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Synthesis and liquid crystalline properties of a disc-shaped molecule with azobenzene at the periphery

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Abstract—A triphenylene-based novel liquid crystal was synthesised whose peripheral cores are six rod-like azobenzene moieties linked through alkyl chains. A disc-shaped molecule 2,3,6,7,10,11-hexakis-[{4-(4-nitrophenylazo)phenoxy}hexyloxy]triphenylene was prepared by using a ferric chloride oxidative trimerisation of 1,2-bis-[{4-(4-nitrophenylazo)phenoxy}hexyloxy]benzene. Differential scanning calorimetry and polarising optical microscopy analysis revealed the existence of a nematic mesophase.

Discotic liquid crystals are usually composed of molecules with a disc-like core and aliphatic tails. Substituted hexaethers of triphenylene have been widely synthesised and studied as discotic mesogens. A number of reported discogens consist of a flat, or nearly flat, rigid core surrounded by a number of aliphatic sidechains having binary, trigonal, tetragonal or hexagonal symmetries. Discotic liquid crystals exhibiting mesophases are used in many device applications.[1,2] The potential uses of these materials as photoconductors,[3] one-dimensional conductors[2,4] and light emitting diodes[5] has attracted considerable attention. Several research groups have been working on the synthesis of functionalised triphenylene-based discotic liquid crystals and their potential applications.[6–10]

An extensive study on the synthesis of discotic liquid crystals, based on a triphenylene, showed most of the compounds to form columnar mesophases.[2,6,11] However, current efforts have been directed towards designing novel molecules, which in some way combine the features of rod-shaped and disc-like molecules having photoactive properties. In one example of the combination of calamitic (rod-shaped) and discotic (disc-shaped) molecules, the discotic and calamitic moieties were incompatible with the molecular topology and induced the formation of a smectic phase.[12] Compatible combination of discotic and calamitic mesogens results in the formation of a nematic phase.[13]

We have reported that when rod-shaped azobenzene moieties were incorporated into discotic triphenylene molecules having an acrylate backbone via ester linkages, a side group liquid crystal polymer was produced.[14] Recent studied by Shimizu et al.[15] on a triphenylene mesogen with peripheral azobenzene units, shows 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 (C_3) alkyl chains using ester bonds.[15]

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 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, optical computing and pattern recognition.[16–20] In the work described here we have incorporated azobenzene moieties into a triphenylene molecule via alkyl chains (C_6) using etherification, giving, triphenylene-based discotic liquid crystals having six peripheral rod-like azobenzene units with terminal nitro groups.

Keywords: Liquid crystals; Nematic phase; Azobenzene; Disc-shaped molecule.

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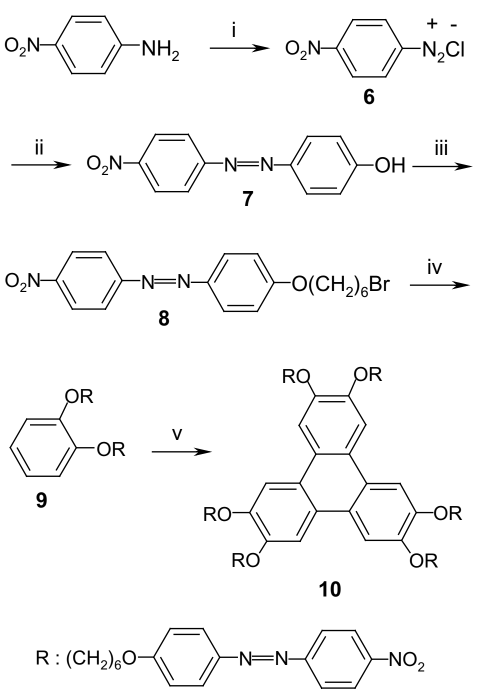

Scheme 1. Reagents and conditions: (i) $NaNO_2$, 3 equiv HCl, 2 °C; (ii) NaOH, C_6H_5OH, 2 °C, 64%; (iii) K_2CO_3, KI, $Br(CH_2)_6$ Br, reflux, 68%; (iv) catechol, K_2CO_3, KI, reflux, 46%; (v) $FeCl_3$, CH_2Cl_2, H_2SO_4, rt, 26%.

