

# Bent-Shaped Molecules with Terminal Trimethylsilyl Group: Synthesis and Characterisation

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## Abstract

The synthesis and characterizations of four symmetric and unsymmetric achiral banana-shaped esters possessing the terminal trimethylsilyl group are described. The chemical structures are confirmed by IR, NMR techniques and further compounds have been examined for liquid crystal properties by polarized light optical microscopy (POM) and differential scanning calorimetry (DSC). In unsymmetric molecule B<sub>1</sub> mesophase has been observed. The remaining compounds are hard to exhibit liquid crystalline property.

**Keywords:** Organosilyl reagents, 4-[2-(trimethylsilyl)ethynyl]benzoates, Banana shape, Liquid crystals, Columnar phases.

## Introduction

Organosiloxane liquid crystals demonstrate a variety of interesting and useful properties for applications due to their mesophase occurrence and crystallization at very low temperatures<sup>1-3</sup>. The LC materials are of great importance for different types of functional materials as display applications<sup>4</sup>, charge carrier materials and in biosensor applications<sup>5,6</sup>. Since the discovery of switchable smectic phases exhibited by achiral compounds composed of bent-shaped molecules, a vast number of such compounds have been synthesized and characterized for the various mesophase possibilities<sup>7,8</sup>. Banana-shaped mesogens have attracted special attention due to their unique properties as for example, spontaneous polar order with alignment and achiral symmetry breaking with formation of chiral superstructures via self assembly and many more<sup>9,10</sup>.

In recent years many research groups are working to attain the possibility of LC phase biaxiality in the nematic phases (N<sub>b</sub> phases) of bent shaped molecules, arise by the restricted rotation of these molecules around the long axis<sup>11-13</sup>. Several different molecular strategies from monomer to polymers and different synthetic approaches have been employed to discover the useful biaxial nematic phases<sup>14</sup> in temperature ranges close to the glass transition temperature with low viscosity. In this regard, elaborated work has been carried out to understand which kind of strategy will play a role for the achieving liquid crystalline properties<sup>15</sup>.

There is a scarcity of the LC work on 4-[2-(trimethylsilyl)ethynyl] benzoic acid. A report exist on synthesis and mesomorphic studies of such acid derivatives of calamitic shape with various linking groups. The polar and non-polar alkyl chain moieties are substituted on the lateral and peripheral positions of the aromatic core composed of trimethylsilyl group. As part of

our continuing program to synthesis and study the properties of compounds composed of trimethylsilyl moiety, we have recently reported a new catalyst for the preparation of trimethylsilyl derived rod-shaped liquid crystal molecules<sup>16-18</sup>. In this piece of work, we report the synthesis of terminal trimethylsilyl alkynyl derived symmetric and unsymmetric banana shaped molecules which contain four, six and seven phenyl rings. Vita et al found that all aromatic rings can favour liquid crystalline property without terminal alkyl chain, flexible spacers and connecting groups. The all aromatic cores such as 2,6-biphenyl naphthalene (PPNPP) and p-quinquephenyl (PPPPP) exhibit Smectic and nematic phases with very high temperatures<sup>19</sup>. This work is motivated us to experiment on our poor mesomorphism expected unsymmetric and symmetric esters of aromatic silyl compounds.

## Materials and Methods

**Materials and characterization:** All chemicals were purchased from Sigma-Aldrich, Sd's, Acros, and Merck make and used as received. Solvents were distilled and dried prior to the reactions. All the reactions were monitored by thin layer chromatography using silica gel precoated on aluminium sheets with 1:4 ratio ethylacetate and petroleum benzene as mobile phase. The final compounds were purified by column chromatography on Acme make silica gel 60-120 mesh size using petroleum benzene as mobile phase. The chemical structures were confirmed by <sup>1</sup>H-NMR spectroscopy (Bruker Biospin 500MHz spectrometer), and FTIR spectroscopy (Shimadzu FTIR-8400 spectrometer). The purities of the final products were confirmed by elemental analysis performed on Carlo-Erba 1106 analyzer. The thermal behaviour was investigated under nitrogen atmosphere by Differential Scanning Calorimetry (DSC) using a Perkin-Elmer, Model Pyris 1 calibrated using indium and zinc standards. The phase characterization and observation of liquid crystal textures

were performed by polarized optical microscope (POM) BX50 Olympus make equipped with a Mettler FP82HT hot stage and Mettler FP90 central processor. The heating and cooling profiles in all cases was at the rate  $5\text{ }^{\circ}\text{C min}^{-1}$ .

