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Calamitic Azobenzene Liquid Crystal Series: Synthesis and Mesomorphic Properties of 1-Methoxyalkyloxy-4`-(4-phenylazo)acetophenone*

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Abstract: New series of calamitic liquid crystal materials with rod-shape azobenzene moieties as a core has been synthesized and characterized by spectroscopic methods. The mesomorphic properties were investigated by differential scanning colorimetry, polarizing optical microscopy and X-ray diffraction. The rod-shaped molecule 1-methoxyalkyloxy-4`-(4-phenylazo)acetophenone was prepared by diazotization of 4-Aminoacetophenone, coupling with phenol and subsequent etherification of 1-bromoalkyloxy-4`-(4-phenylazo)acetophenone in methanol. The presence of smectic A mesophases was confirmed by the textures and X-ray diffraction studies. Compounds 4a-4d (C_3-C_6) exhibits enantiotropic smectic A phase while, compound 4d (C_8) show monotropic smectic A phase.

Key words: Liquid crystal, azobenzene, calamitic, smectic phase

INTRODUCTION

Liquid crystals are fascinating materials with properties intermediate between those of solids and liquids. Fundamentally, liquid crystalline materials are classified as being either thermotropic or lyotropic depending on whether their self-organization occurs only on heating of the pure compounds (thermotropic liquid crystals) or is induced by isotropic solvents (lyotropic liquid crystalline phases) (Tschierske, 1996).

Thermotropic Liquid Crystals (LC) are the most widely used and extensively studied for their linear as well as non-linear optical properties. They exhibit various LC properties as a function of temperature and are often represented as rigid road.

These rigid rods interact with one another and form distinctive ordered structures (Kılıç and Çınar, 2007; Gray, 1987). Conventional thermotropic liquid crystals are composed of rod-like (Calamitic) or discotic molecules (Disc shaped) (Kılıç and Çınar, 2007). Most thermotropic LCs are calamitic structurally (Kılıç and Çınar, 2007; Gray, 1987; Kouwer, 2002). A calamitic mesogen molecule consists of a core, terminal chains and lateral substituents. The core provides rigidity which is required for anisotropy where as the terminal chains provide flexibility to stabilize the molecular alignment within the mesophase (Kılıç and Çınar, 2007; Gray, 1987). The calamitic molecules form both nematic and smectic mesophases depending upon the type of the substituents and their combinations. The nematic liquid crystal phase is technologically the most important mesophase. It is used in almost all commercially available LC displays. On the other hand, the smectic LC phases have found very little commercially successful applications (Gray, 1987; Kouwer *et al*., 2002; Kim *et al*., 2004; Kuo *et al*., 2007; Hsieh *et al*., 2008; Manual *et al*., 2005).

Azobenzene compounds are known to be very attractive for their high thermal stability and for the photoinduced effects as well as for the potential applications in liquid crystal displays and devices,

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reversible optical storage systems, nonlinear optical waveguides, photorefractive switches and holographic gratings (So *et al*., 2006; Lutfor *et al*., 2005; Yu and Ikeda, 2004). In this contribution we report a series of new calamitic low molecular weight azobenzene liquid crystal molecules (4a-4d and 4e) (Scheme 1) which composed of azobenzene with a short acetyl group as a polar terminal unit and alkoxy terminal chains, with methoxy group at the terminal end.

