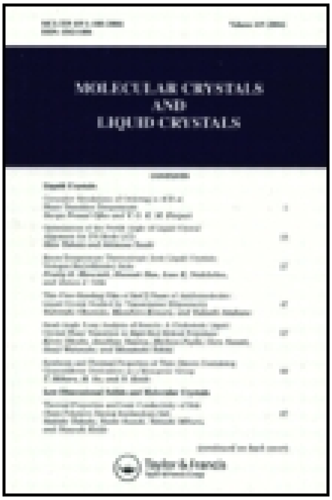

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Novel Non-Symmetric Liquid Crystal Dimer Containing Bisazobenzene Moieties: Synthesis and Characterization

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Novel Non-Symmetric Liquid Crystal Dimer Containing Bisazobenzene Moieties: Synthesis and Characterization

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A new series of calamitic liquid crystalline non-symmetric dimer containing bisazobenzene moiety and a rather short alkoxybiphenyl linked by flexible spacers (4-propyloxy-[4-biphenyloxyalkyl]-4′-(4-phenylazo)azobenzene has been designed, synthesized and characterized by spectroscopic methods. The transition temperatures and phase behaviors were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD) analyses. All the synthesized compounds exhibited enantiotropic phase with dimers containing ***propyl, butyl*** *and* ***octyl*** *flexible alkyl spacers showing SmA and those with* ***pentyl*** *and* ***hexyl*** *spacers exhibited SmA and SmC phases respectively and the stability of the smectic layer depends on the spacer length for the compounds studied.*

Keywords: alkoxybiphenyl; bisazobenzene; liquid crystals; non-symmetric dimer; smectic phase

I. INTRODUCTION

Liquid crystal dimers (Twins) consist of molecules containing two mesogenic units separated by a flexible spacer, most commonly an

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alkyl chain [1–3]. Other flexible spacers includes melonates [4] branched alkyl chain [5], Siloxanes [6,7], lactates [8] 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 [1–12]. The thermal behavior of dimers containing alkyl spacers is quite different from that of conventional low molar mass in particular, their transitional properties exhibits a pronounced alternation on varying the number and parity of methylene groups in the spacer [1–4]. 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 [1–12]. 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 [9,10,13,14].

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 [13] or varying the length and parity of spacer group [1–10]. Dimers of special interest are those based on azobenzene moieties. Azobenzene is well known to undergo reversible trans-cis (E/Z) isomerization upon irradiation with UV/VIS light [11,15]. A survey into the literature composed of 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 [16]. The level of photoinduced birefringence was shown to depend strongly on the type and size of azobenzene groups [16]. 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 [16,17].

We combine bisazobenzene and alkoxybiphenyl mesogenic units through flexible alkyl spacer to produce a calamitic non-symmetric dimer with aims to study the liquid crystalline properties and probably obtained a new promising material that can be utilized for application such, as optical information storage technology. To the best of our knowledge no report is found in the literature of non-symmetric calamitic liquid crystal dimer containing bisazobenzene mesogenic unit with alkoxy substituted biphenyl mesogenic group attached through a flexible spacer units. The phase behavior and the effect of changing the length and parity of the spacer length are discussed.