**General procedure for the synthesis of compounds BTMS-1 to BTMS-4:** A mixture of 4-(2-(trimethylsilyl)ethynyl)benzoic acid (1 mmol) and respective intermediates (1 mmol equivalents for BTMS-1 to BTMS-3; 2 mmol equivalents in case of BTMS-4) was suspended in anhydrous dichloromethane (10 ml). To this was added catalytic amount of 4-*N*, *N*-dimethylamino pyridine (DMAP) (0.005 g) and *N*, *N*-dicyclohexylcarbodiimide (DCC) (1.5-2.5 mmol) and the mixture stirred for 6 h at ambient temperature. The *N*, *N*-dicyclohexyl urea formed as by-product was filtered off and the filtrate diluted with chloroform (25 ml). The combined extract was washed with water (3 x 25 ml) and dried on anhydrous sodium sulphate. The residue obtained on removal of solvent was chromatographed on silica gel (100-200 mesh) using petroleum benzene as an eluent. Removal of solvent from the eluate afforded a colorless material which was crystallized from analytical grade hexane. Yields are in the range of 53-67 %. The analytical data, FT-IR,  $^1\text{H-NMR}$  for the title compounds are summarized as follows:

**Compound (e):** Yield 80 %. IR (Nujol,  $v_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3547 (-OH), 2924 ( $\text{CH}_2$ ), 2854 ( $\text{CH}_2$ ), 1730 (C=O, ester), 1610 and 1454 (C=C, aromatic), 1294, 1176, 1087 (C-O), 842 (C-H).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm)  $\delta$ : 8.25 (dd, 4H,  $J = 8.8$  and  $2.4$  Hz, Ar-H), 7.73-7.57 (m, 4H, Ar-H), 7.49 (m, 1H, Ar-H), 7.29-7.14 (m, 2H, Ar-H), 6.92 (m, 1H, Ar-H), 5.52 (s, 1H, Ar-OH), 2.68 (q, 2H, Ar- $\text{CH}_2$ ), 1.66-1.29 (m, 12H, alkyl - $\text{CH}_2$ -), 0.89 (t, 3H, - $\text{CH}_3$ ), 0.27 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ).  $^{13}\text{C-NMR}$ : 168.3, 151.5, 146.5, 143.4, 132.6, 129.8, 127.6, 127.1, 119.3, 115.9, 35.6, 31.9, 29.5, 29.2, 22.6, 14.1 ppm. Microanalysis calculated for  $\text{C}_{27}\text{H}_{30}\text{O}_3$  (Mol. Wt: 402.53) C, 80.56; H, 7.51; found C, 80.63; H, 7.59 %.

**BTMS-1:** Yield 67 %. IR (Nujol,  $v_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3026 ( $=\text{CH}_2$ ), 2951 ( $\text{CH}_2$ ), 2854 ( $\text{CH}_2$ ), 2158 (acetylene), 1739 and 1722 (C=O, ester), 1602 and 1456 (C=C, aromatic), 1263, 1170, 1134 (C-O), 839 (C-H).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm)  $\delta$ : 8.23 (dd, 4H,  $J = 8.9$  and  $2.4$  Hz, Ar-H), 7.73-7.47 (m, 8H, Ar-H), 7.31-7.16 (m, 4H, Ar-H), 2.68 (q, 2H, Ar- $\text{CH}_2$ ), 1.54-1.28 (m, 12H, alkyl  $\text{CH}_2$ -), 0.89 (t, 3H, - $\text{CH}_3$ ), 0.27 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ). Microanalysis calculated for  $\text{C}_{39}\text{H}_{42}\text{O}_4\text{Si}$  (Mol. Wt: 602.83) C, 77.70; H, 7.02; found C, 77.85; H, 7.23 %.