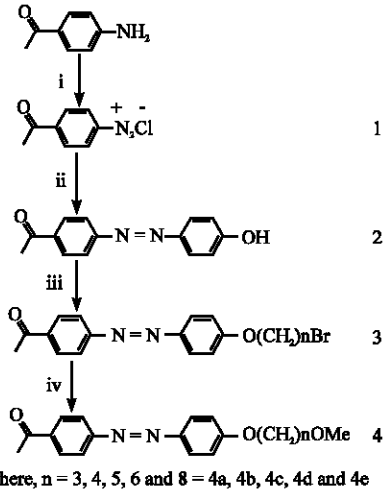
MATERIALS AND METHODS

All materials are of analytical grade unless otherwise stated. 4-acetophenone (Fluka), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck), 1,3-propane, 1,4-dibromobutane (Acros), 1,5-dibromopentane (Acros), 1,6-dibromohexane (Acros) 1,8-dibromooctane (Acros), potassium carbonate (Fluka), potassium hydroxide (Fluka), methanol (Fluka) 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: Elemental analysis was carried out on LECO CHNS-932 analyzer (LECO Corporation USA) 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 on Shimadzu QP5050A (Shimadzu, Japan). Phase transition temperatures and thermodynamic parameters were determined by using a DSC 7 (Perkin Elmer) 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 using an Olympus BX50 (Japan) Optical Polarizing Microscope (OPM) equipped with a Linkam THMSE-600 (Linkam, England) hot stage equipped with a liquid nitrogen cooling system and a TMS 92 control unit to analyze liquid crystal properties. The X-Ray measurements were performed using a nickel-filtered Cu-$K_{\alpha 1}$ radiation with X-Ray Difractometer (PANanalytical, X`Pert-Pro MPD PW 3040/60 XRD.

Synthesis

Scheme 1 illustrates the structures and our synthetic approach to the calamitic azobenzene molecules. The mesogenic part was prepared by diazotization of 4-Aminoacetophenone and then



Scheme 1: Reactions and conditions: (i) $NaNO_3$/HCl; (ii) Phenol, °C; (iii) K_2CO_3/KI, Br(CH_2)nBr, Acetone; (iv) KOH/MeOH

coupling of the resulting diazonium salt, with phenol yielding 4-hydroxy-4`-(4-phenylazo)acetophenone 2, according to literature report (Lutfor *et al*., 2005).

The final compound 1-methoxyalkyloxy-4`-(4-phenylazo)acetophenone **4**, was produced by further reaction with methanol in presence of potassium hydroxide. All compounds in the series were synthesized following similar procedure. A typical procedure for compound 4a is given as follows;

1-Methoxypropyloxy-4`-(4-phenylazo)acetophenone 4a

A mixture of 1-bromopropyloxy-4`-(4-phenylazo)acetophenone (0.5 g, 0.001 M) and potassium hydroxide (0.191 g, 0.003 M) was heated to reflux in methanol (80 mL) for 8 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. The resulting precipitate 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 65.37%, m.p. 129-132°C. Elemental analysis: Found C; C 69.21 H 6.45 N 8.97; Calculated for ($C_{18}H_{20}N_2O_3$), C, 69.34 H 6.49 N 9.02; MS m/z 312 (M^{+1}); IR, (KBr, cm^{-1}): 2926, 2874 (C-H, υ), 1678 (C = O, υ), 1602, 1586, 1500, 1466 (aromatic, υ), 1402 (C-H, δ), 1252, 1124 (C-H, δ), 840 (aromatic, δ). ^{1}H NMR, (400 MHz, $CDCl_3$), δ: 8.08 (2H, d, ArH), 7.93 (4H, d,d, ArH), 7.02 (2H, d, ArH), 4.06 (2H, t, OCH_2), 3.59 (2H, t, OCH_2), 3.22 (3H, s, OCH_3), 2.09 (3H, s, CH_3), 1.64 (2H, m, CH_2). ^{13}C NMR, (400 MHz, $CDCl_3$), δ: 26.82, 29.49 (2C), 58.76, 68.97, 69.04 (3C), 114.78, 122.56, 125.21, 129.34 (8C), 132.54, 137.75, 146.90, 155.25, 162.18, 197.54 (5C).

1-Methoxybutyloxy-4`-(4-phenylazo)acetophenone 4b

Yield 56.77%, m.p. 129-132°C. Elemental analysis: Found C 69.92 H 6.79 N 8.58; Calculated for ($C_{19}H_{22}N_2O_3$), C 70.05 H 6.88 N 8.72; MS m/z 326 (M^{+1}); IR, (KBr, cm^{-1}): 2926, 2874 (C-H, υ), 1678 (C = O, υ), 1602, 1586, 1500, 1466 (aromatic, υ), 1402 (C-H, δ), 1252, 1124 (C-H, δ), 840 (aromatic, δ). ^{1}H NMR, (400 MHz, $CDCl_3$), δ: 8.08 (2H, d, ArH), 7.93 (4H, d, ArH), 7.02 (2H, d, ArH), 4.06 (2H, t, OCH_2), 3.39 (2H, t, OCH_2), 3.34 (3H, s, OCH_3), 2.66 (3H, s, CH_3), 1.84 (2H, m, CH_2)1.60 (2H, m, CH_2). ^{13}C NMR, (400 MHz, $CDCl_3$) δ: 25.95, 26.04, 29.34 (3C), 58.60, 68.20, 72.57 (3C), 114.74, 122.53, 125.20, 129.33 (8C), 137.71, 146.82, 155.25, 162.26, 197.53 (5C).