II. EXPERIMENTAL

2.1.0. Materials

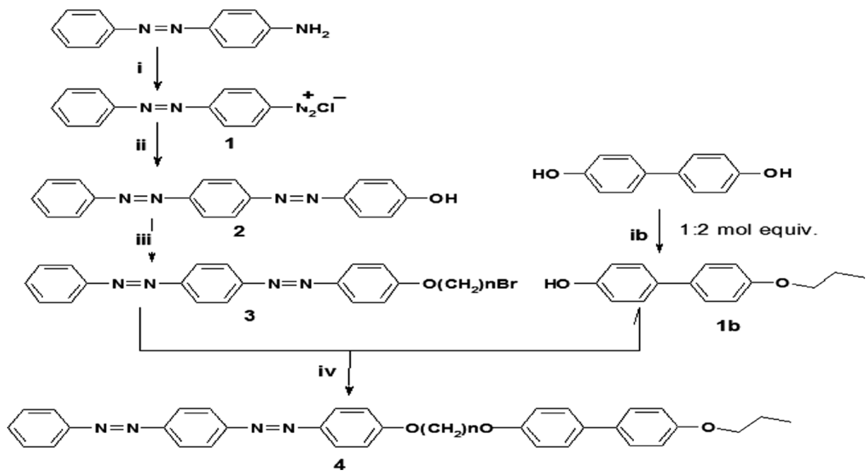
All materials are of analytical grade unless otherwise stated. 4-phenylazoaniline (Fluka), 4, 4′-hydxybiphenyl (Merck), 1-bromopropyl (Fluka), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck), 1,3-dibromopropane (Fluka), 1,4-dibromobutane (Fluka), 1,5-dibromoheptane (Fluka), 1,6-dibromohexane (Fluka), 1,8-dibromooctane (Fluka), potassium carbonate (Fluka), potassium hydroxide (Fluka), methanol and ethanol (Merck) were used as received. Dry acetone was obtained from distilling over phosphorous pentoxide (Merck). Other solvents and chemicals were used without further purification.

2.2.0. Experimental Techniques

The structures of the intermediates and the final compounds were confirmed by spectroscopic methods: FT-IR spectra were measured on a Spectrum BX II FT-IR spectrophotometer (Perkin Elmer). ^{1}H NMR spectra (400 MHz) were recorded on a JEOL ECA 400 spectrometer (JOEL, Japan). Mass Spectra was obtained from Shimadzu QP5050A (Shimadzu Japan). Thermal transition temperatures and thermodynamic parameters of the LC compounds were studied by using a differential scanning calorimeter (DSC 7 Perkin Elmer) under nitrogen atmosphere and the heating and cooling rates were 10°C min^{-1}. Indium was employed as a reference material for the calibration of temperature and enthalpy. The peak maximum or minimum point was taken as the transition temperature. Thermodynamic parameters were obtained from the DSC thermograms. The optical textures of the mesophase formed by the compounds obtained were observed during the second heating and the second cooling scans using an Olympus BX50 (Japan) optical polarizing microscope (OPM) under liquid nitrogen cooling system equipped with a Linkam THMSE-600 (Linkam, England) hot stage and an automatic temperature controller TMS 92 control unit. 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)

2.3.0. Synthesis

Scheme 1 illustrates the structures of intermediates and the final compounds and, our synthetic approach to the calamitic bisazobenzene-alkoxybiphenyl non-symmetric dimer molecule. The mesogenic part was prepared by diazotization of a well known powerful dye,



SCHEME 1 Reactions and conditions: (i) $NaNO_2/HCl$; (ii) Phenol, 2°C; (ib) $Zn/THF/Br(CH)_2CH_3$; (iii) $Br(CH_2)nBr$, K_2CO_3/KI; (iv) $K_2CO_3/KI/DMF$.

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 [18]. Compound **3** 4′-(4-hydroxyphenyl) propyloxybenzene was produce by etherification of 2 moles equivalent of 4′-(4-dihydroxybiphenyl) with 1mole of 1-bromopropane in presence of catalytic amount of Zinc metal in dry THF as solvent according to [19].

