Chapter 4

Synthesis of Some Novel Aromatic Alkynylsilanes: Mesomorphic Characterization of Ethynyl-Substituted Rod Shaped Molecules
PART-A

Introduction

Kenkichi Sonogashira in 1975 reported a palladium-catalyzed substitution reaction that would later be named after him as Sonogashira reaction.²¹⁷ Sonogashira cross-coupling reaction is a powerful tool for the formation of new carbon-carbon single bond. This reaction is used with milder experimental conditions than previous acetylene substitution reactions. It is used in the synthesis of a wide variety of compounds with carbon-carbon triple bond, such as natural products, pharmaceuticals, heterocycles, oligomers and polymers.²¹⁸ Especially in recent years, the Sonogashira reaction has been used for the synthesis of variety compounds in all fields and also in material applications.²¹⁹

\[
R^1\cdot X + H \equiv R^2 \xrightarrow{\text{Pd source, Cul, refluxed}} \text{TEA, refluxed} \rightarrow R^1 \equiv R^2
\]

R¹, R² = Aryl, alkyl; X = Br, I

Scheme IV.1

Trimethylsilylacetylene is an important precursor for Sonogashira coupling reaction. Trimethylsilylacetylene is a versatile two carbon building block of considerable utility in organometallic chemistry. Unlike acetylene itself, which is a gas at room temperature, which is potentially dangerous and difficult to handle, this mono-trimethylsilyl protected synthon is an easily handled stable liquid.

In many instances introduction of the ethynyl group is facilitated by the use of trimethylsilylacetylene (TMSA). It allows chemists to work with conditions that are mild and that do not require pressure or liquid ammonia conditions. It can be used in many
types of synthetic procedures without the taking special precautions and specialized equipment. Most of TMSA chemistry can be applied to introduction of terminal acetylenes. However, easy handing procedures and the unique structural feature of TMSA makes it a very valuable tool in the arsenal of synthetic organic chemists working in the fine chemical industries.\textsuperscript{220}

Trimethylsilylacetylene is an extremely useful and "potentially nucleophilic" two carbon bifunctional equivalent synthon. It can be introduced and subsequently manipulated in a multitude of synthetic transformations that are now well documented in the literature.\textsuperscript{221} TMSA is being used in many areas in the forefront of research such as surface science for the development alignment techniques using new polymers for various applications.\textsuperscript{222}

In continuation of the organosilicon chemistry first initiated by Nagendrappa in our laboratory, the trimethylsilyl group is our prime importance for our ongoing works. Our research is mainly focused on silyl- group containing reagents, their synthesis and reactions. The trimethylsilyl- group acts as a masking agent for the anion rendering it to become an anionic synthon.

In continuation of our Diels-Alder bicyclo[2.2.2]octane cycloadduct reactions of 2-trimethylsilyloxy-1,3-cyclohexadiene with maleimides and synthesis and characterization of arylsilylethers with new Laponite RD catalyst in the Chapters 2 and Chapter-3 respectively, here we are taking diversion to prepare some trimethylsilyl group containing rod shaped compounds, which may show potential as mesogenic materials.
PART-B

A Brief introduction to liquid crystals

The three most common states of matter are solids, liquids and gases. Water, as an example, is a solid below 0 °C, a liquid between 0 °C and 100 °C, and a gas above 100 °C. A transition between the different states of matter (or phases) is generally induced by a change in temperature. The transition from solid to liquid is accompanied by a strong decrease in mutual ordering of the molecules and a large increase in mobility.

In 1888, the Austrian botanist Friedrich Reinitzer discovered an intermediate state of matter between the liquid and solid state. He observed two melting points while heating cholesteryl benzoate.223-226 The cloudy liquid he observed between the two melting points was the first recorded observation of a liquid crystalline phase.

Liquid crystals are class of molecules that show phases that are intermediate between the crystalline solid and the isotropic liquid. This is why these phases are also called mesophases. A simple definition of mesogen or liquid crystal forming material is that when a liquid crystal melts from a solid, it exhibits one or more thermodynamically stable intermediate states called mesophases, and it then finally becomes an isotropic liquid. The word ‘mesophase’ is derived from the Greek word ‘mesos’, meaning between, or intermediate and 'phase’ means state of matter.227 In the overall change from solid to isotropic liquid, there is a stepwise breakdown of the molecular ordering, the molecules can rotate and oscillate rapidly about one or more axes,228 and there is a stepwise collapse of their long range positional ordering, and finally disruption in the short-range order, but the orientational order remains. A liquid crystal mesophase could
be defined as an elastic fluid-like ordered state. Schematic representation of states of matter with liquid crystal state as shown in the Figure IV.1.

**Figure IV. 1.** Schematic representation of states of matter including liquid crystal state

Molecules that exhibit mesophases are usually highly anisotropic in shape, like rods or disks. The molecules in liquid crystalline phases exhibit long-range orientational ordering and sometimes partial positional ordering. The parallel orientation of the long molecular axes is common to all mesophases of rod-like liquid crystals. Figure IV. 2 depict the relationship between the mobility and the order of some condensed (i.e. non-gaseous) phases. Besides the mesophase, which combines the mobility of liquids with the order of crystals, there is the glassy phase, in which the molecules are immobile and behave like a frozen liquid, or a frozen liquid crystal in case of a mesoglass. Scientists soon realised that they had discovered one of the most exciting properties arising from a wide family of synthetic and natural compounds. Liquid crystals have been for a long time the subject of scientific interest since the advent of this fourth state of matter in addition to the known states of solid, liquid and gas.
Liquid crystals are anisotropic, meaning that their physical properties are not identical in all directions, and the anisotropy of the optical, electric, elastic and magnetic properties has led to the use of liquid crystal materials in display devices and as sensors. The diamagnetic anisotropy for instance makes that the molecules can be aligned by an external magnetic field. Other important properties of liquid crystals are that their orientation can easily be influenced by an electric field and by surfaces. These properties have led to their application in display devices such as LCDs. Frequently used classes of liquid crystals are chiral and non-chiral cyanobiphenyls. Because of their chemical stability and suitable temperature range in which the liquid crystalline phase is present, they were for a long time used in LCDs. If the liquid crystalline mesophase is induced (in a certain temperature interval) by the concentration in a solvent they are called lyotropic liquid crystals. This thesis only deals with thermotropic liquid crystals.