1-Methoxypentyloxy-4`-(4-phenylazo)acetophenone 4c

Yield 70%, m.p. 129-132°C. Elemental analysis: Found C 70.56 H 7.11 N 8.23; Calculated for ($C_{20}H_{24}N_2O_3$), C 70.86 H 7.21 N 8.58; MS m/z 340 (M^{+1}); IR, (KBr, cm^{-1}): 2926, 2874 (C-H, υ), 1678 (C = O, υ), 1602, 1586, 1500, 1466 (aromatic, υ), 1402 (C-H, δ), 1252, 1124 (C-H, δ), 840 (aromatic, δ). ^{1}H NMR, (400 MHz, $CDCl_3$), δ: 8.08 (2H, d, ArH), 7.95 (4H, d, ArH), 7.26 (2H, d, ArH), 4.06 (2H, t, OCH_2), 3.40 (2H, t, OCH_2), 3.38 (3H, s, OCH_3), 2.66 (3H, s, CH_3), 1.84 (2H, s, CH_2), 1.62 (2H, m, CH_2), 1.52 (2H, m, CH_2). ^{13}C NMR, (400 MHz, $CDCl_3$) δ: 25.88, 25.93, 29.10 29.57(4C), 58.57, 68.27, 72.71 (3C), 114.77, 122.54, 125.21, 129.34 (8C), 137.75, 146.85, 155.32, 162.32, 197.54 (5C).

1-Methoxyhexyloxy-4`-(4-phenylazo)acetophenone 4d

Yield 65.37%, m.p. 102-105°C. Elemental analysis: Found C 71.16 H 7.39 N 7.90 Calculated for ($C_{21}H_{26}N_2O_3$), C, 71.34 H 3.52 N 9.98; MS, m/z 354 (M^{+1}); IR, (KBr, cm^{-1}): 2926, 2874 (C-H, υ), 1678 (C = O, υ), 1602, 1586, 1500, 1466 (aromatic, υ), 1402 (C-H, δ), 1252, 1124 (C-H, δ), 840 (aromatic, δ). ^{1}H NMR, (400 MHz, $CDCl_3$), δ: 8.08 (2H, d, ArH), 7.93 (4H, d, ArH), 7.02 (2H, d, ArH), 4.06 (2H, t, OCH_2), 3.59 (2H, t, OCH_2), 3.34 (3H, s, OCH_3), 2.66 (3H, s, CH_3), 1.84, (2H, s CH_2), 1.64 (2H, m, CH_2), 1.44 (2H, m, CH_2). ^{13}C NMR, (400 MHz, $CDCl_3$), δ: 25.53, 25.88, 26.81, 29.09, 29.56 (5C), 58.57, 68.27 72.71 (3C), 114.77, 122.54, 125.21, 129.34 (8C), 137.75, 146.85, 155.32, 162.32, 197.54 (5C).

1-Methoxyoctyloxy-4`-(4-phenylazo)acetophenone 4e

Yield 48%, m.p. 129-132°C. Elemental analysis: Found C 72.22 H 7.91 N 7.32 Calculated for ($C_{23}H_{30}N_2O_3$), C 72.54 H 7.98 N 7.53; MS m/z 382 (M^{+1}); IR, (KBr, cm^{-1}): 2926, 2874 (C-H, υ), 1678 (C = O, υ), 1602, 1586, 1500, 1466 (aromatic, υ), 1402 (C-H, δ), 1252, 1124 (C-H, δ), 840 (aromatic, δ). ^{1}H NMR, (400 MHz, $CDCl_3$), δ: 8.08 (2H, d, ArH), 7.93 (4H, d, ArH), 7.02 (2H, d, ArH), 4.06 (2H, t, OCH_2), 3.38 (2H, t, OCH_2), 3.34 (3H, s, OCH_3), 2.66 (3H, s, CH_3), 1.84 (2H, m, CH_2), 1.64 (2H, m, CH_2), 1.44 (2H, s, CH_2) 1.32-1.22 (6H, s, CH_2). ^{13}C NMR, (400 MHz, $CDCl_3$), δ: 25.88, 25.93, 26.81, 29.09, 29.56, 29.70 (6C), 58.57, 68.27, 72.72 (3C), 114.78, 122.56, 125.21, 129.34 (8C), 137.77, 146.86, 155.31, 162.33, 197.53 (5C).