Scheme 1 outlines our synthetic approach. The peripheral units of the mesogenic part were prepared by diazotisation of 4-nitroaniline and then coupling of diazonium salt **6** with phenol yielding 4-(4-nitrophenylazo)phenol **7**. The flexible spacer was introduced by alkylation of phenol **7** with a 10-fold excess of 1,6-dibromohexane in the presence of potassium carbonate as base to give 1-bromo-4-(4-nitrophenylazo)phenoxyhexane **8**. Compound **8** was used to dialkylate catechol, in the presence of potassium carbonate, to give 1,2-bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene **9**. Finally, a disc-like molecule, 2,3,6,7,10,11-hexakis-[4-(4-nitrophenylazo)-phenoxyhexyloxy]triphenylene **10** was prepared by oxidative cyclotrimerisation of **9** with ferric chloride as the oxidant (Scheme 1).

The structures of the intermediates and the final compound were confirmed by spectroscopic analysis. The ^{13}C NMR spectrum of **10** (Fig. 1), had signals corresponding to all the carbon atoms of **10** (only one azobenzene unit is shown in detail in Figure 1, that is, $R = O(CH_2)_6OC_6H_4–4-N_2–C_6H_4–4-NO_2$). There are 18 carbon atoms in the triphenylene core but only three distinct positions (x, y, z). The x, y and z positions correspond to three signals and all other signals correspond to the carbon atoms of the six rod-shaped azobenzene moieties and the alkyl chains (Fig. 1).

Mesomorphic properties: The phase transition temperatures as well as the phase transition enthalpy changes were determined using differential scanning calorimetry (DSC). The DSC thermograms of **10** showed two endothermic peaks at 133.9 and 146.1 °C and the enthalpy changes of these transitions were 49.4 and 1.56 $J g^{-1}$, respectively (Fig. 2). On cooling, two exothermic peaks were also observed at 141.3 and 102.7 °C and the enthalpy changes of these transitions were 2.25 and 46.4 $J g^{-1}$, respectively.

The phase structures were determined by polarising optical microscopy. The polarised optical micrograph of **10**, observed in the liquid crystalline phase upon cooling, is shown in Figure 3. On cooling the isotropic phase, a schieleren texture was observed under the polarising microscope at 136.5 °C (Fig. 3). This schieleren texture is of high fluidity and the optical texture is of a

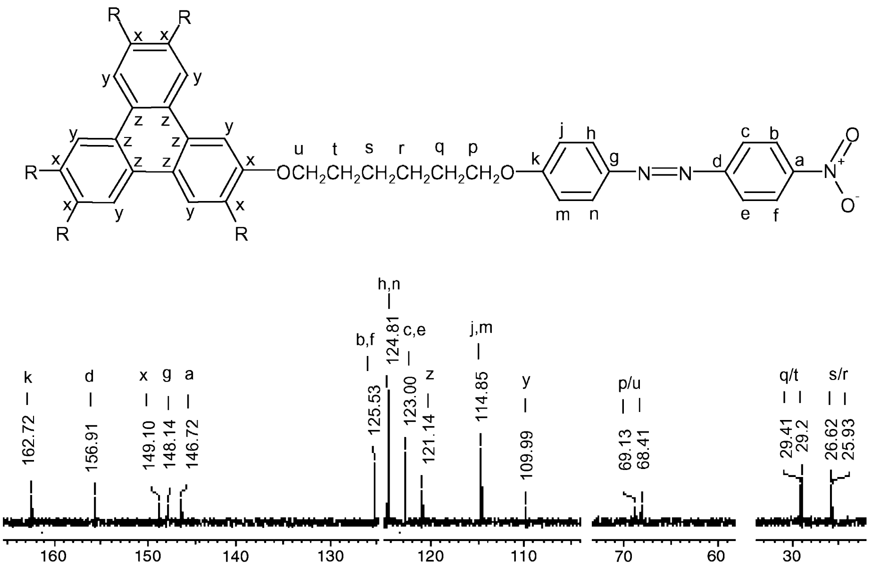

Figure 1. ^{13}C NMR spectrum of **10**. Only one azobenzene unit with an alkyl chain is shown in the chemical structure, that is, $R = O(CH_2)_6OC_6H_4–4-N_2–C_6H_4–4-NO_2$.

