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Synthesis and Characterization of Two Series of Non-Symmetric Liquid Crystal Dimer Containing Bisazobenzene Moiety*

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Abstract: Two series of calamitic non-symmetric liquid crystalline dimer compound containing bisazobenzene moiety and a rather short alkoxybiphenyl linked by flexible spacers 4-propyloxy-[4-biphenyloxyalkyl]-4`-(4-phenylazo)azobenzene has been synthesized and characterized by spectroscopic methods. The transition temperatures and phase behaviours were studied by Differential Scanning Calorimetry (DSC), Polarizing Optical Microscopy (POM) and X-Ray Diffraction (XRD) study. The synthesized compounds exhibited enantiotropic liquid crystal phase with dimer (D_1) containing pentyl flexible alkyl spacer showing smectic A and smectic C phases and dimer (D_2) with hexyl spacer exhibitig SmA and nemetic phases respectively and the stability of the smectic layer depends on the spacer length for the compounds studied.

Key words: Liquid crystal, non-symmetric dimer, nematic phase, bisazobenzene

INTRODUCTION

Liquid crystal dimers (Twins) consist of molecules containing two mesogenic units separated by a flexible spacer, most commonly an alkyl chain (Imrie and Henderson, 2007, 2002; Henderson *et al*., 2005). Other flexible spacers include melonates branched alkyl chain (Achten *et al*., 2004), siloxanes (Olsson *et al*., 2004), lactates (Senthil *et al*., 2006) has been utilized. These materials are gaining much attention as they are regarded as model compounds for main chain and side chain liquid crystalline polymers (Imrie and Henderson, 2007, 2002; Henderson *et al*., 2005; Achten *et al*., 2004; Olsson *et al*., 2004; Senthil *et al*., 2006; Yoshizawa *et al*., 2006; Yelamaggad *et al*., 1999; So *et al*., 2006, 2007). The thermal behaviour of dimers containing alkyl spacers is quite different from that of conventional low molar mass mesogens; in particular, their transitional properties exhibits a pronounced alternation on varying the number and parity of methylene groups in the spacer (Imrie and Henderson, 2007, 2002; Henderson *et al*., 2005).

Dimers containing identical mesogenic units are referred to as symmetric dimers, while dimers consisting of two differing mesogenic groups are referred to as non-symmetric dimers (Imrie and Henderson, 2007, 2002; Henderson *et al*., 2005; Imrie *et al*., 2004; Achten *et al*., 2004; Olsson *et al*., 2004; Senthil *et al*., 2006; Yoshizawa *et al*., 2006; Yelamaggad *et al*., 1999; So *et al*., 2005, 2007). The non-symmetrical dimers are markedly different from those of symmetrical ones as they exhibit interesting polymorphic properties and stabilize wide range of chiral nematic (N*) and smectic A (SmA) mesophases (Yoshizawa *et al*., 2006; Yelamaggad *et al*., 1999; Mori *et al*., 2005; Do *et al*., 2006).

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Normally, the mesogenic units of dimers have at least two rings and typically have a symmetric structure because of synthetic considerations. Non-symmetry is usually introduced into a dimer by connecting two different mesogenic units, by changing the length of the terminal chains or by using different terminal groups (Mori *et al*., 2005) or varying the length and parity of spacer group (Imrie and Henderson, 2007, 2002; Henderson *et al*., 2005; Achten *et al*., 2004; Henderson *et al*., 2001; Olsson *et al*., 2004; Senthil *et al*., 2006; Yoshizawa *et al*., 2006; Yelamaggad *et al*., 1999). Dimers of special interest are those based on azobenzene moieties. Azobenzene is well known to undergo reversible trans-cis isomerization upon irradiation with UV/VIS light (So *et al*., 2005; Yu and Ikeda, 2004). A survey into the literature composed of liquid crystal 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 (Cojocariu and Rochon, 2005). The level of photoinduced birefringence was shown to depend strongly on the type and size of azobenzene groups. 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 (Cojocariu and Rochon, 2005; Zheng *et al*., 2007).

In the study described here, we combine bisazobenzene and alkoxybiphenyl mesogenic units through flexible alkyl spacer to produce a calamitic non-symmetric liquid crystalline dimer with aim to study the liquid crystalline properties and probably obtained a new promising material. To the best of our knowledge no reports are found in the literature of a non-symmetric calamitic liquid crystal dimer containing bisazobenzene mesogenic unit with alkoxy substituted biphenyl mesogenic group attached through a flexible spacer units. The phase behaviour and the effect of changing the length and parity of the spacer length are discussed.

