SYNTHESIS AND CHARACTERIZATION OF TRIPHENYLENE-BASED DISCOTIC LIQUID CRYSTALLINE MONOMERS CONTAINING AZOBENZENE MOIETIES

M. R. Lutfor[1], M. H. Iqbal[1], S. Silong[2], M. Z. A. Rahman[2] and W. M. Z. Wan Yunus[2]
[1]School of Science and Technology, Universiti Malaysia Sabah,
88999 Kota Kinabalu, Sabah, Malaysia
[2]Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 Serdang, Selangor Malaysia

ABSTRACT. *A series of novel discotic liquid crystalline monomer was synthesized where the molecular architecture is composed of a triphenylene unit as central core and six rod-like azobenzene moieties as the peripheral core. The azobenzene mesogen was synthesized based on the acrylate monomer containing an alkyl chain spacer with 6 and 9 methylene units. These peripheral cores were linked to the central core by esterification. This is the first example of the triphenylene based discotic liquid crystalline monomer as 3,6,7,10,11-hexakis-[{4-(4-alkeneloxy)phenylazo}benzoyloxy]triphenylene was prepared by using a ferric chloride oxidation method. Differential scanning calorimetry and polarizing optical microscopy measurements confirmed the existence of columnar mesophases for all compounds. UV-vis spectra showed that the absorption of azobenzene mesogens was a significant tailing, which would allow the use of laser in the visible range to photo induce reorientation of the azo groups for holographic storage.*

KEYWORDS. Azobenzene, chromophore, discotic liquid crystal, polymer liquid crystal

INTRODUCTION

Triphenylene derivatives are the most well known representatives of the discotic liquid crystal forming columnar mesophase (Cammidge and Bushby, 1998; Chandrasekhar, 1998.). The mesophases of these materials having very high charge carrier mobility makes them suitable for use in one-dimensional conductor, photoconductors, light-emitting diode and one-dimensional energy transfer (Kuboshita *et al.* 1991; Kumar and Manickam, 1999). The photo-orientation of the azobenzene units is induced through trans-cis-trans isomerization cycles by irradiating liquid crystalline materials containing the chromophores with linearly polarized light (Ikeda and Tsutsumi, 1995). A significant optical birefringence could be achieved due to the large anisotropy of reorientation of the chromophores. Polymer liquid crystals (PLC) as optical storage materials have became a promising area in fundamental research and industries. Photon mode optical image storage in PLCs has been demonstrated by Goldmann *et al.* (1998). Their system is composed of PLCs with side-chain photochromic azobenzene moieties, and photoirradiation caused isomerization of the photochoromic molecules, inducing grating in the PLC. The grating is produced by the change in the refractive index of the medium resulting from isomerization.

Recently, Stracke *et al.* (2000) introduced discotic liquid crystals called trisazomelamine consisting of a triazine core, linked to three rod-like azobenzene units bearing a C_{12}-alkyl chain for optical storage in smectic mesophases. In this paper, we have prepared triphenylene based discotic liquid crystal monomers having six rod-like azobenzene units via ester groups for novel optical storage.

MATERIALS AND METHODS

Materials

4-Aminobenzoic acid (Fluka), sodium nitrite (BDH), urea (BDH), phenol (Merck), 8-bromo-1-octene (Fluka), 11-bromo-1-undecene (Fluka), veratrole (BDH), boron tribromide (Merck), 1,3-dicyclohexylcarbodiimide (DCC) (Merck), 4-(N,N-dimethylamino)pyridine (DMAP) (Merck), silica gel-60 (Merck) and sodium sulfate (Fluka) were used as received. Dry acetone (Merck) and dry dichloromethane (Merck) were obtained from distilling over phosphorus pentaoxide. Other solvents and chemicals were used without further purification unless otherwise stated.

