



Synthesis and mesomorphic behaviour of new discotic liquid crystalline compounds containing triphenylamine as a core moiety via Sonogashira coupling

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ABSTRACT

Design and synthesis of cholesterol based disk-like liquid crystalline compounds using triphenylamine as a core moiety have been achieved by Pd-catalyzed cross-coupling reaction. The newly synthesized compounds exhibit a cholesteric phase with fingerprint texture as well as oily texture. In the low temperature region, there is a signature of smectic B with characteristic dendritic and mosaic textures. The mesogenic properties were characterized by polarizing microscopy, differential scanning calorimetry and HRXRD studies.

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Discotic liquid crystals (DLCs) are unique nanostructures with remarkable electronic and optoelectronic properties. Mesophase formed by disc-shaped molecules is primarily of two types: nematic and columnar. A few discotic molecules are also reported to form a discotic lamellar mesophase.^{1,2} In the discotic nematic phase, there is an orientationally ordered arrangement of discs with no long-range transitional order, while in the columnar phase, the discs are stacked one on top of another to form columns. Two attractive intermolecular interactions are most probably the main factors responsible for the observation of mesogenic properties. These are core–core attraction (e.g., dispersion forces) and a hydrophobic interaction between aliphatic chains.

Molecules containing triphenylamine (TPA) moiety have been widely investigated as active materials for hole-transport and electroluminescence.³ The amorphous character of these materials offers possibilities to develop active materials for solar cells⁴ with isotropic optical and charge-transport properties. The use of TPA-based materials for photovoltaic conversion has been scarcely considered.⁵ They also play an important role in photorefractive (PR) materials, which have attracted much interest in recent years because of their potential applications in holographic optical data storage and real time imaging processes. Therefore, in continuation of our studies towards the design and synthesis of liquid crystalline compounds,⁶ we became interested in synthesizing a new class of disc-like molecules with TPA and cholesterol via Sonogashira reac-

tion. The palladium and copper co-catalyzed coupling of terminal alkynes with various organic halides is the most straightforward and powerful method for the construction of C(sp²)-C(sp) bonds.⁷ This method has been widely applied to diverse areas such as natural product synthesis and material science.⁸ In our previous Letter⁹, we have reported a disc-shaped molecule containing triphenylamine as core moiety with highly branched terminal alkyl chains which self-assembled (the polar and non-polar regions) to form the columnar mesophase. Now we have undertaken a study to design and synthesize a new class of cholesterol-containing trimeric mesogens for studying their mesomorphic behaviour. Herein we report the results.

The methodology for the synthesis of new discotic liquid crystals (**9a,b**) is depicted in Scheme 1.

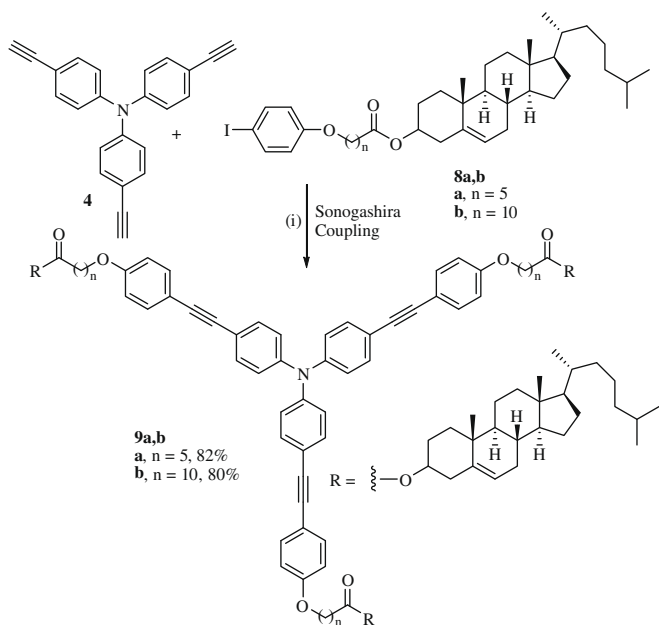
The required precursor **4** was synthesized by deprotection of the TMS group of compound **3** using KF-MeOH. Compound **3** was in turn prepared by Sonogashira coupling of the compound **2** with trimethylsilylacetylene. Compound **2** was prepared by the iodination of triphenylamine (**1**) with I₂ in the presence of HgO in EtOH¹⁰ (Scheme 2).