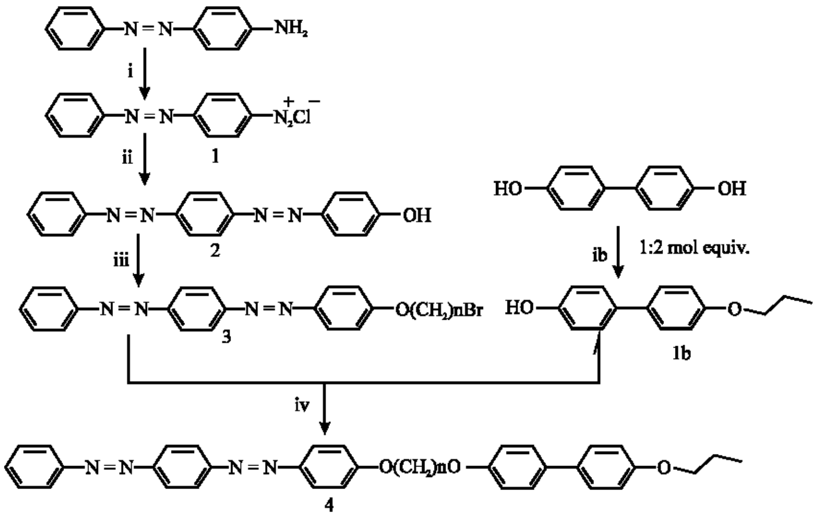
MATERIALS AND METHODS

All materials are of analytical grade unless otherwise stated. 4-phenylazoaniline (Fluka), 4, 4`-hydroxybiphenyl (Merck), 1-Bromopropyl (Fluka), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck), (Fluka), 1,5-dibromoheptane (Fluka), 1,6-dibrohexane (Fluka), potassium carbonate (Fluka), potassium hydroxide (Fluka), methanol (Merck) were used as received. Dry acetone was obtained from distilling over phosphorous pentoxide (Merck). Other solvent and chemicals were used without further purification.

The structures of the intermediates and the final product were confirmed by spectroscopic methods: FT-IR spectra were measured on a Spectrum BX II spectrophotometer (Perkin Elmer). ^{1}H and ^{13}C NMR spectra (400 MHZ) were recorded on a JEOL ECA 400 spectrometer (JEOL Japan). Mass Spectra was obtained on Shimadzu QP5050A (Shimadzu, Japan). Elemental analysis was carried out on LECO CHNS-932 analyzer (LECO Corporation 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 and the heating and cooling rates were 10°C min^{-1}. Phase transition temperatures were collated during the second heating and the second cooling scans. Olympus BX50 (Japan) Optical Polarizing Microscope (OPM) equipped with a Linkam THMSE-600 (Linkam, England) hot stage and a TMS 92 control unit was used to observe phase transition temperatures and optical textures to analyze liquid crystal properties. The X-Ray measurement was performed using a nickel-filtered Cu-K$_{\alpha 1}$ radiation with a Philips X-Ray diffractometer X`PERT PRO PW 3040 (PanAnalytical, Hollands).

Synthesis

Scheme 1 illustrates the structures of intermediates and the final compounds and our synthetic approach to the calamitic bisazobenzene-alkoxybiphenyl dimer molecule. The mesogenic part was



Scheme 1: Reactions and conditions: (I) NaNO$_2$/HCl; (ii) Phenol, 2°C; (ib) Zn/THF/Br(CH)$_2$CH$_3$; (iii) Br(CH$_2$)nBr, K$_2$CO$_3$/KI;(iv) K$_2$CO$_3$/KI/DMF

prepared by diazotization of a well known dye, 4-phenylazoaniline and then coupling of the resulting diazonium salt, with phenol yielding 4-hydroxy-4`-(4-phenylazo)azobenzene 1. The flexible spacer was introduced by alkylation of phenol 1, with a 10-fold excess of an appropriate α, ω-dibromoalkane in the presence of potassium carbonate as base and catalytic amount of potassium iodide to give 1-bromoalkyloxy-4`-(4-phenylazo)azobenzene 2 following modified method reported in by Lutfor *et al.* (2005). Compound 3, 4`-(4-hydroxyphenyl)propyloxybenzene was produce by etherification of 2 mol equivalent of 4`-(4-dihydroxybiphenyl) with 1 mole of 1-Bromopropane in presence of catalytic amount of Zinc metal in dry THF as solvent according to the reported method (Satya and Monika, 2004).