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** (*BA.OnO.3* series). All compounds in the series were synthesized following similar procedure and a typical procedure for compound *BA.*O_3O*.3* is described as follows:

2.2.1. *4-propyloxy-[4-Biphenyloxypropyl]-4′-(4-phenylazo)azobenzene* **BA.O_3O.3**

A mixture of compound **2** (0.5 g, 0.1 mmol), compound **3** (0.23 g, 0.10 mmol) and potassium carbonate (0.26 g, 0.20 mmol) was heated to reflux with stirring in dried freshly distilled N,N′-dimthylformamide (80 ml) for 24 hrs 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 48%, m.p. 116–119°C. Elemental analysis: Found C 75.77 H 6.01 N 9.82, Calculated for ($C_{36}H_{34}N_4O_3$) C 75.52 H 5.85 N 9.42, MS m/z: 570 (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) 4.10 (2H, t, OCH_2), 4.06 (1H, s, OCH_2), 2.06, (1H, d, CH_2), 1.52 (1H, s CH_2), 1.25 (2H, s, CH_3); ^{13}C NMR (400 MHz $CDCl_3$) δ: 13.52 21.04, 29.70, 64.43, 72.29 (6C), 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).

2.2.2. 4-propyloxy-[4-biphenyloxybutyl]-4′-(4-phenylazo)azobenzene: **BA.O$_4$O.3**

Yield 65%, m.p. 122–124°C. Elemental analysis: Found C, 76.00 H 6.21 N 9.58, Calculated for ($C_{37}H_{36}N_4O_3$), C, 75.630; H, 6.12; N, 9.36, MS m/z: 584 (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) 4.10 (2H, t, OCH_2), 4.06 (1H, s, OCH_2), 2.06 (1H, d, CH_2), 1.62 (2H, s CH_2), 1.25 (3H, s, CH_3); ^{13}C NMR (400 MHz $CDCl_3$) δ: 14.32, 21.02, 25.72, 29.70, 68.36, 71.29 (7C), 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).

2.2.3. 4-propyloxy-[4-biphenyloxypentyl]-4′-(4-phenylazo)azobenzene: **BA.O$_5$O.3**

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^+) 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).

2.2.4. 4-propyloxy-[(4-biphenyloxyhexyl)-4′-4-phenylazo]azobenzene: BA.O$_6$O.3

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).

2.2.5. 4-propyloxy-[4-biphenyloxyoctyl]-4′-(4-phenylazo)azobenzene: BA.O$_8$O.3

Yield 48%, m.p. 122–125°C. Elemental analysis: Found C 76.85 H 6.92 N 8.74, Calculated for ($C_{41}H_{44}N_4O_3$), C 76.57 H 6.72 N 8.33, MS *m/z*: 640 (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 (6H, t, OCH_2), 1.82 (6H, q, CH_2), 1.55 (4H, s CH_2), 1.38 (4H, d, CH_2)0.85 (3H, s, CH_3);^{13}C NMR (400 MHz $CDCl_3$) δ: 14.12, 21.02, 25.7, 28.54, 29.05 (8C), 68.06, 70.29 (3C), 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).

III. RESULTS AND DISCUSSIONS

3.1.0. Thermal behavior 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 diffractometry was used to confirm the SmA mesophase 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 two exothermal transitions on heating to the isotropic liquid and

TABLE 1 Phase Transition Temperatures and Enthalpies Obtained from DSC Scans

Compound	Transition temperature (*T*/°*C*) and associated Transition enthalpies values ($\Delta H/JK^{-1}$), heating/cooling
BA.O$_3$O.3	Cr 115.42 (3.4) SmA 127.51 (1.6) I
	I 109.51 (0.2) SmA 87.2 (12.4)Cr
BA.O$_4$O.3	Cr 122.65 (4.2) SmA 138.46 (0.3) I
	I 126.36 (0.4) SmA 92.84 (9.5) Cr
BA.O$_5$O.3	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
BA.O$_6$O.3	Cr 96.35 (2.8) SmA 111.85 (2.3) SmC 131.69 (1.7) I
	I 128.82 (2.2) SmC 94.65 (0.3) SmA 48.84 (9.4) Cr
BA.O$_8$O.3	Cr 120.34 (4.3) SmA 136.19 (0.3) I
	I 133.66 (0.4) SmA 90.18 (7.35) Cr

Abbreviations: Cr = crystal; SmA = smectic A; SmC = Smectic C; I = isotropic phase andTransition enthalpies in parenthesis.

two endothermic transitions on cooling circle, indicating that *BA.O$_3$O.3* exhibited an enantiotropic behavior for SmA phase. The SmA phase was characterized by the formation of bâtannotes and focal-conic textures (127.9°C on heating and 110.2°C on cooling) as observed under polarized light.