The other precursors **8a,b** were synthesized from naturally occurring cholesterol. Esterification of cholesterol (**5**) with the bromoalkanoylchlorides (**6a,b**) was carried out in THF in the presence of pyridine to afford the compounds **7a,b**. The cholesteryl 4-iodo alkyl esters (**8a,b**) were prepared by the reaction of compounds **7a,b** with 4-iodophenol in refluxing acetone in the presence of anhydrous K₂CO₃¹¹ (Scheme 3).

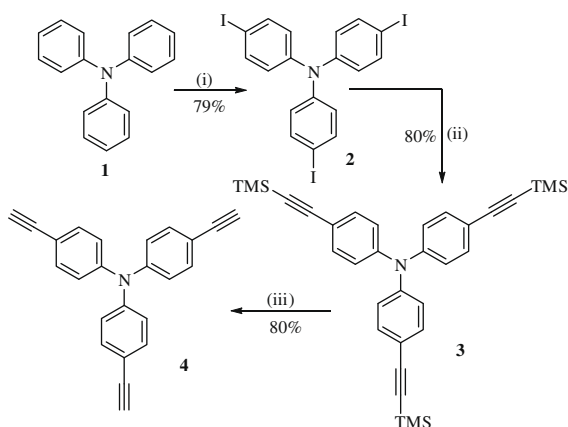
Finally the target compounds (**9a,b**¹²) were successfully obtained by Sonogashira coupling between compound **4** and

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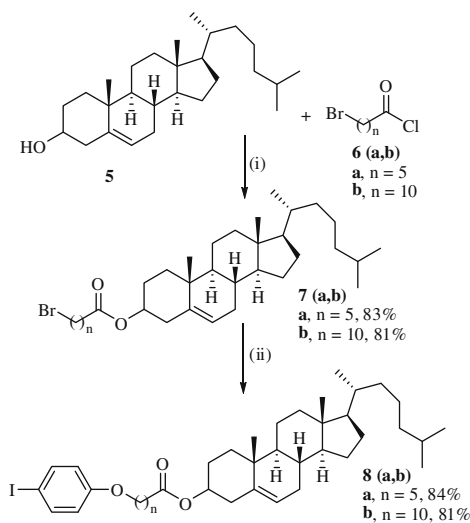
E-mail address: kcm_ku@yahoo.co.in (K.C. Majumdar).



Scheme 1. Synthetic route for the synthesis of new discotic liquid crystals **9a,b**. Reagent and conditions: (i) Pd(PPh₃)₂Cl₂, CuI, DIPEA, THF, rt, 12 h.



Scheme 2. Synthesis of precursor **4**. Reagent and conditions: (i) HgO, I₂, EtOH, rt, 12 h; (ii) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, DIPEA, THF, rt, 12 h; (iii) KF, MeOH, 2 h.



Scheme 3. Synthesis of precursors **8a,b**. Reagent and conditions: (i) THF, pyridine, rt, 12 h; (ii) *p*-iodophenol, K₂CO₃, acetone, reflux, 12 h.

compounds **8a,b** by using Pd(PPh₃)₂Cl₂ (10 mol %) as catalyst, CuI (12 mol %) as co-catalyst, and DIPEA as base in THF.

The phase transitions of the new discotic liquid crystalline materials (**9a,b**) were determined by differential scanning calorimetry (DSC) at a heating rate of 5 °C min⁻¹. The transition temperatures and associated enthalpies are shown in Table 1.

Textural analysis was carried out with the help of a polarizing optical microscope (POM). Compounds **9a,b** exhibited the enantiotropic phase sequence of crystal→Smectic B→TGB→cholesteric→isotropic, when the sample was placed in a glass slide and sandwiched by a cover slip at homogeneous heating conditions. When the compound **9a** was allowed to heat up to isotropic temperature (116.1 °C) and kept for 5 min in isotropic phase and was allowed to cool slowly, the reappearance of the texture was observed at 113.1 °C with four brush cholesteric spherulites (Fig. 1a) which turned to a pellet-like texture at around 112.8 °C (Fig. 1b). This pellet-like texture then transformed to characteristic long pitch cholesteric droplets with different colours corresponding to different twists (Fig. 1c). After lowering the temperature slightly, the coalescence of the cholesteric droplets occurred during the phase ordering process. At around 112.2 °C, the cholesteric fingerprint texture was observed (Fig. 1d). A TGB phase was also observed at a very short range (0.2–0.5 deg, Fig. 1e). When the sample was allowed to cool, there was a sudden change in texture to dendritic form which is often observed in smectic B phase (Fig. 1f). The dendritic texture persisted till room temperature. The sample was heated slowly to observe the textural pattern from dendritic texture, and this texture continuously changed the colour but without any change in texture as the temperature was increased and turned to cholesteric fingerprint texture before transforming to isotropic phase. The textural appearances of the compound **9a** are shown in Figure 1.