These liquid-crystalline phases, textures and molecular arrangements are usually identified using an optical polarising microscope in conjunction with differential scanning calorimetry (DSC) and X-ray diffraction studies.
VI. 1. Classification of Liquid Crystals

There are two main families of liquid crystals: thermotropic and lyotropic liquid crystals. Classifications of liquid crystals are shown in Figure IV.3. The thermotropic liquid crystals exhibit liquid-crystalline mesophases on melting from the crystal phase or cooling from the isotropic liquid, whereas the lyotropic materials exhibit liquid-crystalline mesophases when mixed with particular solvent. Liquid crystals are materials which display characteristics of both the crystalline and liquid states. These liquid crystalline states can be induced using two methods. Firstly by changes in temperature, they are termed as thermotropic and secondly by changes in molecular concentration where they are termed lyotropic.

![Diagram of liquid crystal classification]

**Figure IV.3:** General classification chart of liquid crystals

The typical chemical structure of calamitic (rod shaped) and banana shaped (bent shaped) molecules can be represented by the general formula shown in Figure IV. 4 and Figure IV. 5. Most of the calamitic compounds consist of two or more ring structures, and three or seven ring structures in case of bent shaped molecules, bonded together directly or via covalent bonds or linking groups (L₁-L₅) such as, -N=N, -CH=CH-, -
CH=N-, -COO-, Acetylene, -(CH₂)n-. These groups vary the polarity, direction and flexibility of the molecules.²³⁵

![Figure IV.4: General model of calamitic liquid crystals](image)

Both rod and bent shaped liquid crystals usually have terminal (R₁-R₂) polar groups (CN, NO₂, halogens), and mainly hydrocarbon chains, such as n-alkyl/n-alkoxy/n-alkanoates, sometime small units of lateral substitutions (X₁-X₅) such as halogens, CN, NO₂, aryl/alkyl/alkoxy groups as well. These substituents play an important role in position, volume and bending angle of the molecules.²³⁶

![Figure IV.5: General model of bent shaped liquid crystals](image)

In case of discotic liquid crystals central rigid aromatic core is surrounded different groups by directly or covalent bonds or ionic bond. General template of discotic liquid crystal is shown in Figure IV. 6.

![Figure IV.6: General model for disc shaped liquid crystals](image)
Many discotic cores are known with appropriate substitutions afford discotic liquid crystals. These cores are mainly (a) aromatic hydrocarbons such as, benzene, naphthalene, anthraquinone, phenanthrene, pyrene, perylene, triphenylene, truxene etc. (b) macrocyclic cores such as, metacyclophane, tribenzocyclononatriene, tetrabenzo-cyclo-dodecatetraene, phenylacetylene etc; (c) heterocyclic cores such as, benzopyrane, oxatruexene, thia-truxene, benzotrisfuran etc; (d) metallomesogens such as, diketone complexes, triketone complexes, dioxime complexes, etc, (e) saturated cores such as, cyclohexane, pyranose sugars. Additionally, a number of discotic cores generated through non-covalent H-bonding are also known to display columnar mesophases. In addition to the above types of liquid crystals, Y-shape, H-shape, S-shape, W-shape, V-shape, hockey stick shaped liquid crystals also developed in recent years.

Lytotropic liquid crystals are comprised of amphiphilic molecules, where one end of the individual molecule is hydrophilic, and another end is hydrophobic. Such compounds are shown in Figure IV. 7. Upon interaction between the compound and an appropriate solvent (usually water) at a certain concentration, the molecules arrange into spheres, rods or discs, called micelles and it is upon this basis that lyotropic liquid crystals are prevalent in everyday life. Examples include soap and detergents, whilst not so obvious examples include the structural conformation of biological phospholipid membranes.

![Figure IV. 7: General feature of amphiphilic molecule for lyotropic liquid crystals](image-url)
VI. 2: Types of liquid crystal phases

Thermotropic liquid crystals exhibit mesophases on heating or cooling, and the temperature range over which the mesophases are exhibited varies from material to material. These types of liquid crystals generally have several common characteristics; among these are rod like molecular structures, rigidness of the long axis and strong dipole moments. These mesophases can be classified according to the positional and orientational order of the molecules. Molecules that show liquid crystalline behavior usually have an anisotropic shape; their liquid crystalline properties depend on non-covalent interactions. Several different types of shapes and their corresponding phases can be distinguished. Typically, certain types of molecules exhibit distinct mesophases. It is however not always possible to predict the type of mesophase based on just a molecular shape. Rod-shaped (or calamitic) molecules form most of the traditional liquid crystalline phases: nematic, cholesteric and smectic phases. The nematic mesophase has long-range orientational order and no long-range positional order. The molecules are oriented parallel in a certain domain of a sample (the preferred direction can vary from point to point in a medium). The nematic phase is optically uniaxial (Nu) and is therefore frequently used in display device technology. The biaxial nematic phase (Nb), in which there is an additional correlation of the molecules perpendicular to the director, is a recently recognized sub-class of the nematic phase.

A typical thermotropic transition sequence on heating progresses from the crystalline phase (solid state), then to the smectic phase, next to the nematic and finally to the isotropic phase (liquid state). This can be seen in Figure IV. 8 for rod shaped liquid crystals.
Figure IV. 8: Typical transitions of rod like thermotropic liquid crystal on heating from the crystalline to the isotropic state.