4-(4-Hydroxyphenylazo)benzoic acid (1)

4-Aminobenzoic acid (10 g, 0.0729 mol) was dissolved in 100 ml water, 100 ml acetone and 16 ml of conc hydrochloric acid. The mixture was cooled to 2 C, and sodium nitrite (6.00 g, 0.0869 mol) in 20 ml of water was added drop-wise to the cooled mixture with stirring for 1 h using a mechanical stirrer. Exactly, 5 ml of urea (0.86 g, 0.0143 mol) solution was added with stirring for 10 minutes to decompose the excess sodium nitrite. Phenol (6.86 g, 0.0729 mol) with 10 ml water was added to the diazoted mixture and stirred for 1 h. The reaction was maintained at pH 7-8 by using sodium hydroxide solution and stirred for 2 h. Then 300 ml of water was added to the mixture and the precipitate was collected by filtration. The resulting product was recrystallized from methanol. Yield 8.51 g (48.2 %) and m.p. 186 C. ^{1}H NMR (400 MH_z, Acetone-D_6) : 9.22 (H, ArOH), 8.20 (2H, ArH), 7.94 (4H, ArH), 7.04 (2H, ArH).

4-[4-(1-octeneloxy)phenylazo]benzoic acid (2) and *4-[4-(1-undeceneloxy)phenylazo]benzoic acid* (3)

The appropriate 8-bromo-1-octene (1.52 g, 8 mmol) or 11-bromo-1-undecene (1.86 g, 8 mmol) was dissolved in dry acetone (60 ml) solution of **1** (1.50 g, 6.19 mmol) and potassium carbonate (1.53 g, 10 mmol) with catalytic amount of potassium iodide was refluxed for 16 h under argon. The mixture was then poured into cold water and acidified with dilute hydrochloric acid. The precipitate was filtered off and dissolved in chloroform and water. The organic phase was washed with sodium chloride solution and water successively. Afterwards, the solution was dried by sodium sulfate and the solvent was removed under reduced pressure. Then, the products were recrystallized

Compound **2**: ^{1}H NMR (400 MH_z, Acetone-D_6) : 8.20 (2H, ArH), 7.94 (4H, ArH), 7.04 (2H, ArH 6.08 (2H, CH_2=CH), 5.06 (H, CH=CH_2), 4.01 (2H, OCH_2), 3.24 (2H, CH_2), 2.05 (4H, CH_2CH_2), 1.2 (4H, CH_2CH_2).

Compound **3**: ^{1}H NMR (400 MH_z, Acetone-D_6) : 8.20 (2H, ArH), 7.94 (4H, ArH), 7.04 (2H, ArH 5.85 (2H, CH_2=CH), 5.01 (H, CH=CH_2), 4.03 (2H, OCH_2), 3.47 (2H, CH_2), 1.8 (2H, CH_2), 1.68 (2 CH_2), 1.46 (2H, CH_2), 1.31 (8H, CH_2CH_2 CH_2CH_2).

2,3,6,7,10,11-Hexamethoxytriphenylene (4)

Compound **4** was prepared using a procedure described by Zniber et al. (2002). Iiron (I chloride (48.79 g) was suspended in dichloromethane (250 ml) and 0.7 ml sulfuric acid. The veratrole (13.82 g, 100 mmol) in dichloromethane (50 ml) was added slowly (15 min) to a stirr suspension of iron (III) chloride for 2 h at room temperature. Afterwards, 400 ml of methanol w added and the mixture was stirred for 15 min and the solid product was filtered off and wash several times with methanol (4 × 100 ml). The product was dried in vacuum at 50 C to yie hexamethoxytriphenylene **4** as a gray powder. Yield: 8.5 g (62.5%) and m.p. 312 C. ^{1}H NMR (4 MH_z, DMSO-D_6) : 7.59 (6H, ArH), 4.01 (18H, OCH_3).

2,3,6,7,10,11-Hexahydroxytriphenylene (5)

Demethylation of the compound **4** by using boron tribromide yielded the pheno compound **5** according to the method reported by Zniber et al. (2002). Compound **4** (1.0 g, 2 mmol) was dissolved in dichloromethane (100 ml) and the solution was cooled to 75 C. Bor tribromide (4.4 g, 15 mmol) in 50 ml of dichloromethane was added drop-wise and the reaction w maintained under argon atmosphere. The mixture was then allowed to reach room temperature a stirred for 6 h. The reaction mixture was slowly poured into 150 g of crushed ice and it was stirr until the ice melted. The product was extracted with diethyl ether (4× 100 ml) and the orgar extracts were washed with sodium chloride solution. The solvent was removed under reduc pressure and product was dried in vacuum at 50 C to yield hexahydroxytriphenylene **5**. Yield: 0.2 (26.33%) and m.p. 272 C. ^{1}H NMR (400 MH_z, DMSo-D_6) : 9.26 (6H, ArOH), 7.59 (6H, ArH).