The powder X-ray diffraction pattern was performed on compound **9a** at different temperatures to investigate the supramolecular arrangement of molecules in the liquid crystalline phases. Careful observation of the X-ray diffraction pattern reveals that the compound forms highly ordered liquid crystalline phase. The Debye–Scherrer pattern for the compound **9a** at 95 °C and 105 °C was discussed here as these temperatures corresponds to the smectic B mesophase. The pattern shows two distinct sharp small angle peak at both the temperatures where $2\theta = 2.08^\circ$ and 2.54° for 95 °C indicating the layer spacing in smectic layer $d = 42.47 \text{ \AA}$ and 34.82 \AA , respectively. At 105 °C the $2\theta = 2.048^\circ$ and 2.497° and the layer spacing is pretty close to the previous temperature 95 °C ($d = 43.13 \text{ \AA}$ and 35.38 \AA). In the wide angle region, the scarcity of diffuse peak indicates the presence of long-range order in the smectic layer which indicates that the smectic phase is not fluid. This is quite possible in smectic B type phase. The appearance of two sharp peaks at small angles may probably be due to first and second order transitions. In the smectic B phase, the constituent molecules pack in a hexagonal array with the molecular long axes perpendicular to the layer planes. The molecules are assumed to rotate and the layer is free to slide over one another.¹³ On the basis of the above discussion and shape of the newly synthesized molecules **9a,b**, we have constructed a supramolecular arrangement of the molecule in smectic B phase. The proposed model is supposed to be hexagonal where each corner of the hexagon is occupied by a hand of the two trihand molecules by free rotation (Fig. 2).

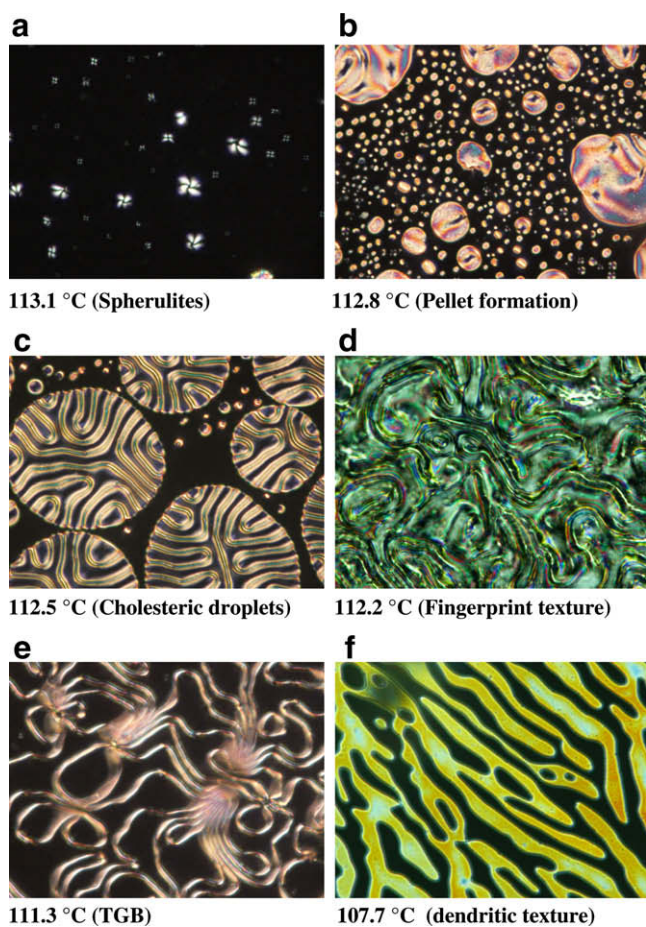
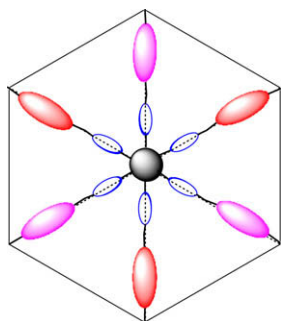
In conclusion, we have succeeded in designing and synthesizing a new class of disc-like mesogens containing both cholesterol and triphenyl amine moieties via Sonogashira coupling as a key step. We have also characterized the mesophases. It is worth mentioning that generally cholesterol-based dimers show Sm A/Sm C phase (among smectic phases)¹⁴ and usually the disc-like molecules with flexible branched alkyl chains self assemble to form columnar phase.¹⁵ At the present instance, the cholesterol moiety is con-