RESULTS AND DISCUSSION

Thermal Behavior and Texture Observation

The phase transition temperatures as well as the phase transition enthalpy changes were determined using Differential Scanning Calorimetry (DSC) and the result of the second heating and cooling scans are summarized in Table 1. Two peaks were observed in the thermograms of compounds 4a-4d for both heating and cooling cycles. A representative DSC trace of these compounds is depicted in Fig. 1. Although, the Cr-SmA and SmA-I phase transitions were observed for compound 4a, 4b, 4c and 4d at the respective temperatures 77.39 and 102.24°C, 81.34 and 106.35°C, 75.88 and 106.35°C and 91.92 and 107.69°C, when they were heated up, the reverse process occurred at 92.24°C (I-SmA) and 46.73 (SmA-Cr), 92.24°C (I-SmA) and 46.73°C (SmA-Cr), 87.66°C (I-SmA) and 42.09°C (SmA-Cr) and 102.99°C (I-SmA) and 64.39°C (SmA-Cr), respectively.

As for compound 4e (C_8), only one transition temperature (Cr-I) 98.66°C was observed during heating process. The enthalpy with respect to this transition (78.7 kJ mol^{-1}) can be associated with transition from crystal to isotropic liquid while, during the cooling process two transition temperatures (I-SmA and SmA-Cr) 90.20 and 69.98°C were observed.

Table 1: The result of the second heating and cooling scans

Compound	n	Transition temperature (T/°C) and associated transition enthalpies values ($\Delta H/JK^{-1}$), heating/cooling
4a	3	Cr 77.39 (39.7) SmA 102.24 (11.9) I 92.24 (34.1) SmA 46.73 (28.3) Cr
4b	4	Cr 81.34 (56.2) SmA 106.35 (2.7) I 95.36 (24.3) SmA 48.96 (29.6) Cr
4c	5	Cr 75.88 (53.3) SmA 103.19 (0.6) I 87.66 (7.9) SmA 42.09 (31.2) Cr
4d	6	Cr 91.92 (66.7) SmA 107.69 (2.5) I 102.99 (8.7) SmA 64.39 (49.1) Cr
4e	8	Cr 98.66 (78.7) I 90.20 (1.23) SmA 69.98 (57.4) Cr

Cr: Crystal, SmA: Smectic A, I: Isotropic phase, transition enthalpies in parenthesis

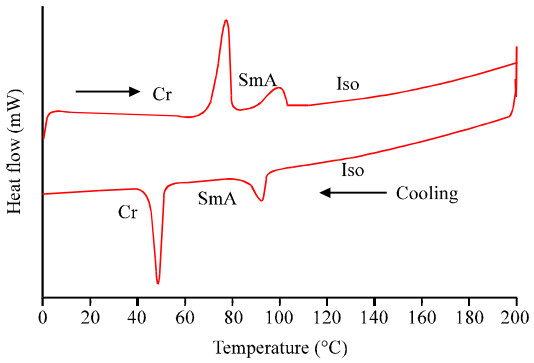


Fig. 1: DSC second heating and cooling traces of compound 4a (10°C min^{-1})

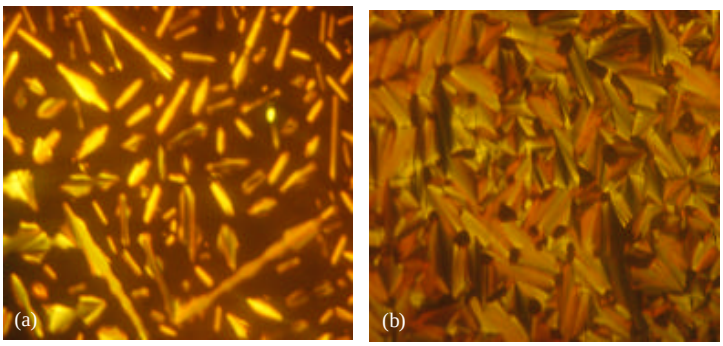


Fig. 2: Optical photomicrograph of 4a (a) Bâtannotes on cooling at 102.5°C (b) Smectic A on heating to the isotropic liquid at 103.6°C (Cross polarizer magnification x200)

