



NEW LIQUID CRYSTALS IN THE SERIES OF 1, 3, 5-TRIAZINE COMPOUNDS CONTAINING AZOBENZENE AT THE PERIPHERAL ARMS

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ABSTRACT

Novel liquid crystal materials whose molecular structures consist of disc-like 1,3,5-triazine unit as a central core and three rod-like azobenzenes as the peripheral arms unit has been prepared and characterized by spectroscopic methods, and X-ray diffraction. The Series of compounds were prepared by nucleophilic addition of the primary amino nucleophile to 1,3,5-triazine electrophilic ring via alkyl spacers in presence of potassium carbonate as hydrochloride acceptor. Differential scanning calorimetry (DSC), polarizing optical microscopy and x-ray diffraction confirmed Smectic mesophase textures of the materials. Increase in the polymethylene spacer length influence the thermal and phase stability of the compounds studied.

Keywords: Liquid crystal, azobenzene, Smectic mesophase, triazine core, discotic

INTRODUCTION

One approach towards oligomeric mesogens with a well defined molecular structure just bridging the gap between monomeric and polymeric mesogens consists in the chemical linkage of a defined number of formed anisotropic sub-units [Kouwer *et al.*2003]. Beside various dimeric mesogens appropriate trimers and tetramers are available by connecting three or four mesogenic groups with a central linking unit. Examples are tetrameric liquid crystals with biphenyl and phenylcyclohexyl groups linked to tetrahedral penta-erythritol unit [Goldman *et al.* 1998], photochromic star-like siloxane liquid crystal incorporating four butoxyazobenzene mesogens in its periphery [Liu *et al.* 2005], Star-shaped glassy liquid crystals containing pentaerythritol as flexible core and ω -[4-(p-alkoxybenzoloxy)phenoxy]valeric acid as side mesogenic arms (Liu *et al.*2005 and zhang *et al.* 2005).

On one hand, there has been much interest in the synthesis and characterization of compounds containing a 1, 3, 5-triazine unit owing to their interesting properties, such as liquid crystalline and non linear optical properties as well as their applications in other fields [Lee *et al.* 2002]. Among these materials, disc-like liquid crystals are particularly gathering attention especially, with respect to their unique optical properties. More recently a 1, 3, 5-triazine has been used as a core [Lee *et al.* 2002, Lee *et al.*2001 and Lee *et al.* 2004]. In addition, from the synthetic view point, the mesogenic 1, 3, 5-triazine compounds have an advantage. Various nucleophilic side groups have been easily incorporated with the triazine ring by their reaction with cyanuric chloride, showing discotic as well as calamitic morphological behaviors depending on their structures (Lee *et al.* 2001). It has been demonstrated that the 1,3,5-triazine ring is a suitable structural element to be

incorporated into thermotropic liquid crystals thus, aromatic esters involving 1,3,5-triazine moiety were found to exhibit calamitic mesophases (Goldmann *et al.* 1998). A series of 2,4,6-triaryl-amino-1,3,5-triazines bearing six long peripheral alkoxy chains which form enantiotropic columnar mesophases were reported, although the molecules are characterized by a lack of inherent molecular planarity. Goldmann *et al.* (1981) attached three rod-like alkoxy substituted azobenzenes molecular sub-units to the 2-, 4- and 6-positions of the 1,3,5-triazine nucleus via secondary amino linkages. These compounds are considered as calamitic homotrimers with a 1,3,5-triazine core as the central linking unit exhibiting nematic phase on cooling from the isotropic phase and upon cooling the nematic phases, focal-conic fan shape textures developed for some of the compounds [Goldmann *et al.* 1998]. Therefore, the question of new molecular design arises as how to modify the substitution pattern of the 1,3,5-triazine ring in such away that liquid crystalline compounds result, probably exhibiting highly ordered Smectic phases. Our approach therefore, consists in attaching three rod-shaped azobenzene molecular sub-units via alkyl spacers to 2-, 4- and 6-positions of the triazine nucleus via secondary amino linkages (Scheme 1). Herein, the series of these compounds are presented.

MATERIALS AND METHODS

All materials are of analytical grade unless otherwise stated. 4-Aminoacetophenone (Fluka), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck), α , ω -dibromoalkanes (Fluka), potassium carbonate (Fluka), potassium hydroxide (Hamberg), ethanol amine (Acros), potassium carbonate (Fluka) and Cyanuric chloride (Acros) were used without further purification. Dry acetone, dry butanone and dry tetrahydrofuran (THF) were obtained from distilling over phosphorous pentoxide (Merck).