Several types of smectic phases exist. Two of the most common, which are the smectic A and smectic C phases. Molecules in smectic A and C phases tend to arrange themselves into planes. Within these planes no positional order exists, so we can consider the positional order to be 1D only. All smectic phases display orientational order. In the smectic A phase the director is perpendicular to the planes, while in the smectic C phase the director makes an angle other than 90° to the planes i.e. it is tilted. Several types of smectic phases exist. In rod shaped liquid crystals SmA and SmC phases are quite common, Smectic phases occur when the thermal energy is enough to overcome the Van de Waals attractive forces between the ends of the rods and so positional order of each layer may be lost. Schematic representation of SmC phase is shown in Figure IV.9.

Figure IV. 9: General structure Smectic C phase of rod like liquid crystal
**Banana phases**

Banana liquid crystals are packing along a bent direction of the molecules, to constitute a polar plane which is perpendicular to the tilt plane. In addition, the tilted molecules exist in layers and produce a layer plane. Thus three different planes exist for a given layer which can be assumed to be three co-ordinates. If these three co-ordinates form a particular handedness (depending on tilt direction with respect to other two-coordinates), the mirror image of this shows the opposite handedness. These are non superimposable mirror images and that’s why the layer becomes chiral though the individual molecules are achiral. Arrangement of achiral banana shaped molecules shown in Figure IV.10.

![Diagram of banana phases](image)

**Figure IV.10:** General schematic arrangement of bent shaped molecules

**Discotic phases**

In discotic liquid crystals molecules are stack one above the other or molecules assemble themselves one on the top of the other in columns packed parallel on a two-dimensional lattice. In columnar mesophases, the molecules may be arranged in a regular ordered manner or aperiodically (disordered). Self-organization of disc-like molecules to form discotic liquid crystals these columns form supramolecular assembly form a variety of discotic phases. Hexagonal columnar mesophase in common in discotic molecules.
Arrangement of discotic mesogens in columns to form columnar phase shown in Figure IV.11.

Figure IV.11: General schematic arrangement of disc shaped molecules in a column for Hexagonal columnar phase.

In all types of liquid crystals, nematic phases are commonly used for displays. In this study we will focus on trimethylsilyl derived calamitic liquid crystals.

Some of the reactions performed and compounds prepared and characterized for the application point of view using our target molecule 4-[2-(trimethylsilyl)ethynyl]phenol.

Yashima et al, synthesized and studied the properties of optically active phenylacetylene monomer as well as phenylacetylenes polymers using the 4-[2-(trimethylsilyl)ethynyl]phenol. However, a copolymer with the phenylacetylene having a bulky tert-butyldiphenylsiloxy group at the para- position is reported to a very intense induced CD which was almost a mirror image to those of the chiral homopolymers in the 300-450 nm wavelength range. These results suggest that the copolymer may possess a reversed helical structure. The specific rotation of the copolymer with the phenylacetylene having bulky tert-butyldiphenylsiloxy groups at the para position
showed a specific rotation about 2 times larger than that of the homopolymers (Scheme IV. 2)\textsuperscript{247}

\[
\begin{array}{c}
\text{Si} \equiv \text{C} \equiv \text{C} \equiv \text{OH} \xrightarrow{\text{(Bu)}_4\text{NF, t-BuPh}_2\text{SiCl}} \text{H} \equiv \text{C} \equiv \text{C} \equiv \text{O} \equiv \text{Si} \equiv \text{C} \equiv \text{C} \equiv \text{OH} \\
\end{array}
\]

Scheme IV. 2

4-[2-(trimethylsilyl)ethynyl]phenol has been used in the synthesis of natural product. Nysol is stimulated the proliferation of estrogen dependent T47D breast cancer cells, and their stimulatory effects were blocked by an estrogen antagonist. In addition, (-) Nysol showed binding affinity for the bovine uterine estrogen receptor\textsuperscript{248}. Akiyama et al. showed the stereoisomer controlled synthesis of natural product (-) Nysol using vinylaluminium reagent and 4-[2-(trimethylsilyl)ethynyl]phenol (Scheme IV. 3)\textsuperscript{249}. The synthesis leads to the absolutely pure (-) nysol compound without any other impurities as byproducts.

\[
\begin{array}{c}
\text{Si} \equiv \text{C} \equiv \text{C} \equiv \text{OH} \xrightarrow{\text{AcO}} \text{Si} \equiv \text{C} \equiv \text{C} \equiv \text{OH} \xrightarrow{\text{HO}} \text{Si} \equiv \text{C} \equiv \text{C} \equiv \text{OH} \\
\end{array}
\]

Scheme IV. 3

Thermally curable, melt processible organic polymeric systems of cyclotriphosphazenes has been reported. This molecule was prepared by the reaction of hexachlorocyclotriphosphazene with sodium salt of 4-[2-(trimethylsilyl)ethynyl]phenol obtained by using sodium hydride in 1,4-dioxane. Cyclotriphosphazenes exhibit useful thermal properties such as self-extinguishibility and flame retardancy. Which are
imparted mainly by the presence of nitrogen and phosphorus atoms in the ring (Scheme IV. 4).\textsuperscript{250}

Ting et al, synthesized the thermal and photoluminescence properties having liquid crystalline polyacetylenes containing 4-alkanyloxyphenyl trans-4-alkylcyclohexanoate as a side group using 4-[2-(trimethylsilyl)ethynyl]phenol. [Rh(nbd)Cl]$_2$, MoCl$_5$ and WCl$_6$ were used as polymeric initiators. Both the compounds exhibit Smectic A and Smectic C phases. X-ray diffraction diagrams reveal that the liquid crystalline polyacetylenes display an interdigitated bilayer structure for the smectic phases and their emission wavelengths are about 500 nm. The photoluminescence intensity increased dramatically when a liquid crystalline polyacetylene was blended with poly(methyl methacrylate) (Scheme IV. 5).\textsuperscript{251}
Kanaru et al. prepared and studied the simple trimethylsilyl derived rod shaped molecules and their desilylated terminal acetylene compounds. These molecules are showed the unstable monotropic liquid crystalline phases, the unstable liquid crystalline phases are probably due to the sterically hindered large trimethylsilyl group. The molecules have been used for the preparation of platinum metal co-ordinate complexes to get liquid crystalline property. These organometalllic complexes have showed stable thermotropic liquid crystal phases (Scheme IV. 6).\(^{252}\)

\[
\begin{align*}
&\text{Si} = C - \text{O} - C - \text{OC}_n \text{H}_{2n+1} \\
&\text{R}^2 \text{O} - \text{C} - \text{Pt} - \text{C} - \text{O} - \text{C} - \text{OR}^1
\end{align*}
\]