**BTMS-2:** Yield 53 %. IR (Nujol,  $v_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3021 ( $=\text{CH}_2$ ), 2924 ( $\text{CH}_2$ ), 2852 ( $\text{CH}_2$ ), 2158 (acetylene), 1732 (C=O, ester), 1602 and 1454 (C=C, aromatic), 1255, 1197, 1163 (C-O), 844 (C-H).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm)  $\delta$ : 8.32 (m, 2H, Ar-H), 8.14 (m, 5H, Ar-H), 7.62-7.40 (m, 11H, Ar-H), 6.96 (d, 2H,  $J = 8.5$  Hz, Ar-H), 4.06 (t, 2H,  $J = 6.5$  Hz, - $\text{OCH}_2$ -), 1.84-1.27 (m, 20H, alkyl - $\text{CH}_2$ ), 0.89 (t, 4H, - $\text{CH}_3$ ), 0.29 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ). Microanalysis calculated for  $\text{C}_{51}\text{H}_{54}\text{O}_9\text{Si}$  (Mol. Wt: 839.05) C, 73.00; H, 6.49; found C, 73.11; H, 6.54 %.

**BTMS-3:** Yield 57 %. IR (Nujol,  $v_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3019 ( $=\text{CH}_2$ ), 2229 (CN), 2158 (acetylene), 1732 (C=O, ester), 1600 and 1452 (C=C, aromatic), 1251, 1161, 1057 (C-O), 759 (C-H).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm)  $\delta$ : 8.33 (m, 4H, Ar-H), 8.15 (m, 5H, Ar-H), 7.77-7.38 (m, 11H, Ar-H), 0.29 (s, 9H,  $\text{Si}(\text{CH}_3)_3$ ). Microanalysis calculated for  $\text{C}_{40}\text{H}_{29}\text{NO}_8\text{Si}$  (Mol. Wt: 679.75) C, 70.68; H, 4.30; N, 2.06; found C, 70.81; H, 4.35, N, 2.21%.

**BTMS-4:** Yield 55 %. IR (Nujol,  $v_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3021 ( $=\text{CH}_2$ ), 2156 (acetylene), 1736 (C=O, ester), 1601 and 1454 (C=C, aromatic), 1250, 1158, 1047 (C-O), 844 (C-H).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm)  $\delta$ : 8.32 (m, 4H, Ar-H), 7.75-6.98 (m, 16H, Ar-H), 0.29 (s, 18H,  $\text{Si}(\text{CH}_3)_3$ ). Microanalysis calculated for  $\text{C}_{56}\text{H}_{46}\text{O}_8\text{Si}_2$  (Mol. Wt: 903.13) C, 74.47; H, 5.13; found C, 74.58; H, 5.23 %.