The final product 4-propyloxy-[4-biphenyloxyalkyl]-4`-(4-phenylazo)azobenzene was synthesized by further etherification of compound 3 with compound 2 to give compound 4 (D$_n$ series). All compounds in the series were synthesized following similar procedure and a typical procedure for compound D$_1$ is described as follows:

4-propyloxy-[4-biphenyloxypentyl]-4`-(4-phenylazo)azobenzene: D$_1$

A mixture of compound 2 (0.5 g, 0.1 mmol), compound 3 (g, 0.00 mmol) and potassium carbonate (0 g, 0.00 mmol) was heated to reflux with stirring in dried freshly distilled N,N`-dimthylformamide (80 mL) for 24 h 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. 300 mL) 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 methanol and ethanol respectively. Yield 59%, m.p. 99-102°C. Elemental analysis: Found C, 76.23; H, 6.40; N, 9.36; Calculated for ($C_{38}H_{38}N_4O_3$), C 76.05 H 6.23 N 9.14, MS m/z: 598, MS m/z: 374 (M$^+$); FT-IR, (KBr, cm^{-1}): 2938, 2862 (C-H, υ), 1602, 1584, 1498, 1474 (aromatic, υ), 1394 (C-H, δ), 1250, 1148 (C-H, δ), 856 (aromatic, δ). ^{1}H NMR (400 MHZ, CDCl$_3$) δ: 8.05 (4H, d, ArH), 7.97 (2H, t, ArH), 7.55 (2H, d, ArH), 7.49 (2H, d, ArH), 7.25 (1H, s, ArH), 7.03 (2H, d, ArH), 7.00 (4H, d, ArH) 4.04 (3H, t, OCH$_2$), 1.76 (6H, q, CH$_2$), 1.55 (2H, s CH$_2$), 0.95 (3H, s, CH$_3$);

^{13}C NMR (400 MHZ $CDCl_3$) δ: 29.70, 14.12, 22.13, 29.54, 68.06, 72.29 (8C), 114.78, 114.9 (6C), 122.99, 123.00, 123.42, 123.75, 125.07, 129.12 (16C) 131.25, 147.08, 152.78, 153.30, 153.98, 162.00 (8).

4-propyloxy-[(4-biphenyloxyhexyl)-4`-4-phenylazo]azobenzene: D_2

Compound D_2 was produced following same procedure as D_1 above. Yield 63%, m.p. 95-96°C. Elemental analysis: Found C 76.44 H 6.58 N 9.14, Calculated for ($C_{39}H_{40}N_4O_2$), C 76.17; H, 5.92; N, 8.73; MS m/z: 612 (M^+) IR, (KBr, cm^{-1}): 2938, 2862 (C-H, υ), 1602, 1584, 1498, 1474 (aromatic, υ), 1394 (C-H, δ), 1250, 1148 (C-H, δ), 856 (aromatic, δ). ^{1}H NMR (400 MHZ, $CDCl_3$) δ: 8.05 (4H, d, ArH), 7.97 (2H, t, ArH), 7.55 (2H, d, ArH), 7.49 (2H, d, ArH), 7.25 (1H, s, ArH), 7.03 (2H, d, ArH), 7.00 (4H, d, ArH) 4.04 (3H, t, OCH_2), 1.76 (6H, q, CH_2), 1.51 (4H, s CH_2), 0.85 (3H, s, CH_3); ^{13}C NMR ^{13}C NMR (400 MHZ $CDCl_3$) δ: 14.12, 21.02, 25.72, 28.54, 29.70, 68.06, 72.29 (9C), 114.78, 114.9 (6C), 122.99, 123.00, 123.42, 123.75, 125.07, 129.12 (16C) 131.25, 147.08, 152.78, 153.30, 153.98, 162.00 (8).

RESULTS AND DISCUSSION

Thermal Behaviour and Texture Observation

The phase transition temperatures as well as the phase transition enthalpy changes were studied using Differential Scanning Calorimetry (DSC) and the result of the second heating and second cooling scans are summarized in Table 1. The optical textures were Observed on Polarizing Microscope (OPM). Small angle X-ray diffraction was used to confirm the SmA phase of a representative sample of the compounds. Table 1 summarizes the data relating to the thermal transitions and the nature of the mesophases of the compounds; including enthalpy changes of the phase transitions. All materials are very stable crystals at room temperature.

The DSC thermograms show three exothermal transitions on heating to the isotropic liquid and three endothermic transitions on cooling circle, indicating that D_1 exhibited an enantiotropic behaviour for SmA ad SmC phase. The SmA phase was characterized by the formation of bâtannotes and focal-conic textures (117.26°C on heating and 110.2°C on cooling) as observed under polarized light [Do, imrie].

We have recently observed an enantiotropic nematic phase on a low molecular weight bisazobenzene liquid crystal molecule with a (C_4) alkyl terminal unit with mothoxy group at the end from our laboratory. On further lengthening of the alkylene chain to C_6 in D_2, the DSC thermograms also showed three thermal transitions on both heating and cooling circles respectively (Fig. 1).

