm), which could verify the tilted smectic layered structures of the SmC phase in compound **5f**. The broad peak at the wide angle of 2θ =13.82° corresponds to the average distances between rigid rods of SmC phase, which should be irrelevant to their molecular chain lengths [18]. The formation of smectic phase by rod-disc shaped mesogen is presumably due to a side-by-side organization of azobenzene base peripheral units which lie parallel to each other. The layer distance is a bit less than one half of the molecular length in a conformation as shown in Figure 6 derived from MM2 computations of CS Chem Draw 3D (version 5) program.



Figure 4. The intensity versus 2θ profile for the X-ray diffraction pattern of compounds **5f** at 140°C during the cooling process.



Figure 5. The intensity versus 2θ profile for the X-ray diffraction pattern of compounds **5f** at 100°C during the cooling process.

The aromatic rod-like cores are organized in common layers together with the disc-like triphenylene cores. It can be deduced that the rod-like peripheral arms will determine the type of mesophase because the alkyl spacer (n=5 until 10) linking the linearly benzothiazole azo and triphenylene core is flexible enough to allow the pheripheral to rotate freely [18]. Hence, the smectic and nematic layers are formed by these rod-like units and the triphenylene unit acts only as linking unit interconnecting the rods. A related azobenzene triphenylene linked by flexible chain (Figure 7) had been reported by Shimizu *et al.*



Figure 6. Molecular model of compound **5b** in which six rod-like benzothiazole azo as the peripheral units are connected to a triphenylene core



Figure 7. The structure of compound 2,3,6,7,10,11-hexakis(4-*n*-decyloxyphenylazophenyl-4-propylenecarboxy)triphenylene, reported by Shimizu et al [12].

In the present compounds **5a-5f**, the triphenylene core and peripheral benzothiazole moieties with azo unit are linked by more flexible spacers. This system allows conformational change. Thus, the rod-shape segment could easily align in parallel arrangement resulting in layered structure characteristics of smectic phase.

3.3 Absorption spectra

The preliminary studies of the photochemical properties were carried out on the compounds **5a-5f** consisting of azo -N=N- linkage. The UV-Visible absorption spectra for all the compounds are depicted in Figure 8 and the absorption maximums are listed in Table 9. The absorption spectra for all the six compounds are found to be almost identical. This can be attributed to the fact that the compounds possess almost the same molecular structures with only the variation of the length of methylene unit $-(CH_2)_n$, where n=5-10. One of the remarkable trend that we can infer from the absorption spectra is that for the peaks which appeared in high-intensity at 427.50-430.50 nm can be associated with the π - π * transition of the *trans*-configuration of azobenzene. This observation complies with the previously reported rod-disc shaped liquid crystals containing triphenylene and azobenzene with *trans*-configuration of which the absorption fell within the range from 392 to 460 nm [16].



Figure 8. UV-Visible absorption spectra of compound 5a-5f in chloroform

	Absorbance, nm
Compounds	λ_{\max}
5a (n=5)	427.50
5b (n=6)	429.00
5c (n=7)	430.00
5d (n=8)	431.50
5e (n=9)	431.50
5f (n=10)	430.00

Table 9. UV-Visible results of compounds 5a-5f

4. Conclusion

A new series which consists of both discotic and calamatic bearing a triphenylene as central core and six rod-like benzothiazole azo as the peripheral units was prepared. The combination of calamitic and discotic units led to a nematic phase although the molecule is disc-shaped. It seems that the triphenylene unit acts only as a linking unit, interconnecting the rod-like units (oligomer effect) rather than as a disc-like unit, which would lead to a columnar organisation. The homologue with n = 5 displayed monotropic nematic phase. However, the higher homologues (n = 8 to 10) exhibited nematic phase and upon cooling showed monotropic smectic C phase.

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Highlights

- Newly derived triphenylene armed by peripheral azo-bridged benzothiazole-phenyl ethers.
- The member with shorter spacer (n=5) exhibits predominantly monotropic N phase.
- The members with longer spcaer (n=8-10) show enantiotropic N and monotropic SmC phase.
- Central core of triphenylene acts as a linking unit rather than as a disc-like entity.
- XRD data reveals the presence of smectic C without any discotic columnar phase

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