On increasing the length of the alkyl spacer to C_4 in *BA.O$_4$O.3*, two thermal transitions were observed on the DSC thermograph during heating and cooling circles respectively.

Texture observation carried out on *BA.O$_4$O.3* under polarized light revealed that it exist as an enantiotropic smectogen displaying SmA phase during heating and cooling circle respectively, as observed on heating (122.2°C) to the isotropic phase and, the reverse on cooling process (125.8°C) from the isotropic liquid phase, respectively.

The SmA flashes upon shearing, which appeared optically homoetropic see Figure 2a. There was no additional phase transition until it crystallized at 92.84°C.

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 in our laboratory [21]. On further lengthening of the alkylene chain to C_5 and C_6 in *BA.O$_5$O.3* and *BA.O$_6$O.3,* the DSC thermograms showed three thermal transitions on both heating and cooling circles respectively.

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 *BA.O$_5$O.3* when it was heated up, the reverse process

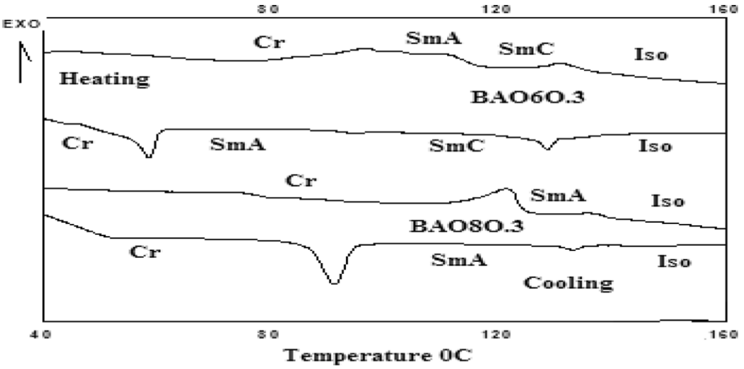


FIGURE 1 Representative DSC thermograph for compounds *BA.*O_6*O.3* and *BA.*O_8*O.3*.

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 *BA.*O_6*O.3* the Cr-SmA, SmA-SmC and SmC-I phase were observed at a respective temperatures 96.34°C, 111.85°C and 131.69°C when heated up, the reverse process occurred at 128.82°C, 94.65°C and 48.84°C respectively. Texture observation for these compounds under polarized light showed that, both SmA and SmC phases appeared during heating and cooling circle. Typical examples in regards to texture observation under polarized light for *BA.*O_5*O.3* and *BA.*O_6*O.3* is shown by *BA.*O_5*O.3* in Figure 2. The focal-conic fan shaped and Schlieren textures in the isotropic matrix were observed during heating and the cooling process for both compounds.

BA.O_8*O.3* exhibited enantiotropic behavior showing SmA only in both heating and cooling cycle. Two peaks were observed in its thermograms during heating as well as cooling cycles. A representative DSC trace of these compounds is depicted in Figure 1.

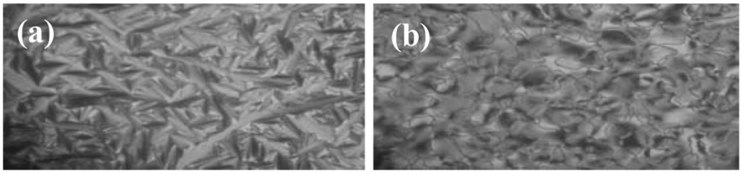


FIGURE 2 Photomicrograph of (a) Smectic A (Focal-conic texture) of compound *BA.*O_3*O.3* on cooling from isotropic liquid at 125°C (b) Smectic C texture of compound *BA.*O_5*O.3* on cooling from isotropic liquid at 160.2°C after mechanical stress (Cross polarizer magnification × 200).