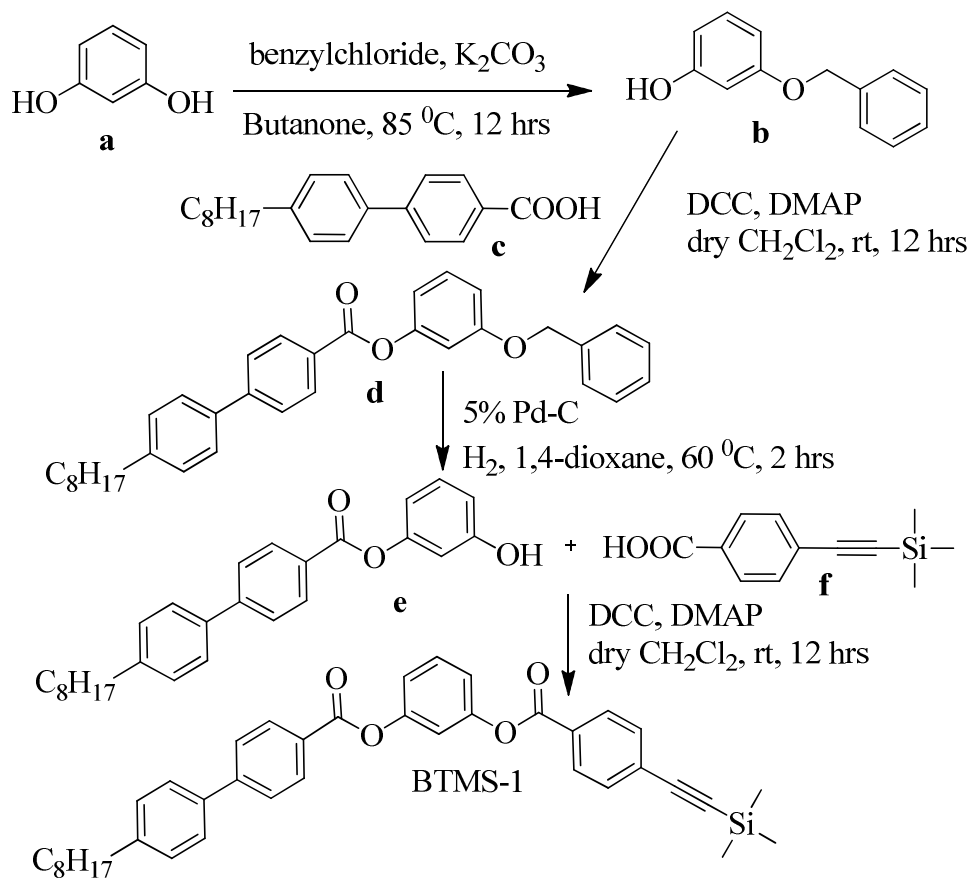
## Results and Discussion

We had earlier reported the preparation of 4-[2-(trimethylsilyl)ethynyl]benzoic acid (f) and this compound was used for the preparation of rod shaped esters with variety of connecting groups<sup>20</sup>. We now report the use of 4-[2-(trimethylsilyl)ethynyl]benzoic acid for the synthesis of the bent-core compounds BTMS-1 to BTMS-4. The synthetic strategy is shown in Scheme 1 for BTMS-1.

Resorcinol a was refluxed with benzyl chloride in presence of anhydrous potassium carbonate as a base at  $85^{\circ}\text{C}$  in butanone for overnight to get 3-benzyloxyphenol b. The 3-benzyloxyphenol was reacted with 4-*n*-octylbiphenyl-4'-carboxylic acid using DCC coupling esterification reaction to get intermediate d. Catalytic hydrogenation was then carried out using 5% Pd on carbon in hydrogen atmosphere to get key precursor e in 80% yield. Finally, the target bent-core trimethylsilyl (BTMS) esters were achieved by DCC coupling reaction with 4-(trimethylsilylethynyl) benzoic acid f in presence of DMAP and dry  $\text{CH}_2\text{Cl}_2$  over 12 hours of stirring.

Figure-1 shows the bent-core molecules of BTMS-2 to BTMS-4. The required intermediates for target compounds BTMS-2 to BTMS-4 were synthesised according to the procedures reported in the literature<sup>21-25</sup>. The synthetic procedure used for the terminal trimethylsilyl derived compounds BTMS-2 to BTMS-4 is same as that of BTMS-1.

The chemical structures of all the new 4-[2-(trimethylsilyl)ethynyl] benzoic acid derivatives BTMS-1 to BTMS-4 were confirmed by standard spectroscopic techniques. All the compounds exhibited prominent carbon-carbon triple bond stretching frequency at  $2100\text{ cm}^{-1}$  and ester stretching frequency at approximately  $1730\text{ cm}^{-1}$ . Compound BTMS-3 shows cyano and trimethylsilyl acetylene stretching frequencies at 2200 and  $2100\text{ cm}^{-1}$  respectively which confirms the formation of BTMS-3 as depicted in figure 2 (a). The liquid crystalline properties was established by the combination of POM and DSC.



