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SYNTHESIS AND CHARACTERIZATION OF A STAR-SHAPED NEMATIC DISCOTIC LIQUID CRYSTAL CONTAINING 1, 3, 5-TRIAZINE CORE AND BISAZOBENZENE AT THE PERIPHERAL ARMS

Abdulsalam, A. Salisu
Department of Pure and Industrial Chemistry, Bayero University Kano, P. M. B. 3011 Kano, Nigeria
aasalisu@yahoo.com

ABSTRACT
A new three arm liquid crystalline material containing bisazobenzene and 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 behaviors were studied by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The synthesized compounds exhibited nematic discotic phase and the stability of the layer depends on the spacer length for the compounds.

Keywords: Liquid Crystal, Star-shaped, Nematic discotic, Bisazobenzene,

INTRODUCTION

In recent years, discotic liquid crystals (DLCs) have attracted considerable attention because of their unique optical and electronic properties, like charge and energy migration phenomena along the column axis [Kumar 2005]. Conductivity along the column in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction (Kumar *et al.* 2005). Liquid crystal assembly of disk like molecules is influenced not only by the mesogenic shape anisotropy, but also by the inter-core interaction along the disk normal. The columnar phase is normally predominant over nematic phase for discotic LCs owing to the fact that conventional discogenic cores are usually very flat structures consisting of □-electron-rich aromatic rings with strong inter-core interaction (Lee *et al*., 2001; Kumar 2005).

There are few numbers of reported compounds exhibiting discotic nematic phases. Among them are the derivatives of Naphthalene substituted triphenylene (wu *et al.* 2001), Hexa- and Penta-alkynyl benzene substituted triphenylene [Goodby *et al.* 1995] and Oxadiazole substituted triethynylbenzene [Lee *et al.* 2004]. Recently, some three armed planar star shaped molecules composing of a small polar core have been reported to exhibit nematic discotic phases (Lee and Yamomoto 2001; Meier *et al.,* 2004; Zheng *et al..* 2007: Liu *et al.,* 2005).

Due to the higher viscosity and multidomain scattering of columnar phase, nematic phase is often preferred for the electrooptic application of discotic LCs (Lee *et al.* 2004; Wu *et al.* 2000). Nematic discotic liquid crystalline materials, which exhibit negative birefringence, have demonstrated their potential for applications as compensation film for wide viewing angle liquid crystal displays (LCDs) (Wu *et al.* 2000])

Liquid crystal materials containing azobenzene moieties have been attracting considerable attention owing to their potential technological applications in reversible optical information storage, variable transmitting materials, optical switching and photonic devices (Liu *et al.* 2005). Although chromophores having only one azo group in their chemical structure (monoazobenzenes) have been primarily studied, systems with bisazobenzene moieties are also being investigated for optical storage applications (Cojocariu and Rochon 2005). The photoinduced birefringence per azobenzene structure in bisazobenzene-based polymers was reported to be five times larger than that in azobenzene-based polymers.

In this research, we are reporting a new three arm star-shaped molecule containing bisazobenzene as peripheral arm with 1, 3, 5-triazine core exhibiting nematic discotic phase. The design, synthesis and phase behavior are discussed.