Co-ordinate complex

**Scheme IV. 6**

Hennrich et al. applied a standard Sonogashira coupling protocol for the preparation of unsymmetric linear phenylacetylenes, incorporating terminal biphenyl substituent in rod shaped compounds. The mesomorphic study of target compounds of biphenylacetylenes forms SmA mesophase, which was identified from the homeotropic texture to confirm the type of mesophase. X-ray diffraction experiments were performed and the patterns obtained present a diffuse halo corresponding to a mean distance of 4.4 Å. This feature is characteristic of the liquid-like order of the aliphatic chains in a liquid crystal phase. A set of sharp maxima in the low angle region confirms the Smectic phase (Scheme IV. 7).\(^{253}\)
Mohamed et al., have shown that Sonogashira coupling with aqueous ammonia is tolerable for the reaction of aryl iodides or alkynes bearing an azobenzene group. The Sonogashira coupling reaction of (4-heptyloxyphenyl)ethyne with (4-heptyloxyphenyl)-(4-iodophenyl)diazene gives the corresponding azotolane in 87% isolated yield. Coupling reactions of alkynes with aryl halides, in which an azo group is incorporated in the molecule, produce azotolanes in good to excellent yields. The reaction was also found to be applicable for substrates bearing a protic functional group such as -NH₂ or -OH on the aromatic ring. The reaction provides a practical azotolane synthesis that enables to design derivatives bearing a wide range of functional groups and alkyl groups with different chain length directed toward holographic materials of high performance. However, none of the these molecules possess mesomorphic property (Scheme IV. 8).²⁵⁴

\[
\begin{align*}
\text{Si} & \equiv \text{N=N} & \text{OC}_7\text{H}_{15} \\
\text{NC} & \equiv \text{N=N} & \text{OC}_7\text{H}_{15}
\end{align*}
\]

Scheme IV. 8

In 2010, Ho and co-workers designed and synthesized the novel amphiphilic liquid crystals that contain β-D-galactopyranoside end-group and 4-[1,2,3]-triazolephenyl 4-alkoxybenzoates using trimethylsilyl group with Sonogashira coupling and simple esterification reactions. The catalyst used is the highly hygroscopic 1-(3-
dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride at -20 °C to get target molecules (Scheme IV. 9).

![Chemical structure diagram](image)

**Scheme IV. 9**

In addition to liquid crystal property self-assembling, amphiphiles segregation strength properties in solution phase also have been carried out with good results.

Liao *et al.*, designed and synthesized ferroelectric liquid crystal monomer and structurally similar dimer molecule. The monomer displays a characteristic Schlieren texture for nematic mesophase and broken fan texture of the smectic mesophase along with broken fan shaped structure for the indicating the formation of the SmC* phase. The size and flexibility effects of the monomer molecules have profound influences on their SmC* mesomorphic behavior (Scheme IV. 10).

![Chemical structure diagram](image)

**Scheme IV. 10**
Present work:

Since our laboratory is primarily interested in organosilicon chemistry, we were interested in synthesis and characterization of some novel low molar mass liquid crystals. In this regard, aryl silanes and aryl acetylenes are highly reactive potential candidates for material science. Substituted aromatics with long alkyl chains have been reported to reveal solid polymorphism and mesomorphism.

All the compounds in the references aforesaid are able to self-organize and exhibit interesting properties in materials science with linear and non-linear optical properties, electrical conductivity, electroluminescence, which may be useful as energy storage materials for solar cell and exhibit of variety of liquid crystalline phases.

In continuation of our studies and in the light of importance of the above reported works in literature, it was of our interest to attempt the preparation and study the liquid crystal properties of some low molar mass silyl- substituted rod shaped molecules.

Here we report the simple and efficient synthesis of some 4-[2-(trimethylsilyl)ethynyl] phenyl ester derivatives using Sonogoshira cross-coupling reaction and simple DCC esterification reaction to obtain alkynyl aromatic esters. The chemical structure characterization and study of mesomorphic properties of prepared molecules is discussed. The study has led to the preparation of new potential synthetic intermediates and as well as materials for applications. All benzoic acid derivatives 46-55 were prepared according the procedures described in the literature.\textsuperscript{257-261} The synthesis of trimethylsilyl derived rod shaped compounds 55-65 is outlined in the synthetic Scheme IV. 11.
Scheme IV. 11. Synthetic scheme of trimethylsilyl- derived rod shaped compounds 55-65.

The synthesis of trimethylsilyl- substituted rod shaped molecules can be achieved in different ways. One of the earliest reported methods is Sonogashira coupling of aryl iodide and alkynyls which employs costly reagents and harsh reaction conditions, such as high heating temperatures, prolonged reaction timings, costly and hazardous reagents. This synthesis involves partial alkylation of aryl iodides. However, homocoupling leads to many inorganic side products, with very low yield of desired product. This prompted us to look the simple method to synthesis of trimethylsilyl- compounds. In this context, we prepared the 1-[4′-(hydroxyphenyl)]-2-trimethylsilylacetylene 45 by altered reaction conditions of Sonogashira reaction.

We now report a simple method for the preparation of rod shaped molecules. Our procedure simplifies laborious synthesis a range of rod shaped compounds with variation of terminal unit using compound 1-[4′-(hydroxyphenyl)]-2-trimethylsilylacetylene (45).
Compound 45 was used to prepare rod shaped molecules 56-65 by simple and efficient DCC coupling with various substituted benzoic acids without having any side product according to the general procedure given in experimental section.