2,3,6,7,10,11-Hexakis-[{4-(4-octeneloxy)phenylazo}benzoyloxy]triphenylene (6)
2,3,6,7,10,11-Hexakis-[{4-(4-undeceneloxy)phenylazo}benzoyloxy]triphenylene (7)

The appropriate 4-[4-(1-octeneloxy)phenylazo]benzoic acid (0.390 g, 1.11 mmol) or 4-[4-(undeceneloxy)phenylazo]benzoic acid (0.437 g, 1.11 mmol) was dissolved in 50 ml of d dichloromethane at 2 C. Then DCC (0.247 g, 1.19 mmol) and DMAP (0.013 g, 0.11 mmol) we

added at 2 C and the mixture was allowed to reach room temperature and stirred for 48 h under argon atmosphere. The white precipitate was removed by filtration and the solvent was removed by reduced pressure. The product was purified by column chromatography on silica gel with dichloromethane as eluant. The solid was recrystallized from ethanol and methanol repeatedly. Yield: 0.290 g and 0.310 g, respectively.

Compound **6**: ^{1}H NMR (400 MH_z, Acetone-D_6) : 8.20 (2H, ArH), 8.02 (1H, ArH), 7.94 (4H, ArH), 7.04 (2H, ArH), 6.08 (2H, CH_2=CH), 5.06 (H, CH=CH_2), 4.01 (2H, OCH_2), 3.24 (2H, CH_2), 2.05 (4H, CH_2CH_2), 1.27 (4H, CH_2CH_2).
Compound **7**: ^{1}H NMR (400 MH_z, Acetone-D_6) : 8.20 (2H, ArH), 8.04 (1H, ArH), 7.94 (4H, ArH), 7.04 (2H, ArH), 5.85 (2H, CH_2=CH), 5.01 (H, CH=CH_2), 4.03 (2H, OCH_2), 3.47 (2H, CH_2), 1.8 (2H, CH_2), 1.68 (2H, CH_2), 1.46 (2H, CH_2), 1.31 (8H, CH_2CH_2 CH_2CH_2).

Characterization

^{1}H NMR spectra of the samples were recorded with a Bruker-DRX (400 MHz) Spectrometer. The thermotropic properties of compounds **6** and **7** were characterized with a Perkin Elmer DSC-7 instrument. The rate of heating and cooling was 5 C min^{-1}, the sample weight was about 3 mg and indium was used for calibration. The peak maximum was taken as phase transition temperature. Optical textures were observed by using Olympus BX50 polarizing optical microscope, equipped with a Linkam THMSE 600 heating stage. Sony digital color video camera (Hyper HAD) and Sony digital color printer (FVP-1E) was used to obtain the optical micrographs. UV-vis spectra of compounds **6** and **7** were recorded with a Shimadzu-2100 UV-vis Spectrometer using chloroform (1 x 10^{-6} mol L^{-1}) solution.

RESULTS AND DISCUSSION

Synthesis

The novel disk shaped monomers were prepared based on the synthetic approach as shown in Figure 1. The peripheral core of the mesogenic part was prepared from the starting material of 4-aminobenzoic acid in which the amino group was diazoted by sodium nitrite in the presence of 2.5 equivalence of hydrochloric acid at 2 C, the diazonium salt was converted into 4-(4-hydroxyphenylazo)benzoic acid **1** by coupling with phenol. Then, the flexible spacer of the liquid crystalline moiety was introduced by alkylation of the compound **1** with 8-bromo-1-octene and 11-bromo-1-undecene to give the corresponding 4-[4-(1-octeneloxy)phenylazo]benzoic acid **2** and 4-[4-(1-undeceneloxy)phenylazo] benzoic acid **3**, respectively in the presence of potassium carbonate base.