The Cr-SmA and SmA-I occurred at 120.34°C and 136.19°C when heated up, the reverse process occurred at, 133.66°C and 90.18°C respectively. Texture observation for this compound under polarized light showed that, SmA appeared during heating and cooling circle respectively (Fig. 3).

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 *BA.*O_6*O.3*. 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 [20]. The diffraction patterns display one sharp and intense reflection at low angle 46.8 Å ($2\theta = 2.06°$) 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 above.

The dependence of the phase transition temperatures on the length and parity of the flexible spacer is shown in Figure 4. The melting transition temperatures appeared to show an odd-even effect as a function of the parity and the length of the spacer and it decreases with increasing spacer length for the compounds studied. Similarly, the SmA-SmC transitions decreases with increase in transition temperatures of the methylene spacers. The liquid crystal to isotropic transition temperatures shows some alternation on increasing the

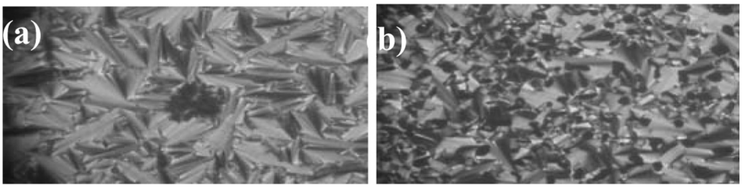


FIGURE 3 Optical photomicrograph of (a) Bâtonates forming SmA at 105.6°C and (b) SmA (Focal-conic texture) of compound *BA.*O_6*O.3* at 94.8°C (c) SmA of compound *BA.*O_8*O.3* obtained on cooling from isotropic liquid at 90.4°C with a polarizing microscope.

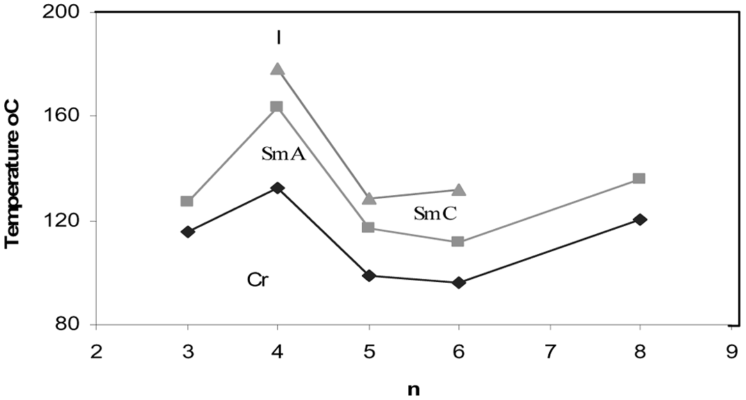


FIGURE 4 The dependence of the transition temperatures on the number of carbon atoms in the alkyl spacer for *BA.OnO.3* series.

spacer length for the compounds. This result seems to show that there is tendency towards smectic polymorphism to increase with increase in the length of the flexible alkylene spacer.

IV. CONCLUSION

A series of five novel calamitic non-symmetric liquid crystals dimer based on 4-propyloxy-[4-biphenyloxyalkyl]-4′-(4-phenylazo)azobenzene (*BA.OnO.3 series,* $n = 3–6$ *and 8*) has been synthesized and characterized. All compounds were found to be enantiotropic mesogens with compounds $BA.O_3O.3$, $BA.O_4O.3$ and $BA.O_8.O.3$ exhibiting smectic A in both heating and cooling circle, while $BA.O_5O.3$ and $BA.O_6.O.3$ exhibits smectic A and SmC phases in both heating and cooling cycles respectively. The thermal behavior 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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