Compounds we have synthesized constituted of polar terminal substituents like cyano-, nitro-, groups varying the terminal alkyl groups as mono-, di- and trialkoxy-groups with two aryl ring compounds as indicated in Scheme IV. 11. The trimethylsilyl derived rod shaped low molar mass chemical structures and their melting points for the compounds 56-65 are given in the Table IV. 1.

Figure IV.12. General Sonogashira reaction mechanism
Table IV. 1. Chemical structures and melting points (in °C) of compounds 56-65.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical structure</th>
<th>Melting Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>TMS-苯-O-C-苯-CN</td>
<td>137-139</td>
</tr>
<tr>
<td>57</td>
<td>TMS-苯-O-C-苯-NO₂</td>
<td>126-128</td>
</tr>
<tr>
<td>58</td>
<td>TMS-苯-O-C-苯-OCH₃</td>
<td>86-88</td>
</tr>
<tr>
<td>59</td>
<td>TMS-苯-O-C-苯-O-苯</td>
<td>165-167</td>
</tr>
<tr>
<td>60</td>
<td>TMS-苯-O-C-苯OC₆H₁₃</td>
<td>Viscous liquid</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>TMS-苯-O-C-苯OC₁₀H₂₁</td>
<td>50-52</td>
</tr>
<tr>
<td>62</td>
<td>TMS-苯-O-C-苯OC₇H₁₅</td>
<td>84-85</td>
</tr>
<tr>
<td>63</td>
<td>TMS-苯-O-C-苯OC₁₄H₂₉</td>
<td>70-72</td>
</tr>
<tr>
<td>64</td>
<td>TMS-苯-O-C-苯-C₁₂H₂₅</td>
<td>90-92</td>
</tr>
<tr>
<td>65</td>
<td>TMS-苯-O-C-苯-O-C-苯OC₁₆H₃₃</td>
<td>102-104</td>
</tr>
</tbody>
</table>
All compounds 56-65 were evaluated for the liquid crystalline properties using the combination of Differential Scanning Calorimetry and Polarized Optical Microscope techniques. Compounds 56 and 57 did not exhibit liquid crystalline property. The compounds with methoxy- 58, benzyloxy- 59, tri-hexyloxy- 60 and di-decyloxy- 61 moieties also did not show any liquid crystalline property. This prompted us to increase the substituent by one more aryl ring to verify the structure property relationships of the liquid crystals.

In this regard, we synthesized the 2-trimethylsilylacetylene group containing known monotropic SmA phase compound 62 and non-mesogenic compound 63. These compounds 62 and 63 and their respective acetylenes show thermodynamically unstable mesophases, probably due to steric hindrance of the much larger trimethylsilyl group present in the terminal position of the molecule.

To overcome this, and to achieve thermodynamically stable mesophase, we prepared the compounds 64 and 65 by increasing length of the molecule with one phenyl ring and single long alkyl chain. Compound 64 a biphenyl derivative without connecting group; and 65 with ester connecting group possess long alkyl chains which favor the mesomorphic property.

**Liquid crystal property**

Melting and isotropic transition points, liquid crystalline behaviors were deduced by the combination of Differential Scanning Calorimetry and polarized optical microscopic observations. The samples were sandwiched between untreated glass plate and cover slip for the observation of mesophase through the polarized optical microscope.
The compounds 64 and 65 show fan shaped texture of Smectic A phase enantiotropically, compound 64 shows long range Smectic A mesophase at about 80 °C, which melts from crystalline to liquid crystalline state at 90 °C then it went to isotropic state at 160°C. Upon cooling from isotropic liquid, peculiar fan shaped texture of Smectic A mesophase appears at 157 °C. The material crystallizes at 70 °C. Compound 64 has lower mesophase stability and width of the mesophase than that of the molecule 65. The ester linkage of 65 gives additional stability in relation to the physical properties such as mesophase range, melting and isotropic temperatures. Liquid crystal phase transition temperatures are shown in **Table IV. 2**.

**Table IV. 2**: Transition temperatures of compounds 64 and 65 scanning rate at 5 °C/min

<table>
<thead>
<tr>
<th>Compound</th>
<th>Heating scan</th>
<th>Cooling scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>64*</td>
<td>Cr</td>
<td>90 °C SmA 160 °C Iso</td>
</tr>
<tr>
<td>65*</td>
<td>Cr</td>
<td>102 °C SmA 176 °C Iso</td>
</tr>
</tbody>
</table>

* = Temperatures were determined by POM
**Figure IV. 13.** Optical photomicrograph of compound 65 Smectic A phase obtained on cooling from isotropic state at 120 °C.

![Smectic A phase images](image)

Jewel kind of texture was observed for SmA phase in heating cycle (a) and in cooling cycle, beginning of growing a typical fan shaped focalconic texture is observed for the Smectic A phase (b), complete grown fan shaped SmA phase (c) for compound 64 and complete grown fan shaped SmA phase for compound 65 is shown in **Figure IV.13.** Smectic and nematic phases are common phases in regular rod shaped liquid crystals.

Polarised Optical Microscopic observations were not sufficient to confirm the whether it is Smectic A phase. For the further confirmation of the phase we have done the X-ray analysis for the compound 64 at liquid crystal state. There are two peaks which have been observed. In the small angle region a sharp peak corresponding to spacing
35.09 Å and in the wide angle region spacing 4.63 Å was indicative of liquid like order. Typical scattering pattern of peaks and local molecular structure is confirming the SmA mesophase. The intensity versus 2θ plot derived from the diffraction pattern as shown in Figure IV.14.

![Graph showing X-ray diffractogram of compound 64 in the mesophase at 110 °C.]