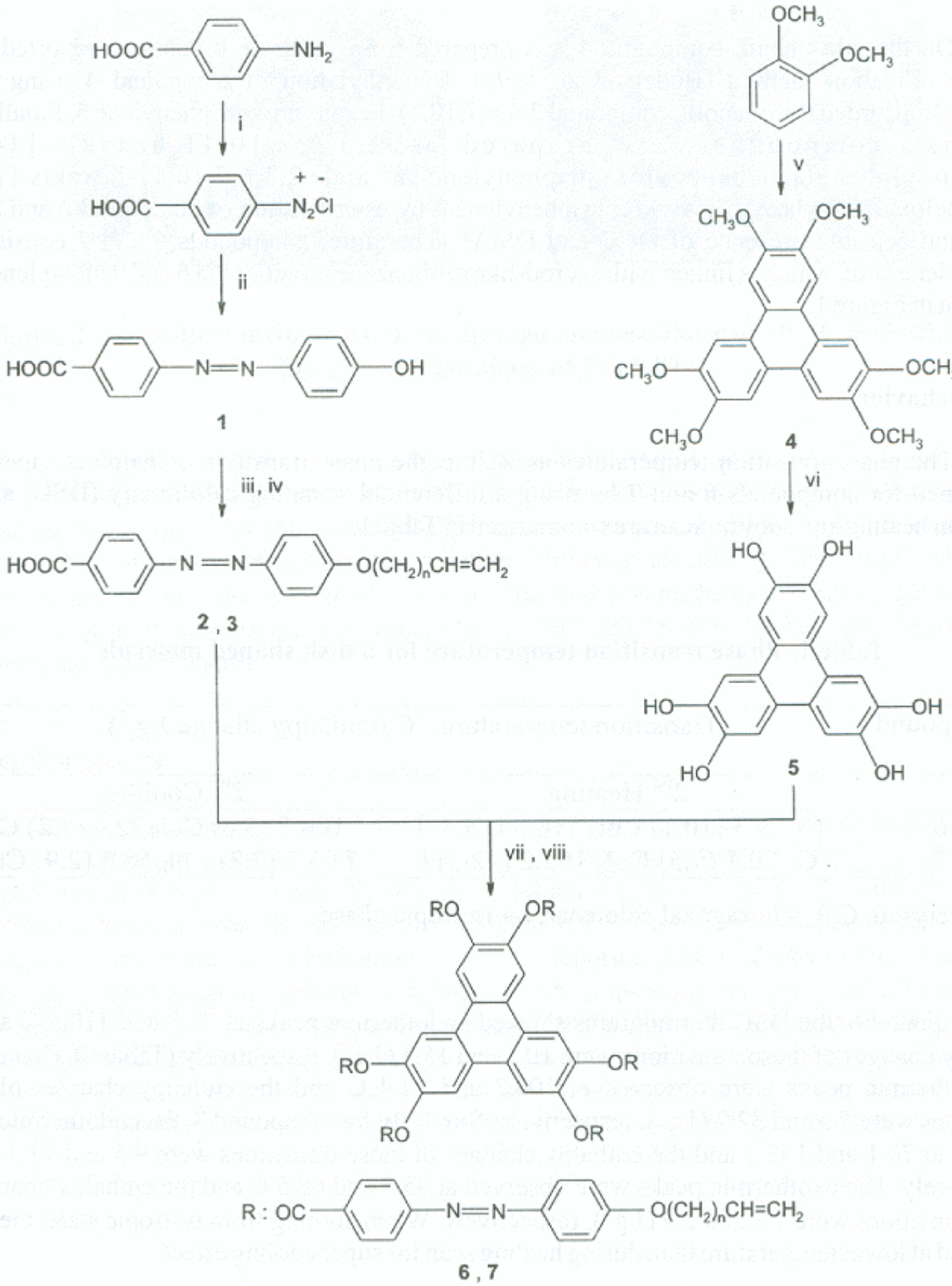


Figure 1. Synthesis of triphenylene derivatives. Reagents and conditions: i, $NaNO_2$, HCl, 2 C; ii, NaOH, C_6H_5OH; iii and iv, K_2CO_3, KI, $Br(CH_2)_n$ $CH=CH_2$ [n = 6 and 9]; v, $FeCl_3$, CH_2Cl_2, H_2SO_4; vi, BBr_3, CH_2Cl_2; vii and viii, DCC, DMAP, compound 5 and compound 2 or 3.