MATERIALS AND METHODS

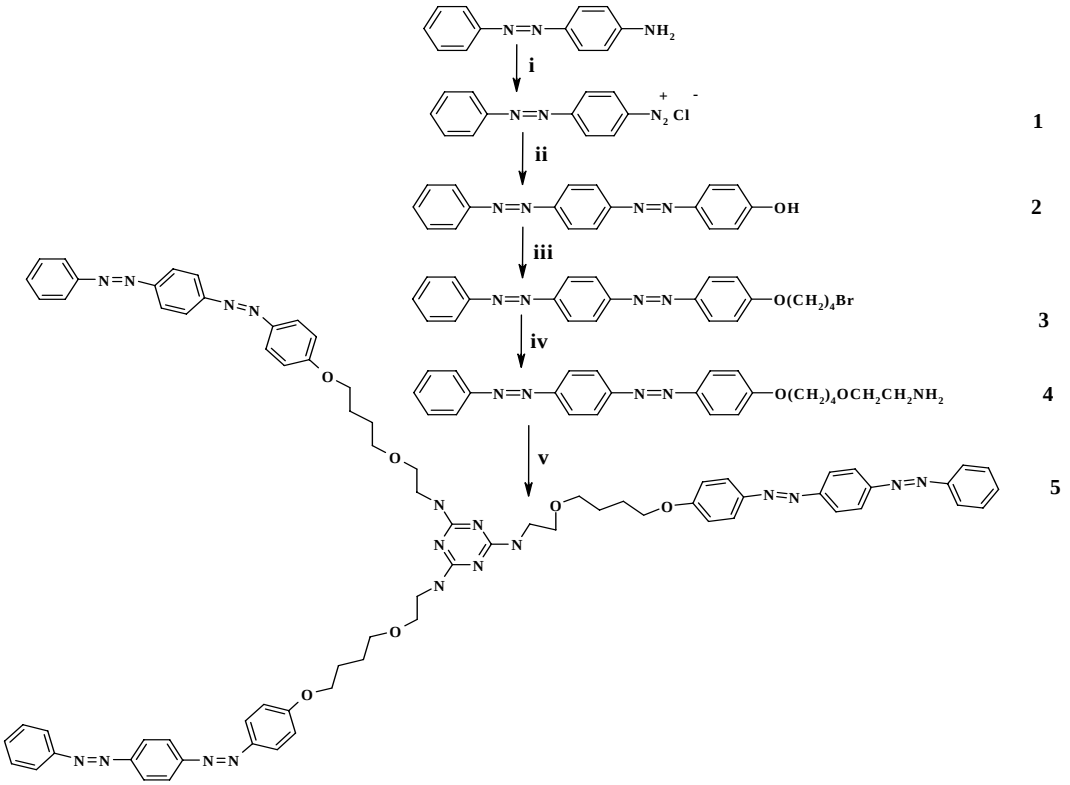
All materials used are of analytical grade unless otherwise stated. 4-Aminoacetophenone (Fluka), Sodium nitrite (BDH), Urea (BDH), Phenol (Merck), 1,4-dibromohexene (Fluka), Potassium carbonate (Fluka), Potassium hydroxide (Hamburg), ethanol amine (Acros), and Cyanuric chloride (Acros) were used as received. Dry acetone, dry butanone and dry Tetrahydrofuran (THF) were obtained from distilling over Phosphorous pentoxide (Merck). Other solvents and chemicals were used 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 (Perking Elmer). ^{1}H 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 10^0C 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.

Synthesis

Scheme 1 illustrates the structures and the synthetic approach to the disc-shaped, molecule. The synthesis follows the general methodology of azobenzene synthesis. The peripheral units of the mesogenic part were prepared by diazotization of a well known powerful dye, 4-phenylazoaniline and then coupling of the resulting diazonium salt, with phenol yielding 4-hydroxy-4`-(4-phenylazo)azobenzene **2**. The flexible spacer was introduced by alkylation of phenol **2**, with a 10-fold excess of 1,4- dibromohexane in the presence of potassium carbonate as base to give 1-bromobutyloxy-4`-(4- phenylazo)azobenzene **3** according to literature report (Lutfor *et al.*, 2005].



Scheme 1: Reaction and conditions: (i) $NaNO_2$/HCl, 0^0C; (ii) Phenol, 0^0C; (iii) Acetone K_2CO_3, $Br(CH_2)_4Br$, reflux; (iv) Methanol, KOH, Ethanol amine, reflux; (v) Cyanuric chloride, Butanone/THF, K_2CO_3, reflux**.**

Compound **3** was further alkylated with ethanolamine by Williamson`s ether synthesis reaction to produced 2-{4-[4-(4-Phenylazo-phenylazo)-phenoxy]-butoxy}-ethylamine **4.** Finally, compound **5** was produced by nucleophilic substitution of the primary amine nucleophile into the 2, 4,and 6 positions of 1,3,5-triazine ring to give a disc-liked molecule N,N`,N``-Tris(2-{4-[4-(4-phenylazophenylazo)-phenoxy]-butoxy}-ethyl)-[1, 3, 5]-triazine-2,4,6-triamine **4**.

The structures of the intermediates and the final compound were confirmed by spectroscopic analysis. The ^{13}C NMR spectrum of **5**, had signals corresponding to all the carbon atoms. There are 3 carbon atoms in the triazine core but only one distinct position, corresponding to one signal and all other signals correspond to the carbon atoms of the three rod-shaped bisazobenzene moieties and the alkyl chains.