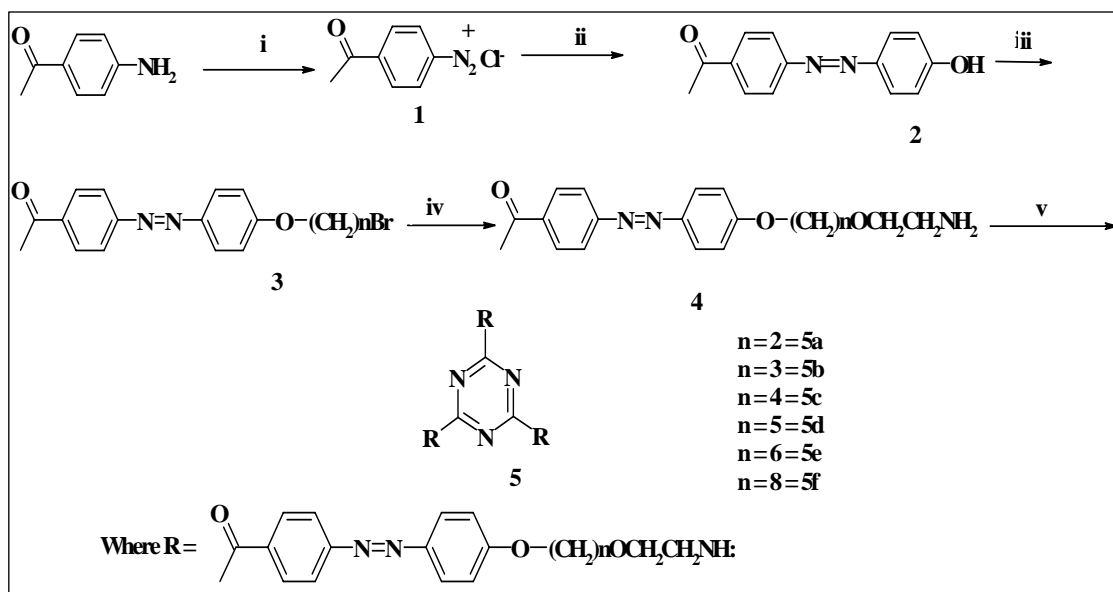
Other solvents and chemicals were used also without further purification. Silica gel 60 (230-460nm) was used for column chromatography. FT-IR spectra were measured on a BX spectrum II FT-IR spectrometer (Perkin Elmer). ^1H NMR spectra (400 MHz) were recorded on a Jeol ECA 400 NMR spectrometer (Jeol, Japan). Phase transition temperatures and thermodynamic parameters were determined by using a DSC 7 (Perkin Elmer) and DSC 8 (diamond DSC, Perkin Elmer) equipped with a liquid nitrogen cooling system under nitrogen atmosphere. The heating and cooling rates were $10^\circ\text{C min}^{-1}$. Phase transition temperatures were collected during the second heating and the second cooling scans. An Olympus (Leica, Germany) polarizing optical microscope equipped with a Linkam THMSE-600 (Linkam, England) hot stage was used to observe phase

transition temperatures and optical textures to analyze liquid crystal properties of the new material. The X-Ray measurement was performed using a nickel-filtered $\text{Cu-K}\alpha_1$ radiation with a Philips X-Ray diffractometer X'PERT PRO PW 3040 (PanAnalytical, Holland).

RESULTS AND DISCUSSION

Synthesis

Scheme 1 illustrates the structures and the synthetic route to the 1,3,5-triazine compounds. The peripheral arm units of the mesogenic part for all the compounds studied were prepared by diazotization of 4-Aminoacetophenone and then coupling of diazonium salt, with phenol yielding 4-(4-acetylphenylazo)phenol **2**.