On the other hand, compound **4** was prepared from veratrole by using a reported ferric chloride oxidation method (Boden et al. 1993). Demethylation of compound **4** using boron tribromide afforded the phenolic compound 2,3,6,7,10,11-hexahydroxytriphenylene **5**. Finally, two disk-like compounds were prepared as 2,3,6,7,10,11-hexakis-[{4-(4-octeneloxy)phenylazo}benzoyloxy]triphenylene **6** and 2,3,6,7,10,11-hexakis-[{4-(4-undeceneloxy)phenylazo}benzoyloxy]triphenylene **7** by esterification of compound **2** and **3** with compound **5** in the presence of DCC and DMAP. Therefore, compounds **6** and **7** consist of a triphenylene core, which is linked with six rod-like azobenzene moieties via 6 and 9 methylene units as shown in Figure 1.

Phase behavior

The phase transition temperatures as well as the phase transition enthalpy changes were determined for compounds **6** and **7** by using a differential scanning calorimetry (DSC) and the results on heating and cooling scan are summarized in Table 1.

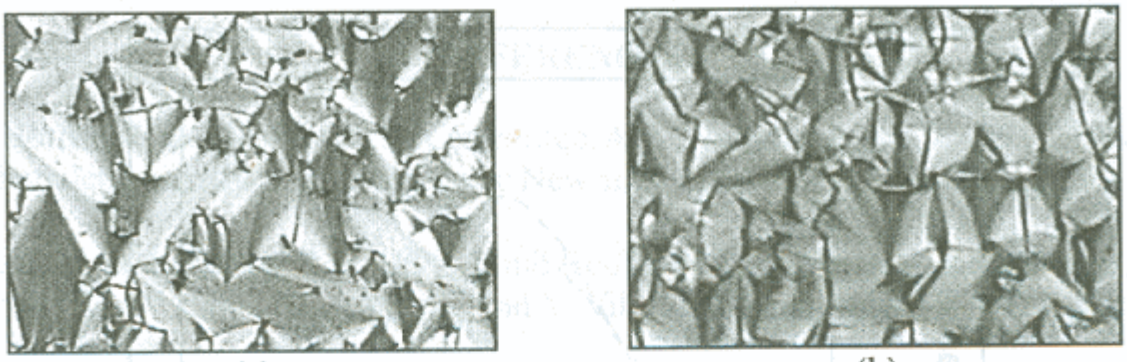
Table 1. Phase transition temperature for a disk shaped molecule [a]

Compound	Transition temperature, °C (enthalpy change J g^{-1})	
	2nd Heating	2nd Cooling
6	Cr 78.3 (10.1) Col_h 110.5 (15.3) I	I 104.2 (5.6) Col_h 72.4 (3.2) Cr
7	Cr 70.1 (9.5) Col_h 105.2 (12.3) I	I 95.7 (7.8) Col_h 68.5 (2.9) Cr

[a] Cr = crystal, Col_h = hexagonal columnar, I = isotropic phase

For compound **6**, the DSC thermograms showed endothermic peaks at 78.3 and 110.5 C and the enthalpy changes of these transitions were 10.1 and 15.3 (J g^{-1}), respectively (Table 1). On cooling, the exothermic peaks were observed at 104.2 and 72.4 C and the enthalpy changes of these transitions were 5.6 and 32.2 (J g^{-1}), respectively. Similarly for compound **7**, the endothermic peaks showed at 70.1 and 105.2 and the enthalpy changes of these transitions were 9.5 and 12.3 (J g^{-1}), respectively. The exothermic peaks were observed at 95.7 and 68.5 C and the enthalpy changes of these transitions were 7.8 and 2.9 (J g^{-1}), respectively. When cooling from isotropic state, the peaks appeared at lower temperature than during heating scan for super cooling effect.

The phase structures were observed by optical polarizing microscopy when cooling from isotropic point and their liquid crystalline phases are shown in Figure 2a and Figure 1b.



(a) (b)

Figure 2. (a) Optical texture of 6 in the hexagonal mesophase at 102°C and (b) also hexagonal mesophase of 7 at 94°C

On cooling the isotropic phase **6**, a typical pseudo focal conic texture was observed at 102 C (Figure 2a). This pseudo focal conic is a typical texture of hexagonal columnar (Col_h) phase, which is a broad transition from 102 to 80°C. A crystalline texture was observed when cooling from the Col phase and the compound is enantiotropic in nature. Similarly, on cooling the isotropic phase **7**, a focal conic texture was observed at 94°C (Figure 2b) and it is probably the hexagonal columnar (Col_h) phase. A crystalline texture was observed when cooling from the Col phase and the compound is also enantiotropic in nature.