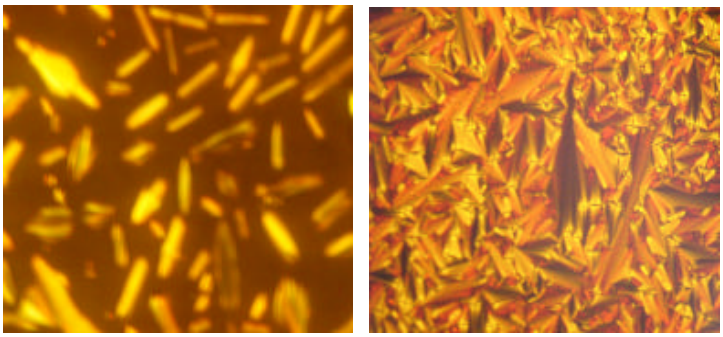


Fig. 3: Optical Photomicrograph of 4d obtained with a Polarizing Microscope (a) Bâtannotes appearing on cooling from isotropic liquid at 98.5°C (b) Smectic A on heating to the isotropic liquid 109.5°C (Cross polarizer magnification x200)

The phase structures were determined by polarizing optical microscope, heating/cooling rate 10 min^{-1}. Texture observation for these compounds under polarized light shows that SmA phase appeared during heating and cooling cycles. The SmA phase was characterized by the formation of bâtannotes and focal-conic textures as for compound 4a in Fig. 2 above.

Also texture observation carried out on 4b, 4c and 4d under polarized light revealed, they exist as enantiotropic smectogens displaying SmA phase during heating to the isotropic liquid at 82.2°C (Cr-SmA) and 105.6°C (SmA-I), 78.9°C (Cr-SmA) and 108.3°C (SmA-I) and 92.5°C (Cr-SmA) and 110.2 (SmA-I) and the reverse on cooling process from the isotropic liquid (92.24°C (I-SmA) and 46.73°C (SmA-Cr), 87.66°C (I-SmA) and 42.09°C (SmA-Cr),) cycle respectively.

The SmA flashes upon shearing, which appeared optically homoetropic (Fig. 3). There were no additional phase transitions on further cooling until crystallization of these compounds.

As for compound 4e (C_8), only one phase transition temperature 101.2°C (Cr-I) was observed during heating process while, during the cooling process two phase transition temperatures 91.4 and 69.8°C (I-SmA and SmA-Cr) were observed under polarized light respectively. The smectic A phase was also characterized by the homoetropic regions observed under optical polarizing microscope, formation of bâtannotes and fan-shaped textures as in Fig. 3. The clearing temperatures decrease with increase in spacer length for the compounds studied. These materials are very stable crystals at room temperature.

To complement DSC and POM 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 4d. Powder sample was placed on the Pt heating strip and then thermally processed. The heating/cooling rate was 10°C, followed by collection of data for 4 min at 90°C according to the method described by Blanton *et al.* (1997). The diffraction patterns display one sharp and intense reflection at low angle 38.64 Å (2θ = 2.28°) which indicates a lamellar structure corresponding to smectic layers. In the wide-angle region, a broad halo centered at about 2θ = 20.02°, which corresponds to an average intermolecular distance of approximately 4.43 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. The mesophase behavior exhibited by these compounds might be connected to the presence of the short acetyl group and the methoxy group at the end of the alkyl terminal units which, have might have promotes the microphase separation between the molecules which is a driving force to smectic phase formation. This is also in conformity with the general observation that for conventional low molar mass materials increasing the length of the terminal alkyl chain promotes smectic behavior (Imrie and Henderson, 2007).

CONCLUSION

A series of five novel calamitic liquid crystals based on 1- methoxyalkyloxy-4`-(4-phenylazo)acetophenone (4a-4d and 4e) with different terminal group and bulky methoxy group has been synthesized and characterized. Compounds with short to medium terminal groups (4a-4d) were found to be enantiotropic mesogens exhibiting Smectic A phase in both heating and cooling cycles respectively. Compounds 4e with longer alkyl (C_8) group showed a monotropic smectic A phase on cooling process from the isotropic liquid. The presence of bulky methoxy group at the terminal end and the short polar acetyl group at the azobenzene terminal were observed to improve the enantiotropic behavior, thermal and mesophase stability throughout the series of these compounds. In order to exploit the possible potential application of these compounds further studies such as the photoisomerization, birefringence and so on should be carried out.

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