Scheme-1  
Synthetic route for the target bent-core molecule BTMS-1

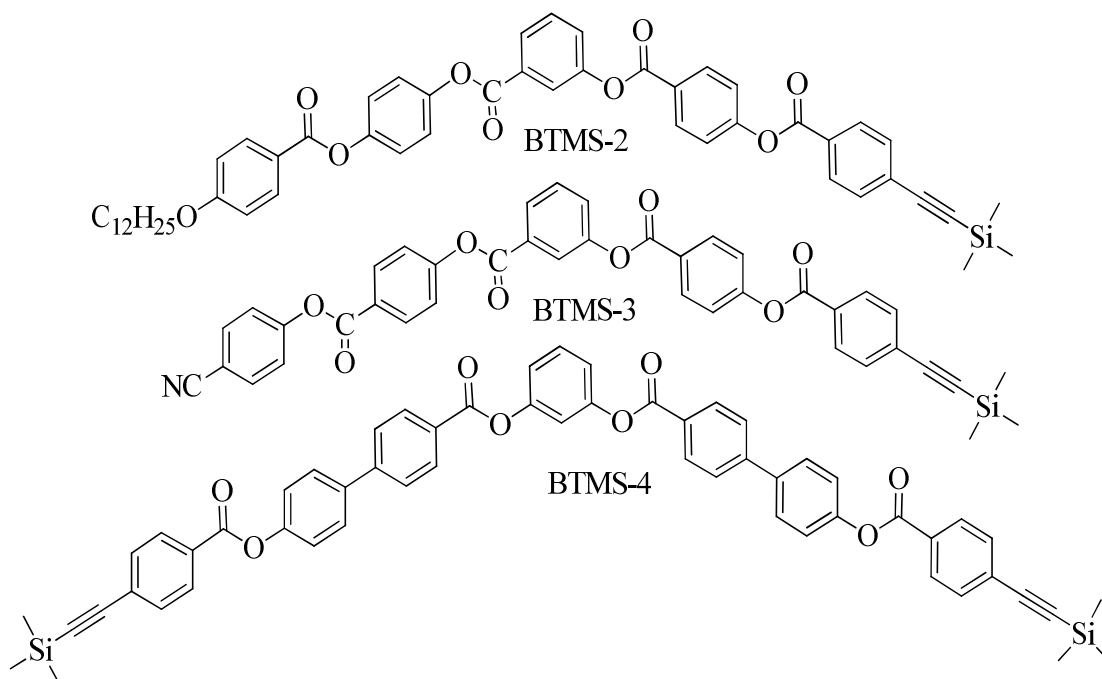
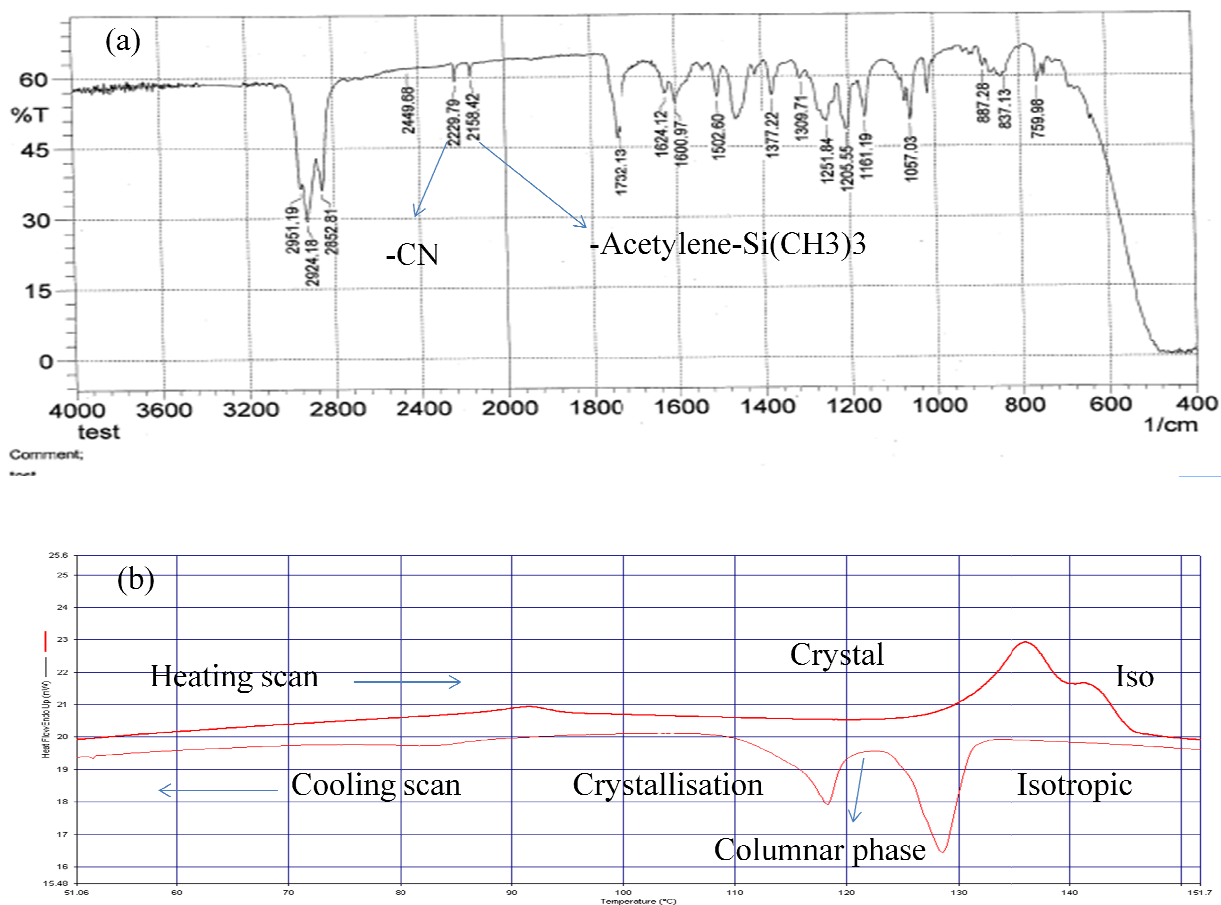