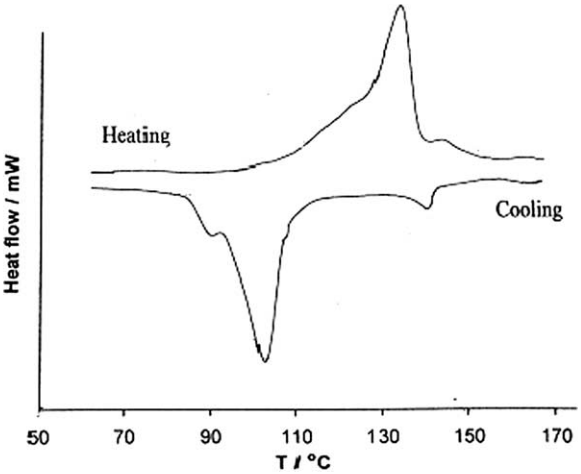

Figure 2. DSC heating and cooling traces of compound **10** (10 °C min^{-1}).

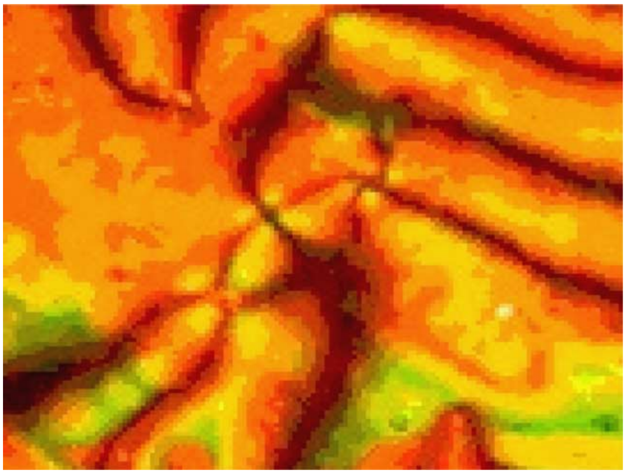

Figure 3. Optical micrograph of **10** showing nematic phase at 136 °C.

typical nematic phase. There was no further phase transition on continued cooling, except for crystallisation.

Shimizu et al.[15] described the unusual behaviour in mesophase formation for a disc-shaped molecule. The triphenylene core and peripheral azobenzenes are commonly linked by flexible chains, which allowed the conformational change in mesophase formation. Thus, the rod-shaped parts can easily recognise each other and form a smectic layered structure but with less molecular recognition along the central core. Therefore, fluid nematic and layered smectic mesophases occur in disc-shaped molecules.

In conclusion, a disc-shaped molecule was prepared whose molecular architecture was composed of a triphenylene central core and six rod-like azobenzenes as the peripheral units linked through alkyl chain spacers. The combination of calamitic and discotic units led to a nematic mesophase 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.

4-(4-Nitrophenylazo)phenol **7**: 4-Nitroaniline (10 g, 0.0724 mol) was dissolved in methanol (200 ml) and water (50 ml) with 25 ml of concd hydrochloric acid and the mixture was cooled to 2 °C. Sodium nitrite (5 g, 0.0924 mol) in water (20 ml) was added dropwise and the mixture stirred for 1 h. After this, phenol (6.8 g, 0.0724 mol) in acetone (100 ml) and water (50 ml) was added and the mixture was maintained at pH 8–9 using sodium hydroxide solution, and stirred for 2 h. Then, dilute hydrochloric acid (ca. 80 ml, 10%) and water (300 ml) were added and the resulting precipitate was collected by filtration. The product was crystallised twice from methanol and ethanol, respectively. Yield: 11.2 g (64%) and mp 207 °C. ^{1}H NMR (600 MHz, acetone-d_6) δ: 8.33 (2H, d, $J = 8.6$ Hz, Ar-H), 7.94 (4H, dd, $J = 8.5$ Hz, $J = 5.8$ Hz, Ar-H), 7.00 (2H, d, $J = 5.7$ Hz, Ar-H), 5.88 (1H, s, Ar-OH).