RESULTS AND DISCUSSION

Phase transitions by DSC:

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.

Table 1: Phase transition temperatures and enthalpies obtained from DSC scans of 5[a].

	Transition temperature (*T/^{0}C)* and associated Transition enthalpies values ($\Delta H/Jg^{-1}$)
2nd Heating	Cr 128.54 (29.4) N 163.65 (0.57) I
2nd Cooling	I 159.53 (0.65) N 119.39 (27.6) Cr

Key: Cr = crystal, SmA = smectic A, I = isotropic phase

The DSC thermogram of compound **5** is shown in Figure 1. Two exothermic peaks were found on heating to the isotropic liquid. The enthalpy change at the N transition is higher than at the N-Iso transition which is usually observed for this type of phase transition [Lee *et al.* 2001 and Lutfor *et al.* 2005].

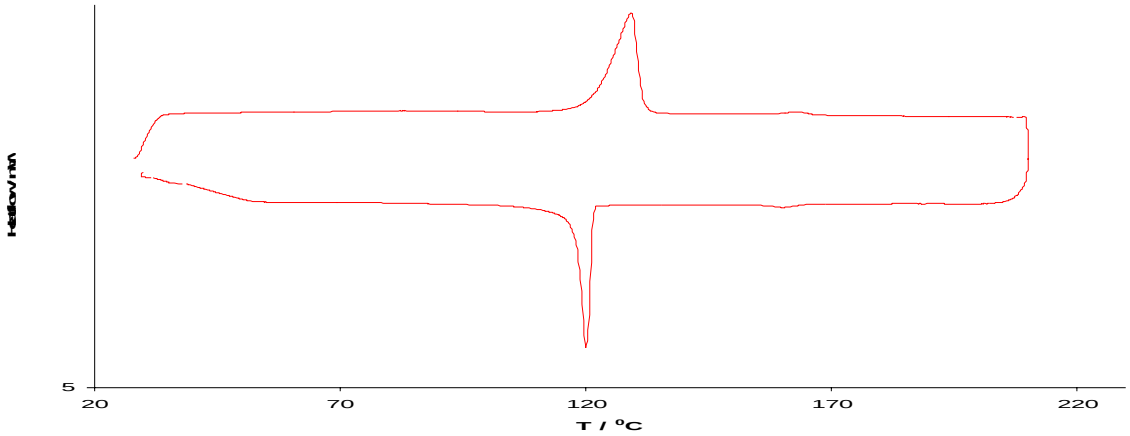


Figure 1: DSC heating and cooling traces of compound 5 (10^0C min^{-1}) Diamond DSC

Intermolecular hydrogen bonding of secondary amino groups and π-π interactions between aromatic rings were expected to play an important role in molecular ordering (Lee *et al.* 2004). Aliphatic tails would provide the mobility necessary to molecular arrangement into an ordered structure (Lee *et al.*, 2002; Zheng *et al.*, 2007).

Phase Structures by OPM:

The phase structures were determined using optical polarizing microscope (OPM). The polarized micrograph of **5,** observed in the liquid crystalline phase in the second heating and cooling cycle, is shown in Figure 2. On heating to the isotropic phase, a nematic texture was observed under the optical polarizing microscope at 152 ^{0}C (Figure. 2). The texture was very stable and it is typical of a nematic phase with four point brush desclinations (Henderson and Imrie, 2008).

On cooling the isotropic liquid a stable nematic phase also was observed at 142 ^{0}C. There was no additional phase seen until the sample crystallized at 131 ^{0}C. The stability of the nematic discotic phase exhibited by these compounds might be due the hydrogen bonding of the secondary amino group and the π-π interaction of the aromatic 1, 3, 5-triazine core.