Figure-1  
Target bent-shaped molecules of BTMS-2 to 4



**Figure-2**  
 (a) IR spectrum of BTMS-3 and (b) DSC scan of compound BTMS-2

**Table-1**

**Phase type, transition temperatures (°C) and enthalpies (kJ mol<sup>-1</sup>; in parentheses) of banana-shaped molecules**

Compound	Heating scan	Cooling Scan
BTMS-1	Cr 137.2 (86.4) Iso	Cr 95.5 (67.1)
BTMS-2	Cr 136.5 (58.5) B <sub>1</sub> 142.2 (20.85) Iso	Cr 118.2 (15.8) B <sub>1</sub> 129.5 (20.8) Iso
BTMS-3	Cr 175.9 (67.6) Iso	Cr 93.3 (57.3) Iso
BTMS-4	Cr 178.7 (139.3) Iso	Cr 102.9 (38.9) Iso

Note: Cr = crystal; B<sub>1</sub> = columnar phase; I = isotropic phase.

**Thermal and liquid crystal properties:** The transition temperatures and their associated enthalpy values for trimethylsilyl group derived bent-core compounds BTMS-1 to BTMS-4 have been obtained using the combination of polarizing optical microscopy and differential scanning

calorimetry. The findings are summarized in Table-1. In general, the samples were sandwiched between untreated glass plate and a cover slip and heated up to its isotropic point using temperature controlled hot stage and then slowly cooled from the isotropic liquid and observed under a optical polarizing microscope to verify the LC textures.

The sample was sandwiched between untreated glass plate and cover slip and it was kept in the hot stage in which heating and cooling process was taken place by automated programming at the rate of 5°C/min. The whole hot stage setup was kept under the polarised optical microscope for the observations of crystal-mesophase-isotropic transitions with liquid crystal textures. For instance compound BTMS-1 directly went to isotropic state at 137.2°C (ΔH = 86.4), again it was cooled down to crystalline state at 95.5°C (ΔH = 67.1) without showing LC property. Notable changes were occurred in the next member BTMS-2. The DSC spectrum of BTMS-2 shown in Figure-2(b). Compound BTMS-2 melted at 136.5°C (ΔH = 58.5) to show columnar phase, then it went to isotropic state at 142.2°C (ΔH = 20.85). Further, it was cooled from the isotropic state and

129.5°C ( $\Delta H = 20.8$ ), a characteristic optical photomicrograph of sandy texture having small focal-conics were seen as shown in Figure-3 (a) and (b), which can be assigned to a columnar phase, which was finally crystallized at 118.2°C ( $\Delta H = 15.8$ ). Whereas unsymmetric compound BTMS-3 with polar cyano group and the symmetric compound BTMS-4 with trimethylsilyl group at both the ends of the molecules did not show any LC property. Both the compounds showed crystal to isotropic and isotropic to crystal transition states at 175.9°C ( $\Delta H$

= 67.6), 178.7°C ( $\Delta H = 139.3$ ) and 93.3°C ( $\Delta H = 57.3$ ) 102.9°C ( $\Delta H = 38.9$ ) respectively on heating and cooling scans.

We were unable to probe X-ray measurements and identify its molecular lattice arrangements in the columnar mesophase, due to short thermal range of BTMS-2 compound. The phase was deduced and assigned on the basis of pattern of the textures observed for columnar phases in the literature<sup>26</sup>.