Scheme 1: Reactions and conditions: (i) NaNO_2/HCl , $\text{C}_6\text{H}_6\text{O}$, 0°C ; (ii) $\text{K}_2\text{CO}_3/\text{KI}$, $\text{Br}(\text{CH}_2)_6\text{Br}$, Acetone; (iii) $\text{C}_2\text{H}_7\text{NO}$, MeOH , KOH ; (iv) $\text{C}_3\text{Cl}_3\text{N}_3$, K_2CO_3 , THF /butanone

The flexible spacers were introduced by alkylation of phenol **2**, with a 10-fold excess of appropriate dibromoalkane in the presence of potassium carbonate as base to give 1-bromo-4-(4-acetylphenylazo)phenoxyalkane **3** according to reported literature procedure [Lutfor *et al.* 2005, Lutfor *et al.* 2007]. Compound **3** was further alkylated with ethanolamine by Williamson's ether synthesis reaction to produce 4-(4-acetylphenylazo)phenoxyalkylethylamine **4**. Finally, a disc-like molecule 2,4,6-tris-4-(4-acetylphenylazo)phenoxyalkylethylamine-1,3,5-triazine **4** was produced by nucleophilic addition of the primary amino nucleophile to 1,3,5-triazine electrophilic ring in presence of potassium carbonate as hydrochloride acceptor (Scheme 1). A general procedure for compound **4** and **5d** is given as described in the previous paper [A. A. Salisu, 2008].

4-(4-acetylphenylazo)phenoxyhexyloxyethylamine 4
A mixture containing compound **3** (2.00g, 4.9mmol), ethanolamine (0.302g, 4.9mmol), and potassium hydroxide (0.274g, 4.9mmol) were refluxed for 10 h under nitrogen atmosphere with stirring in methanol (180ml). The reaction mixture was allowed to cool down to room temperature, then poured into ice-cold water and acidified with dilute hydrochloric acid. The resulting yellowish precipitate, was collected by filtration and recrystallized from methanol. Yield 1.86g (86%), m.p. = $105-107^\circ\text{C}$. FT-IR, (KBr , cm^{-1}): 2938, 2862 (C-H, u), 1674 (C=O, u), 1598, 1498, 1470 (aromatic, u), 1396 (C-H, δ), 1358 (OH, δ), 1188 (C-O-C, u), 1254, 1126 (C-H, δ), 842 (aromatic, δ). ^1H NMR, (400MHz, CDCl_3), δ : 8.08 (2H, d, $J = 8.2$ Hz, ArH), 7.93 (4H, d, $J = 8.7$ Hz, d, $J = 5.8$ Hz, ArH), 7.02 (2H, d, $J = 8.9$ Hz, ArH), 4.06 (2H, t, $J = 6.4$ Hz, OCH_2), 3.44 (2H, t, $J = 5.2$ Hz, OCH_2), 2.66 (3H, s, CH_3), 1.93-1.84 (4H, m, CH_2) 3.58 (2H, m, N-H).

3.3

2,4,6-tris-4-(4-acetylphenylazo)phenoxyhexyloxyethylamine-1,3,5-triazine 5

A mixture consisting of a solution of compound **4** (1.5g, 3.91 mmol) in dry butanone (80ml), cyanuric chloride (0.239g, 1.30 mmol) and potassium carbonate ((0.539g, 3.91 mmol) were refluxed for 24 h under nitrogen atmosphere. The reaction mixture was brought to the room temperature, poured into ice-cold water and acidified with dilute hydrochloric acid. The resulting precipitate was collected by suction filtration and recrystallized twice from methanol and ethanol respectively. Yield: 0.762g (24%) m. p. = 95-97°C. FT-IR (KBr, cm⁻¹): 2938, 2862 (C-H, u), 1674 (C=O, u), 1598, 1498, 1470 (aromatic, u), 1396 (C-H, δ), 3076 (N-H, u) 1188 (C-O-C, u), 1254, 1126 (C-H, δ), 842 (aromatic, δ). ¹H NMR, (600MHz, CDCl₃), δ: 8.08 (2H, d, J = 8.2 Hz, ArH), 7.93 (4H, d, J = 8.7Hz, d, J = 5.8 Hz, ArH), 7.02 (2H,

d, J = 8.9 Hz, ArH), 4.06 (2H, t, J = 6.4 Hz, OCH₂), 3.44 (2H, t, J = 5.2 Hz, OCH₂), 2.66 (3H, s, CH₃), 1.93-1.84 (4H, m, CH₂), 7.02 (3H, m, N-H). Elemental analysis: calculated for C₆₉H₈₄N₁₂O₉ (1225.51) C, 69.63%; H, 6.91%; N, 13.75%. Found C, 67.42%; H, 6.72%; N, 13.83%.

Phase transitions

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. Compounds with short to medium spacer length **5a - 5e** (C₂-C₆) exhibited an enantiotropic smectic A mesophases while, compound **5f** (C₈) possessed a monotropic phase on cooling from the isotropic liquid as shown in table 1. The clearing temperatures decrease with increase in spacer length for the compounds studied. These materials are very stable crystals at room temperature.