Absorption spectra

The compounds **6** and **7** were used for the photochemical properties and absorption spectra were obtained from chloroform solution. Both compounds **6** and **7** exhibited absorption maximum at about 430 and 432 nm, respectively (Figure 3), which is related to the π -π^* of the azobenzene trans-configuration. A weak shoulder is observed at about 555 and 556 nm which is related to the n-π^* of the azobenzene trans-configuration. It was reported that 3-{2-[4-(4 ethoxyphenylazo) phenoxy]ethoxy}-4-methylthiophene exhibited π-π^* transitions of the azobenzene trans-configuration about 365 nm (Levesque and Lecerc, 1997). The UV-vis spectra recorded for the compound showed that the absorption wavelength does not change for any of the structures studied. It was observed that the absorbance of azo compounds shows significant tailing at and even beyond 550 nm, which would allow the use of laser in the visible range to photoinduce isomerization.

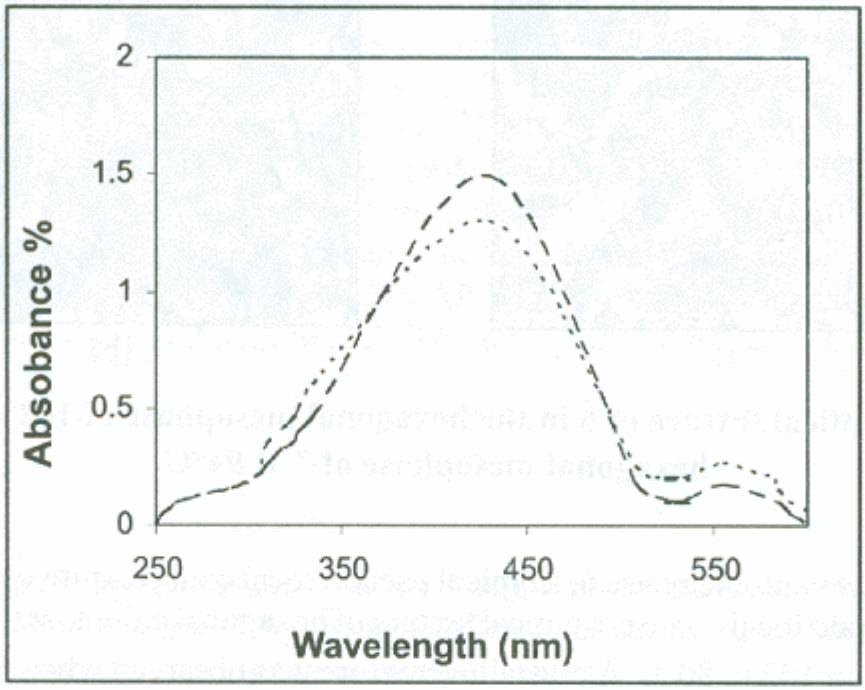


Figure 3. UV-vis spectra of compound 6 (dot line) and compound 7 (dash line).

CONCLUSION

This is the first example of a triphenylene based discotic liquid crystalline monomers as 3,6,7,10,11-hexakis-[{4-(4-alkeneloxy)phenylazo}benzoyloxy]triphenylene were prepared by using a ferric chloride oxidation method. Differential scanning calorimetry and polarizing optical microscopy measurements confirm the existence of columnar mesophases for all compounds. DSC thermograms showed two endothermic peaks when heating from room temperature and on cooling from isotropic state, the two exothermic peaks were observed at lower temperature than heating scan. A typical pseudo focal conic texture and a focal conic texture were observed for both compounds, which showed hexagonal columnar (Col_h) mesophases. UV-vis spectra of the compounds reveal that the absorbance of azo compounds shows significant tailing at and even beyond 550 nm, which would allow the use of laser in the visible range to photoinduce isomerization.

ACKNOWLEDGEMENT

This research was supported by the UMS Fundamental Research Grant (CR1: B-0901-01-ER/U35) and the German Academy Exchange Service (DAAD), The Federal Republic of Germany.

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