Table 1Phase transition temperatures (°C) associated enthalpies (ΔH , KJ mol⁻¹) of the compounds in the heating and cooling cycles are summarized below

Compound	Phase Transition (Heating cycle)	Temperature	Enthalpy	Phase Transition (cooling cycle)	Temperature	Enthalpy
9a	Cr–SmB	87.9	71.9	I–N*	113.1	72.8
	SmB–TGB	104.8	–	N*–TGB	111.3	–
	TGB–N*	105.1	66.5	TGB–SmB	111.4	75.9
	N*–I	116.2	7.7	SmB–Cr	rt	–
9b	Cr–SmB	90.5	36.3	I–N*	142.2	6.5
	SmB–TGB	139.0	–	N*–TGB	140.3	4.6
	TGB–N*	139.6	5.4	TGB–SmB	138.1	10.1
	N*–I	145.9	6.5	SmB–Cr	rt	–

Cr = Crystalline phase, SmB = Smectic phase, TGB = Twist Grain Boundary phase.

– = Not detected in DSC.

**Figure 1.** Polarizing micrographs of compound **9a**.**Figure 2.** Supramolecular arrangement of compound **9a,b**.

nected at the terminal position of the triphenyl amine core via alkyne linkages (relatively rigid) to study the structure-property relationship and a higher order Sm B phase has been observed. We are continuing this work and a full account will be communicated in due course.

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- General procedure for the synthesis of discotic molecules 9a,b via Sonogashira coupling*: Nitrogen gas was purged through a solution of compound **4** (50 mg, 0.16 mmol), **8a** (278.3 mg, 0.55 mmol) and DIPEA (4 mL) in dry THF (10 mL) for 30 min. Then catalyst Pd(PPh₃)₂Cl₂ (16.6 mg, 0.02 mmol) and co-catalyst CuI (6.00 mg, 0.157 mmol) were added and stirred for 12 h at rt. THF was removed followed by extraction with CHCl₃ (3 × 30 ml) and the extract was washed with H₂O (2 × 20 ml) followed by brine (10 ml) and dried (Na₂SO₄), and the solvent was evaporated to give the crude product which was purified by column chromatography over silica gel by EA/PE (1:9) as eluent to afford the compound **9a**. Similar treatment of **8b** with compound **4**, afforded the compound **9b**. Compound **9b**: Yellow solid, yield 80%. IR (KBr, cm⁻¹) ν_{max}: 2931, 2214, 1735, 1513; ¹H NMR (400 MHz, CDCl₃): δ_H = 0.66–2.31 (m, 183 H), 3.92 (t, J = 6.1 Hz, 6H), 4.59–4.62 (m, 3H), 5.36 (d, J = 4.0 Hz, 3H), 6.84 (d,

$J = 8.6$ Hz, 6H), 7.03 (d, $J = 8.5$ Hz, 6H), 7.38 (d, $J = 8.6$ Hz, 6H), 7.41 (d, $J = 8.5$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): $\delta_{\text{C}} = 18.7, 19.2, 21.0, 22.5, 22.8, 23.8, 24.3, 25.0, 27.8, 28.0, 28.2, 29.2, 29.3, 29.4, 29.5, 31.8, 31.9, 34.7, 35.8, 36.2, 36.6, 37.0, 38.2, 38.7, 39.5, 39.7, 42.3, 50.0, 56.1, 56.6, 68.1, 73.7, 87.8, 89.3, 114.5, 115.3, 118.3, 122.6, 124.0, 132.5, 133.0, 139.7, 146.4, 159.1, 173.2$. Anal. Calcd for $\text{C}_{156}\text{H}_{219}\text{NO}_9$: C, 83.19; H, 9.80, N, 0.62. Found: C, 83.44; H, 9.92, N, 0.78.

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