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

Compound	n	Transition temperature ($T^{\circ}\text{C}$) and associated Transition enthalpies values ($\Delta H/\text{JK}^{-1}$), heating/cooling
5a		Cr 68.70 (57.8) SmA 96.80 (3.6) I 78.79 (6.7) SmA 42.56 (22.6) Cr
5b	3	Cr 73.39 (39.7) SmA 102.24 (11.9) I 92.24 (34.1) SmA 46.73 (28.3) Cr
5c	4	Cr 79.32 (46.3) SmA 109.26 (1.9) I 98.72 (7.8) SmA 49.8 (46.2) Cr
5d	5	Cr 75.88 (53.3) SmA 103.19 (0.6) I 87.66 (7.9) SmA 42.09 (31.2) Cr
5e	6	Cr 91.92 (66.75) SmA 107.69 (2.5) I 102.99 (8.69) SmA 64.39 (49.5) Cr
5f	8	Cr 98.66 (78.7) I 90.20 (1.23) SmA 69.98 (57.4) Cr

^aAbbreviations: Cr = crystal, SmA = smectic A, I = isotropic phase, transition enthalpies in parenthesis

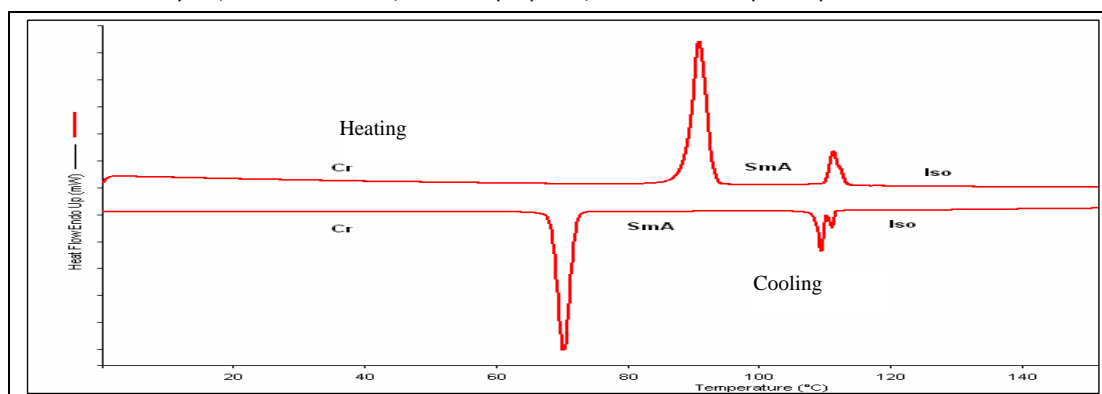


Figure 1: DSC second heating and cooling traces of compound 5b (10°C min⁻¹)

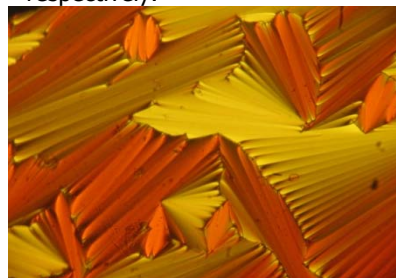
Phase structures

The phase structures were determined by polarizing optical microscope (POM). The representative polarized optical micrograph of series of prepared



5a

compounds (**5a-5e** and **5f**) observed in the liquid crystalline phase for the second heating and cooling cycle, is shown in Figure 3 for compound **5a** and **5c** respectively.



5b

Figure 3: Optical photomicrograph of 5a on heating to isotropic liquid at 124.2 °C and 5b on cooling from the isotropic liquid at 114.2 °C (Cross polarizer magnification ×200).

On heating to the isotropic phase and cooling from the isotropic phase smectic A textures were observed under the polarizing optical microscope for compounds with short to medium spacers (C_2 - C_6). Thus, exhibiting enantiotropic SmA liquid crystal phases. Compound **5f** (C_8) shows a monotropic phase on cooling from the isotropic liquid with no mesophase on heating to isotropic liquid. The enthalpy change associated with this transition is as a result of crystal to isotropization temperature. The texture is typical of a broken Fan-shaped focal-conic texture. It has been demonstrated that the presence of intermolecular hydrogen bonding of secondary amino groups and interactions between aromatic rings is expected to play an important role in molecular ordering. The aliphatic spacer would provide

the mobility necessary for molecular arrangement into an ordered smectic structures (Goldmann *et al.* 1998).