**Figure IV. 14.** X-ray diffractogram of compound 64 in the mesophase at 110 °C.

Thermal degradation stability also has been carried out for some compounds by thermogravimetric analyzer instrument. Two compounds 56 and 65 have been used for the stability studies. These compounds have good thermal stability up to 200 °C - 250 °C and temperatures at which 100% weight loss occurred between 210 °C - 500 °C. The representative thermo gravimetric analysis curves shown in **Figure IV. 15.**

![Graph showing Thermo Gravimetric Analysis curves of compounds 56 and 65.]

**Figure IV. 15.** Representative Thermo Gravimetric Analysis curves of compounds 56 and 65.
This study illustrated the effect of highly polar and non-polar alkoxy substituents in the molecular structure on liquid crystal property of rod shaped molecules derived from aryl 2-(trimethylsilyl)ethynyl functionality. We observed that polar substituent at the terminal position does not favor the mesomorphism in the low molecular weight compounds having ethynyltrimethylsilyl group.

Conclusions

A Novel set of 4-trimethylsilylethynyl group substituted benzoates and aryloxydiacetylene rod shaped molecules have been synthesized with simple and efficient coupling procedures. All chemical structures have been confirmed by standard spectroscopic techniques. The bulky and tetrahedron geometry of trimethylsilyl group does not favor the mesomorphic property without elongation of the molecular length. On the other hand only terminal monoalkylated with extended phenyl ring compounds shows mesomorphic property.
**Experimental and supporting information**

**Procedure for the preparation of 4-\(\text{[2-(trimethylsilyl)ethynyl]}\)phenol (45)**

To a solution of 4-iodophenol (2.5g, 1.0 mmol) copper acetate monohydrate (1.35g, 1.07 mmol) and palladium chloride (1.8g, 1.07 mmol) in triethylamine (10 mL) was added drop wise trimethylsilylacetylene (TMSA) (1.36 g, 1.20 mmol) over 30 min. The reaction mixture was refluxed at 80 °C for 24h under nitrogen atmosphere. The reaction was monitored by TLC, after completion of reaction mixture was cooled filtered through Buchner funnel. Volatile solvents were removed under reduced pressure. Resulting crude light brown coloured viscous oil was extracted into ether, washed with saturated potassium bicarbonate solution, dried over anhydrous sodium sulphate, and concentrated. Finally silylated product was purified by column chromatography on silica gel with 3% ethyl acetate in hexane as an eluent. Yield 2.0g (93%).

**IR-Spectrum of 4-\(\text{[2-(Trimethylsilyl)ethynyl]}\)phenol (45)**
General procedure for the preparation of Trimethylsilylbenzoates

A mixture of 4-(2-(trimethylsilyl)ethynyl)phenol (0.200g, 1mmol), 4-substituted benzoic acid (0.155g, 1mmol), N,N-dicyclohexylcarbodiimide (DCC) (0.250g, 1.2 mmol) and catalytic quantity of the N,N-dimethylaminopyrimidine (DMAP) in anhydrous dichloromethane (10ml) was stirred at room temperature for 2 hrs. After completion of reaction N,N-dicyclohexylurea formed was filtered off and filtrate diluted with dichloromethane. This solution was washed successively with water (2 x 30 mL), 5% aqueous sodium hydroxide solution (2 x 25 mL), water (2 x 25 mL); it was then dried over anhydrous sodium sulphate. The residue obtained on removal of solvents was chromatographed on silica gel and 2% ethyl acetate in petroleum ether as an eluent. Removal of solvent from eluate afforded white solid material which was crystallized from hexane Yield 0.170 g (75%).

4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

Mp: 137-139 °C; IR: 2926, 2821, 2233, 2160, 1747, 1597, 1502, 1454, 1404, 1257, 1195, 1066, 1016, 761, 686 cm⁻¹; ¹H-NMR (ppm, CDCl₃): 8.2 (d, 2H, J = 2.1 Hz), 7.8 (d, 2H, J = 2.0 Hz), 7.5 (d, 2H, J = 1.9 Hz), 7.1 (d, 2H, J = 1.8 Hz), 0.26 (s, 9H); ¹³C-NMR (ppm, CDCl₃): 164.6, 159.7, 150.9, 133.1, 130.5, 129.6, 122.6, 121.6, 120.3, 114.5, 104.2, 94.3, 55.5, 0.02; GC-MS: 319.8 (m/e, relative intensity), 318.8 (4.02), 304.9 (0.96), 303.8 (3.17), 276.2 (0.59), 174 (3.29), 146 (6.65), 130 (100), 115 (2.56), 105 (4.46), 102 (48.54), 75 (12.81), 51 (9.83), 42 (6.46); Elemental analysis C₁₉H₁₇NO₂Si requires C, 71.44; H, 5.36; N, 4.38; found: C, 71.19; H, 5.19; N, 4.50.
IR-Spectrum of 4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

\[ \text{IR Spectra Image} \]

$^1$H-NMR Spectrum of 4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

\[ \text{H-NMR Spectra Image} \]

$^{13}$C-NMR Spectrum of 4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

\[ \text{C-NMR Spectra Image} \]
Gas Chromatogram of 4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

Mass Spectrum of 4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

Elemental Analysis of 4-[2-(Trimethylsilyl)ethynyl]phenyl 4-cyanobenzoate (56)

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GHV Heat value: 7777.025 (Kcal)
NHV Heat value: 7485.361 (Kcal)

4-[2-(Trimethylsilyl)ethynyl-phenyl]-nitrobenzoate (57)

Mp: 126-128 °C; IR: 2922, 2854, 1745, 1527, 1498, 1456, 1348, 1261, 1201, 1078, 1014, 850 cm⁻¹; ¹H-NMR (ppm, CDCl₃): 8.3 (s, 4H), 7.5 (d, 2H, J = 8.8 Hz), 7.2 (d, 2H, J = 8.8 Hz), 0.26 (s, 9H); ¹³C-NMR (ppm, CDCl₃): 162.9, 151, 150.4, 134.7, 133.3, 131.3, 123.8, 121.5, 121.4, 103.9, 94.9, 0.02; GC-MS: 339 (m/e, relative intensity), 207 (1.43), 135
193 (0.26), 150 (19.08), 146 (1.5), 134 (2.75), 120 (2.10), 104 (11.77), 76 (11.92), 73 (11.46), 63 (1.58), 55 (7.05), 44 (64.42), 40 (100); Elemental analysis C_{18}H_{17}NO_{3}Si requires C, 63.70; H, 5.05; N, 4.13; found: C, 63.86; H, 4.99; N, 4.17.