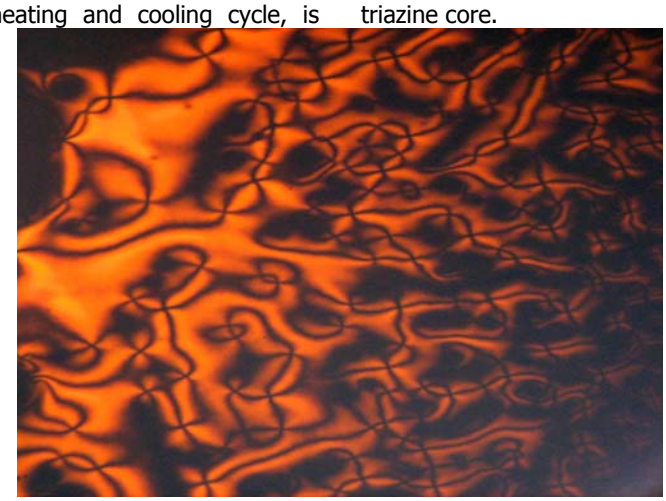


Figure 2: Polarized optical micrograph of discotic mesogen

The formation of nematic phases requires necessary reduced inter-core interactions; Therefore, DLCs with smaller core are appropriate system for this purpose [Wu *et al.* 2001, Zheng *et al.* 2007]. The three armed planar star-shaped molecules composed of small core and a few extended rigid mesogenic units as the side-chain liquid crystal arms, which is different from conventional rod-like or discotic molecules. But most star-shaped molecules having high molecular order usually crystallize, instead of vitrifying into a glassy state, during cooling from the isotropic melt (Zheng *et al.* 2007).

CONCLUSION

A new liquid crystalline molecule that shows nematic discotic liquid crystal phase was prepared based on 1,3,5-triazine central core and three rod shaped bisazobenzene as the peripheral arm units connected through alkyl spacers by secondary amino linkages. The material is enantiotropic molecule exhibiting discotic nematic liquid crystal phase in both heating and cooling cycle respectively.

The formation of nematic discotic phase is believed to be due to the smaller core and the extended bisazobenzene is acting as connecting units to the 1, 3, 5-triazine ring.

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REFERENCES

Cojocariu C., and Rochon P., (2005), Thermotropic side-chain liquid crystalline copolymers containing both mono- and bisazobenzene mesogene: Synthesis and properties, *Macromolecules,* 38, 9526-9538.

Goodby J. W., Hindmarsh P., Watson M. J., Hird M., (1995) Investigation of the effect of bulky lateral substituents on the discotic mesophase bahavior of triphenylene benzoates, *J. Mat. Chem.* **5:** 2111-2123.

Henderson P. A., Seddon J. M. and Imrie C. T., (2005). Methylene- and ether-linked liquid crystal dimers II. Effects of mesogenic linking units and terminal chains length, *Liq. Cryst.* 32, 11–12, 1499–1513**.**

Henderson, P. A., Cook, A. G., Imrie, C. T., (2004). "Oligomeric liquid crystals: From monomers to trimers " *Liq Cryst* **31** 1427–1434

Kumar, S. (2005) "Recent development in the chemistry of triphenylene-based discotic liquid crystals", *Liq. Cryst.,* **31**: 1037-1059

Lee C. J., Lee S. J. and Chang J. Y. (2002). Synthesis of a polymerizable discotic liquid crystalline compound with a 1,3,5-triazine core, *Tetrah. Lett.* **43:** 3863-3866.

Lee C. H. and Yamamoto T., (2001). Synthesis and characterization of a new class of liquid-crystalline, highly luminescent molecules containing a 2,4,6-triphenyl-1,3,5-triazine unit, *Tetrah. Lett.* **42:** 3993-3996.

Lee H., Kim D., Lee H. K., Qiu W., Oh N. K., Zin W. C. and Kim K., (2004). Discotic liquid crystalline materials for potential nonlinear optical applications: synthesis and liquid crystalline bahavior of 1,3,5-triphenyl-2,4,6-triazine derivatives containing achiral and chiral alkyl chains at the periphery*, Tetrah. Lett.* **45:** 1019-1022.

Lutfor, M. R., Yusoff, M., Tshierske, C., Pelz, K., Baumeister, U., Sidik, S. (2005). Nematic and Smectic Mesophase formation by a Novel Triphenylene-Azobenzene Hybride Molecule, *Elect. Liq. cryst. com.* at http://www.e.lc.org/docs/2005_06_26_21_47_19*.*

Wu L. H., Janarthanan N. and Hsu C. S.,(2001), Synthesis and characterization of naphthalene-substituted triphenylene discotic liquid crystals, *Liq. Cryst.*, **28:** 17-24.

Zheng Z., Wang L., Su Z., Xua J. , Yang J. and Zhang Q., (2007) *J. Photochem. and Photobio. A:* Chemistry **185:** 338–344.