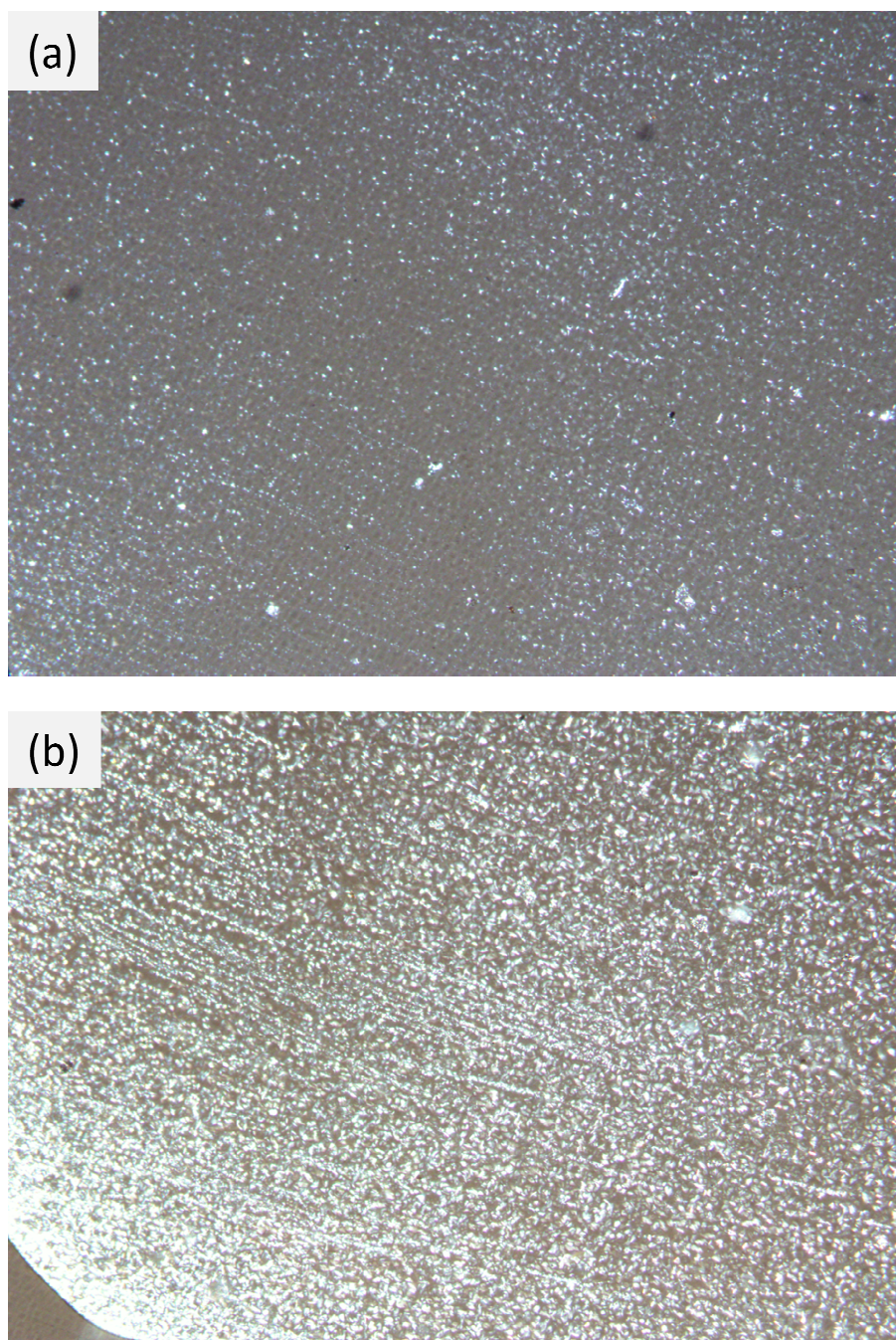


Figure-3  
Optical textures of BTMS-2 on cooling cycle (a) at 128°C (b) at 120°C

Compounds BTMS-1 and BTMS-2 possess relatively lower transition temperatures than compounds BTMS-3 and BTMS-4. The study proves that the removal of alkyl chain in symmetric and unsymmetric molecules enhances the isotropic temperatures as well as suppression of the mesophase. Interestingly, introduction of the polar nitrile and trimethyl silyl groups at terminal position suppress the mesophase in compound BTMS-3 and BTMS-4 respectively. This may be due the reduction of the flexibility at terminal positions of the molecules.

## Conclusion

Four examples of terminally connected 4-(2-(trimethylsilyl)ethynyl) with bent-core molecules have been synthesized and investigated for LC properties. Only one molecule BTMS-2 has enantiotropic B<sub>1</sub> phase (rectangle columnar) whereas the other members hard to exhibit mesomorphism. This investigation evidenced that the elimination of mesophases due to insufficient requirements of LC molecules. This would mean that the polar cyano, tetrahedral trimethylsilyl group and reducing core length of bent-cores reported herein do not provide that degree of favourism which would be required for the existence of LC property. Probably, by keeping the trimethylsilyl group at one end and increasing the chain length at another end of the molecule as in BTMS-2 leads to achieve LC properties.

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