IR Spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl]4-nitrobenzoate (57)

$^1$H-NMR Spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl]4-nitrobenzoate (57)

$^{13}$C-NMR Spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl]4-nitrobenzoate (57)
Gas Chromatogram of 4-[2-(Trimethylsilyl)ethynyl-phenyl]-4-nitrobenzoate (57)

Mass Spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl]-4-nitrobenzoate (57)

4-[2-(Trimethylsilyl)ethynyl]phenyl 3-methoxybenzoate (58)

**Mp:** 86-88 °C, **IR:** 2960, 2837, 2158, 1730, 1600, 1504, 1465, 1276, 1199, 1039, 908, 746 cm⁻¹; **¹H-NMR** (ppm, CDCl₃): 7.7 (m, 1H), 7.6 (m, 1H), 7.5 (d, 2H, J = 2.0 Hz), 7.4 (t, 1H, J = 8.0 Hz), 7.1 (m, 3H), 3.9 (s, 3H), 0.26 (s, 9H); **¹³C-NMR** (ppm, CDCl₃): 163.2, 150.4, 133.3, 133.1, 132.4, 130.6, 121.4, 117.7, 117.1, 103, 94.8, 0.02; **GC-MS:** 324 (m/e, relative intensity), 309 (0.55), 174 (2.67), 146 (4.43), 136 (8.25), 135 (100), 107 (20.88), 92 (14.73), 77 (25.86), 64 (7.60), 63 (6.37), 53 (2.77), 50 (2.59), 43 (3.19); Elemental analysis C₁₉H₂₀O₃Si requires C, 70.34; H, 6.21; found: C, 70.38; H, 6.10.
IR-Spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl 3-methoxy]benzoate (58)

$^1$H-NMR Spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl 3-methoxy]benzoate (58)

$^{13}$C-NMR spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl 3-methoxy]benzoate (58)
Gas Chromatogram of 4-[2-(Trimethylsilyl)ethynyl-phenyl 3-methoxy]benzoate (58)

Mass spectrum of 4-[2-(Trimethylsilyl)ethynyl-phenyl 3-methoxy]benzoate (58)

4-[2-{(Trimethylsilyl)ethynyl-phenyl 4-benzyloxy}]benzoate (59)

Mp: 165-167 °C; IR: 2922, 2852, 2162, 1724, 1606, 1462, 1280, 1074, 987, 744 cm⁻¹;

¹H-NMR (ppm, CDCl₃): 8.1 (d, 2H, J = 9.0 Hz), 7.5 (d, 2H, J = 8.8 Hz), 7.4 (m, 5H), 7.1 (d, 2H, J = 8.8 Hz), 7.0 (d, 2H, J = 9.0 Hz), 5.1 (s, 2H), 0.26 (s, 9H); Elemental analysis C₂₅H₂₄O₂Si requires C, 74.97; H, 6.04; found: C, 75.03; H, 6.18.

IR Spectrum of 4-[2-{(Trimethylsilyl)ethynyl-phenyl 4-benzyloxy}]benzoate (59)
$^1$H-NMR Spectrum of 44-[2-{(Trimethylsilyl)ethynyl-phenyl 4-benzyloxy}]benzoate (59)

4-[2-{(Trimethylsilyl)ethynyl-phenyl 3,4,5-tris-hexyloxy}]benzoate (60)

Viscous liquid, IR: 2929, 2856, 2119, 1735, 1585, 1502, 1452, 1338, 1247, 1188, 1045, 842 cm$^{-1}$; $^1$H-NMR (ppm, CDCl$_3$): 7.5 (d, 2H, J = 8.8 Hz), 7.4 (d, 2H, J = 2.6 Hz), 7.1 (d, 2H, J = 8.7 Hz), 4.0 (m, 6H), 1.8-1.2 (m, 24H), 0.9 (m, 9H), 0.26 (s, 9H); Elemental analysis C$_{36}$H$_{54}$O$_5$Si requires C, 72.68; H, 9.15; found: C, 72.51; H, 9.21.

IR Spectrum of 4-[2-{(Trimethylsilyl)ethynyl-phenyl 3,4,5-tris-hexyloxy}]benzoate (60)
IR Spectrum of 4-[2-{(Trimethylsilyl)ethynyl-phenyl 3,4,5-tris-hexyloxy}]benzoate (60)

4-[2-{(Trimethylsilyl)ethynyl-phenyl 3,4-bis-decyloxy}]benzoate (61)

Mp: 50-52 °C, IR: 2920, 2852, 2152, 1735, 1597, 1462, 1377, 1273, 1138, 1018, 842, 754 cm⁻¹,¹H-NMR (ppm, CDCl₃): 7.8 (d, 1H, J = 2.0 Hz), 7.6 (d, 1H, J = 2.0 Hz), 7.5 (d, 2H, J = 8.8 Hz), 7.1 (d, 2H, J = 1.8 Hz), 6.9 (d, 1H, J = 8.8 Hz), 4.2 (t, 4H, J = 6.5 Hz), 1.8 (m, 4H), 1.6-1.2 (m, 28H), 0.9 (tt, 6H, J = 3.1 Hz and 3.0 Hz), 0.25 (s, 9H);

Elemental analysis C₇₈H₅₈O₄Si requires C, 75.20; H, 9.63; found: C, 75.11; H, 9.59.