X-ray diffraction studies

The Smectic structures of the liquid crystal phases were confirmed by XRD studies. The representative X-ray pattern of the Smectic A form recorded at 80 °C for compound **5b** contains a diffuse band at 4.4 Å° (wide angle), which shows that the alkyl chains have a liquid-like structure and are segregated from the aromatic cores. However, the presence of two sharp reflections at 33.73 and 16.22 Å° (small angle) in a ratio of 1:2 indicates unambiguously the presence of layers (Kouwer *et al.*, 2002).

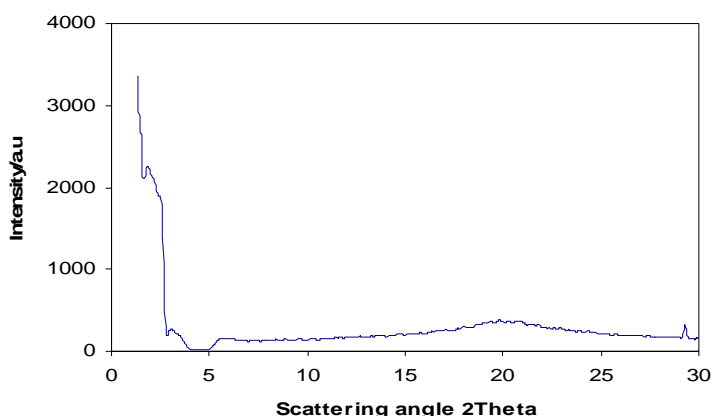


Figure 3: Powder X-ray diffraction pattern of compound 4 in the liquid crystal state (80 °C)

It has been shown previously that a parallel arrangement of at least two rod-like sub-units is most preferable for liquid crystalline oligomers with three or four mesogenic moieties attached to the same central linking compound like compounds (**5a- 5d** and **5f**) in such a fork-like conformation [Goldman *et al*/1998]. If assumed this conformation, the layer distance shall be less than half of the molecular length for all the compounds studied (Figure 4). This means that, the rod-like azobenzene units determine the mesophase i.e. the Smectic layers should be formed by the rod-

like units and the core 1,3,5-triazine units act only as linking unit interconnecting the rods. It is assumed that the aromatic rod-like cores are organized in common layers together with the disc-like 1,3,5-triazine core. The spacer units are located within the aromatic sublayers and form sublayers with a reduced concentration of the azobenzene segments. In such an arrangement, the layer spacing is amounting to value between $1/3$ and $1/2$ of the total molecular length L , depending on the degree of intercalation of the azobenzene moieties (Lutfor *et al.* 2005).

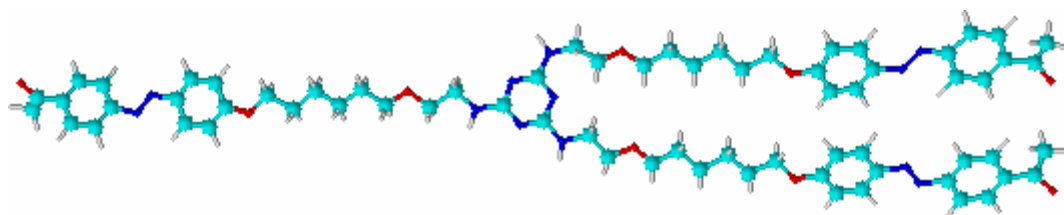


Figure 4: 3D Optimized molecular model of compound 5 representative of the series where, 1,3,5-triazine central core is linked to three azobenzene moieties as the peripheral units

Lutfor *et al.* (2005) described a related azobenzene with triphenylene as central core, where the smectic layer is reported to be formed by the rod-like azobenzene units and the triphenylene unit act only as linking unit interconnecting the rods. In compound **5**, the 1,3,5-triazine core and peripheral azobenzenes are

linked by more flexible spacers (hexamethylene and ethylene via ether linkage, no semi rigid -COO group) which allows a much easier conformational change. Thus, the rod-shaped part can easily align parallel to form a smectic layer structure.

Conclusion

New series of disc-shaped liquid crystal molecules were prepared based on 1,3,5-triazine central core, and three rod-like azobenzenes as the peripheral arm units connected through alkyl spacers via secondary amino linkages. Increase in the polymethylene spacer length influence the thermal and phase stability of these compounds. The substitution pattern through alkyl spacer units lead to the formation of well-ordered Smectic A phase due to the assembly of the mesogenic rod-shaped azobenzene parts. The 1,3,5-triazine core seems only to be linking unit,

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