1-Bromo-4-(4-nitrophenylazo)phenoxyhexane **8**: Compound **7** (2.40 g, 9.87 mmol) was dissolved in dry acetone (130 ml) and potassium carbonate (10 g, 74 mmol), potassium iodide (50 mg) and a 10-fold excess of 1,6-dibromohexane (24 g, 98.7 mmol) were added and the mixture was refluxed for 24 h under argon. The reaction mixture was filtered hot and the acetone was removed under reduced pressure. Then, hexane was added to remove excess 1,6-dibromohexane, the product was insoluble in hexane. The product was collected by filtration and was dissolved in dichloromethane and water (1:1). The organic phase was washed with dilute hydrochloric acid (ca. 50 ml, 10%), sodium carbonate solution (ca. 50 ml, saturated) and water successively. The organic fraction was dried with sodium sulfate and the solvent was removed under reduced pressure. The product was recrystallised from ethanol. Yield: 2.62 g (68%) and mp 128 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.33 (2H, d, $J = 8.4$ Hz, Ar-H), 7.94 (4H, dd, $J = 8.6$ Hz, $J = 5.9$ Hz, Ar-H), 7.02 (2H, d, $J = 8.6$ Hz, Ar-H), 4.05 (2H, t, $J = 6.6$ Hz, OCH_2), 3.42 (2H, t, $J = 5.5$ Hz, CH_2Br), 1.86–1.82 (4H, m, CH_2), 1.55–1.48 (4H, m, CH_2).

1,2-Bis-[4-(4-nitrophenylazo)phenoxyhexyloxy]benzene **9**: Compound **8** (2.03 g, 5 mmol) was dissolved to dry acetone (120 ml) and catechol (0.275 g, 2.5 mmol), potassium carbonate (0.675 g, 5 mmol) and potassium iodide (50 mg) were added and the mixture was refluxed for 40 h under argon. The mixture was poured into ice-cold water and acidified with dilute hydrochloric acid (ca. 10 ml, 10%). The resulting precipitate was filtered off and partitioned between dichloromethane and water. The organic phase was washed with sodium carbonate solution and water, dried with sodium sulfate and the solvent was evaporated under reduced pressure. The product was recrystallised from ethanol. Yield: 1.67 g (46%) and mp 137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.33 (4H, d, $J = 8.4$ Hz, Ar-H), 7.93 (8H, dd, $J = 7.5$ Hz, $J = 6.1$ Hz, Ar-H), 6.97 (4H, d, $J = 8.6$ Hz, Ar-H), 6.88–6.82 (4H, m, Ar-H), 4.03 (8H, m, OCH_2), 1.86–1.82 (8H, m, OCH_2CH_2), 1.55–1.49 (8H, m, CH_2).

2,3,6,7,10,11-Hexakis-[4-(4-nitrophenylazo)phenoxyhexyloxy]triphenylene **10**: Compound **9** (0.55 g, 0.723 mmol) was added to a stirred suspension of iron(III) chloride (0.325 g, 2 mmol) in dichloromethane (25 ml) containing 2 drops of concd sulfuric acid. The mixture was stirred for 2 h and then excess iron(III) chloride was removed by filtration. About 60 ml of methanol was added to quench the reaction and the resulting precipitate was washed several times with methanol. The product was purified by column chromatography on silica gel with chloroform as eluant. The solid was recrystallised from ethanol: chloroform (10:1); yield 0.14 g (26%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.32 (12H, d, $J = 8.4$ Hz, Ar-H), 7.92 (24H, dd, $J = 8.6$ Hz, $J = 5.9$ Hz, Ar-H), 6.98 (12H, d, $J = 8.9$ Hz, Ar-H), 6.88 (6H, s, Ar-H), 4.03 (24H, tt, $J = 6.5$ Hz, $J = 5.7$ Hz, OCH_2), 1.85–1.82 (24H, m, $OCH_2\mathit{CH}_2$), 1.55–1.48 (24H, m, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 26.01, 26.02, 29.25, 29.41, 68.41, 69.13, 109.99, 114.85, 121.14, 123.0, 124.61, 125.53, 146.72, 148.14, 149.10, 155.91, 162.72. Elemental analysis calcd for $C_{126}H_{126}N_{18}O_{24}$ (2276.45): C, 66.48; H, 5.58; N, 11.08. Found: C, 66.25; H, 5.32; N, 11.32%.

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