IR Spectrum of 4-[2-{(Trimethylsilyl)ethynyl-phenyl 3,4-bis-decyloxy}]benzoate (61)
$^1$H-NMR Spectrum of 4-[2-\{(Trimethylsilyl)ethynyl-phenyl 3,4-bis-decyloxy\}]benzoate (61)

4-[2-(Trimethylsilyl)ethynyl-phenyl 4-heptyloxy]benzoate (62)

Mp: 83.9 °C; IR: 2906, 2854, 2160, 1741, 1608, 1510, 1454, 1377, 1251, 1201, 1165, 1066, 842 cm$^{-1}$; $^1$H-NMR (ppm, CDCl$_3$): 8.1 (d, 2H, $J = 2.0$ Hz), 7.5 (d, 2H, $J = 1.9$ Hz), 7.1 (d, 2H, $J = 1.8$ Hz), 6.9 (d, 2H, $J = 1.7$ Hz), 4.0 (t, 2H, $J = 6.5$ Hz), 1.8-1.2 (m, 10H), 0.9 (t, 3H, $J = 6.7$ Hz), 0.25 (s, 9H); Elemental analysis C$_{25}$H$_33$O$_2$Si requires C, 73.49; H, 7.89; found: C, 73.58; H, 8.01.

4-[2-(Trimethylsilyl)-ethynyl-phenyl 4-tetradecyloxy]benzoate (63)

Mp: 70.4 °C; IR: 2924, 2854, 2158, 1732, 1606, 1508, 1458, 1251, 1165, 1068, 842 cm$^{-1}$; $^1$H-NMR (ppm, CDCl$_3$): 8.1 (d, 2H, $J = 2.0$ Hz), 7.5 (d, 2H, $J = 1.9$ Hz), 7.1 (d, 2H, $J = 1.8$ Hz), 6.9 (d, 2H, $J = 1.8$ Hz), 4.0 (t, 2H, $J = 6.5$ Hz), 1.8-1.2 (m, 24H), 0.9 (t, 3H, $J = 6.6$ Hz), 0.25 (s, 9H); Elemental analysis C$_{32}$H$_{46}$O$_3$Si requires C, 75.84; H, 9.15; found: C, 76.01; H, 9.08.
IR Spectrum of 4-[2-(Trimethylsilyl)-ethynyl-phenyl 4-tetradecyloxy] benzoate (63)

\[ \text{IR Spectrum of 4-[2-(Trimethylsilyl)-ethynyl-phenyl 4-tetradecyloxy] benzoate (63)} \]

\[ \text{1H-NMR Spectrum of 4-[2-(Trimethylsilyl)-ethynyl-phenyl 4-tetradecyloxy] benzoate (63)} \]

4-[Dodecyl biphenyl-4'-carboxylic acid 4-(trimethylsilanyl)ethynyl]phenylester (64)

IR: 2922, 2852, 2162, 1730, 1606, 1502, 1454, 1377, 1247, 1203, 1080, 840 cm\(^{-1}\);  
\[ 1^H-NMR \text{ (ppm, CDCl}_3\text{): 8.2 (d, 2H, } J = 1.9 \text{ Hz)}, \text{ 7.7 (d, 2H, } J = 2.0 \text{ Hz)}, \text{ 7.5 (m, 4H)}, \text{ 7.3 (d, 2H, } J = 8.1 \text{ Hz)}, \text{ 7.1 (d, 2H, } J = 2.0 \text{ Hz)}, \text{ 2.6 (t, 2H, } J = 7.5 \text{ Hz)}, \text{ 1.6-1.2 (m, 20H)}, \text{ 0.9 (t, 3H, } J = 6.8 \text{ Hz)}, \text{ 0.26 (s, 9H)}; \text{ Elemental analysis } C_{36}H_{56}O_2Si \text{ requires } C, \text{ 79.65; H, 9.28; found: C, 79.80; H, 9.31.} \]
IR Spectrum of 4-[Dodecyl biphenyl-4'-carboxylic acid 4-(trimethylsilyl)ethynyl]phenylester (64)

$^1$H-NMR Spectrum of 4-[Dodecyl biphenyl-4'-carboxylic acid 4-(trimethylsilyl)ethynyl]phenylester (64)

4-[4'-Hexadecyloxybenoyloxy-benzoic acid 4-(trimethylsilanylethyynyl)]phenyl ester (65)
IR: 2922, 2852, 2158, 1738, 1608, 1512, 1462, 1377, 1282, 1166, 1018, 846 cm$^{-1}$;

$^1$H-NMR (ppm, CDCl$_3$): 8.2 (dd, 2H, $J = 2.0$ Hz & 8.8 Hz), 8.1 (d, 2H, $J = 8.8$ Hz), 7.7 (d, 1H, $J = 8.8$ Hz), 7.5 (d, 1H, $J = 8.8$ Hz), 7.3 (d, 2H, $J = 8.5$ Hz), 7.1 (d, 1H, $J = 8.7$ Hz), 7.0 (m, 3H), 4.0 (t, 2H, $J = 6.5$ Hz), 1.8-1.2 (m, 28H), 0.9 (t, 3H, $J = 6.6$ Hz), 0.26 (s, 9H); Elemental analysis C$_{41}$H$_{54}$O$_5$Si requires C, 75.19; H, 8.31; found: C, 75.23; H, 8.52.
IR Spectrum of 4-[4’-Hexadecyloxybenzoyloxy-benzoic acid 4-(trimethylsilyl)ethylene]phenyl ester (65)

$\text{O} \quad \text{C} \quad \text{O} \quad \text{O} \quad \text{C}_{16}H_{33}$

$\text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}_{16}H_{33}$

$^1$H-NMR Spectrum of 4-[4’-Hexadecyloxybenzoyloxy-benzoic acid 4-(trimethylsilyl)ethylene-phenyl ester (65)

$\text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}_{16}H_{33}$

$\text{O} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{O} \quad \text{C}_{16}H_{33}$