Although, the Cr-SmA, SmA-SmC and SmC-I phase transitions were observed at a respective temperatures 98.58, 117.26°C and 124.24°C for D_1 when it was heated up, the reverse process occurred at 161.4°C (I-N), 116.23°C (I-SmC), 96.49°C (SmC-SmA) 48.62°C (SmA-Cr), respectively. Also, for D_2 the Cr-SmA, SmA-SmC and SmC-I phase were observed at a respective temperatures 96.34, 111.85 and 131.69°C when heated up, the reverse process occurred at 128.82, 94.65 and 48.84°C as in Fig. 1 and Table 1, respectively.

Texture observation for these compounds under polarized light showed that, both SmA and SmC phases appeared during heating and cooling circle (Henderson *et al*., 2005).

Table 1: Phase transition temperatures and enthalpies obtained from DSC scans

Compounds	Transition temperature (T/°C) and associated transition enthalpies values (ΔH/JK^{-1}), heat/cool
D_1	Cr 98.58 (3.6) SmA 117.26 (1.8) SmC 124.24 (1.8) I
	I 121.23 (1.2) SmC 96.49 (0.2) SmA 48.62 (10.2) Cr
D_2	Cr 96.35 (2.8) SmA 111.85 (2.3) SmC 131.69 (1.7) I
	I 128.82 (2.2) SmA 94.65 (0.3) N 48.84 (9.4) Cr

Cr: Crystal, N: Nematic, I: Isotropic phase

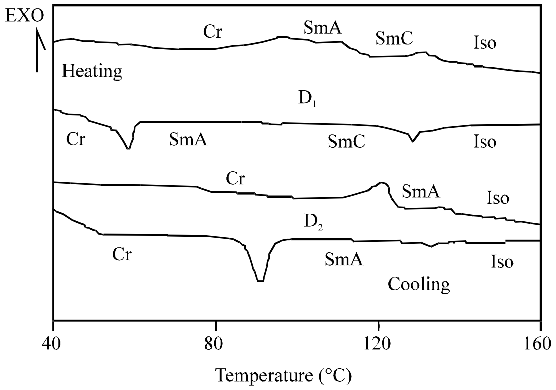


Fig. 1: DSC traces of compounds D_1 and D_2.

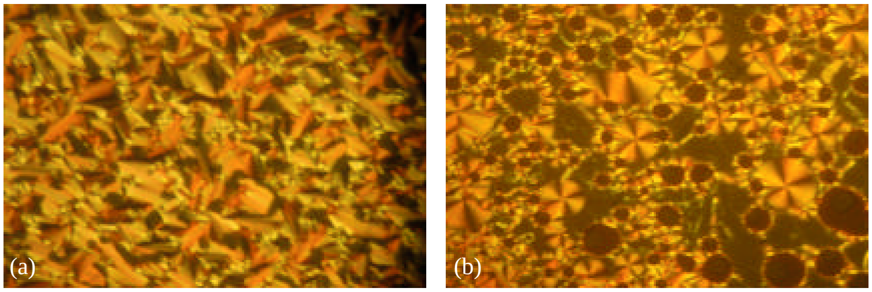


Fig. 2: Optical photomicrograph of (a) SmA (Focal-conic texture) of compound D_1 at 98.8°C and (b) SmC of compound D_1 obtained on cooling from isotropic liquid at 121.4°C with a optical polarizing microscope

Typical examples in regards to texture observation under polarized light for D_1 and D_2 is shown by D_1 (Fig. 2a,b). The focal-conic fan shaped and schieleren textures in the isotropic matrix were observed during heating and the cooling process for both compounds.

X-Ray Diffraction

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 D_2. Powdered sample for *in situ* high temperature XRD analysis was placed on the Pt heating strip and then thermally processed. The heating/cooling rate was 10°C, followed by data collection for 4 min at, 78°C according to the method described in the literature (Blanton *et al*., 2001). The diffraction patterns display one sharp and intense reflection at low angle 46.8Å ($2\theta = 2.06°$) which indicates a lamellar structure corresponding to smectic layers. In the wide-angle region, a broad halo centered at about $2\theta = 20°$, 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 as shown earlier.

CONCLUSION

A series of calamitic non-symmetric liquid crystal dimer based on 4-propyloxy-[4-biphenyloxyalkyl]-4`-(4-phenylazo)azobenzene (D_n series, n = 5 and 6) has been synthesized and characterized. All compounds were found to be enantiotropic mesogens with compounds D_1 exhibiting smectic A and SmC phases and D_2 showing in both heating and cooling cycles respectively. The thermal behaviour appeared to show odd-even effect for the compounds studied and there is increasing tendency of smectic polymorphism as the length and parity of the flexible spacer increases.

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