ABSTRACT

Influence of substituent and linking moiety on chirality in achiral bent core mesogens: synthesis and characterization

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By

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Bent-core or banana liquid crystals (BLCs) came into prominence in recent years because of its great potential in applications due to their distinct properties viz., polar order, chirality, 2D splay modulated layer undulated phases etc. Most of the bent-core compounds consist of five or more aromatic rings exhibiting smectic, nematic phases and have in general higher transition temperatures appeared in literature. The four ring bent-core compounds exhibiting banana mesomorphism is still eluding and remains unexplored. The purpose of this dissertation describes the influence of substituent and linking moiety on chirality in achiral bent core mesogens. The highlight of this work is design, synthesis and characterization of novel unsymmetrical four ring achiral bent-shaped mesogens exhibited chiral B7 phase and also the attention has been focused to these BLCs exhibiting exotic nematic phases in which photochromic azo moiety is incorporated as one of the linking moiety, responsible for light induced trans-cis isomerization.

Chapter 1:
This chapter deals with the general attribute of different liquid crystalline system along with a concise introduction about these materials, including brief description of chirality in achiral banana-shaped molecule. Also includes a description about the liquid crystal phases and their structures of bent-core molecules.

Chapter 2:
This chapter contains review of literature and the work contributed on banana-shaped liquid crystals of different molecular structures around the world in quest for proposed plan of work. Different types of synthesized bent-shaped liquid crystalline materials and their liquid crystalline property was discussed.

Chapter 3:
This chapter includes detailed synthetic procedure for efficient and elegant route towards the successful synthesis of the desired compound and characterization involving different techniques have been describes for confirmation of molecular structures and its composition with the spectral data of the synthesized compound.
Chapter 4(a):  
Molecular structure of the designed and synthesized compound is:

![Molecular structure diagram]

Achiral unsymmetrical four-ring bent-core liquid crystals with strongly polar cyano moiety as substituent at one end and alkyloxy group (butyl to dodecyl) at the other end have been successfully synthesized by a simple and straightforward synthetic method. The four phenyl rings are connected through azo, ester and imine linkages respectively and the bent unit is derived from 3-aminobenzoic acid with 2-methyl substituent in the transverse direction of the molecule. The materials thermal behaviour and phase characterization have been investigated by differential scanning calorimetry and polarizing optical microscopy. All the compounds exhibit enantiotropic nematic phase over a wide temperature range. The light induced cis-trans isomerization is also discussed.

Chapter 4(b):  
The designed and synthesized compounds are:

1-n: n-2M-o-Cl-CN, n = 4, 6, 12; Y = Cl, Z = H  
2-n: n-2M-o-CH₃-CN, n = 4, 6, 12; Y = CH₃, Z = H  
3-n: n-2M-m-Cl-CN, n = 4, 6, 12; Y = H, Z = Cl  
4-n: n-2M-m-CH₃-CN, n = 4, 6, 12; Y = H, Z = CH₃
Chapter 4(b) describes the design, synthesis and influence of polar, non-polar lateral substituents and non-polar methyl substituent at the transverse direction on mesomorphism in four ring bent-core mesogens. All the compounds consists of imine, ester and photochromic azo as linking groups with strongly polar cyano moiety as substituent at one end and alkyloxy group (butyl, hexyl and dodecyl) at the other end have been successfully synthesized. The influence of lateral substitution of methyl and chloro moieties in peripheral phenyl rings reduce the melting as well as clearing temperatures from its parent unsubstituted compounds.

Chapter 4(c):

The designed and synthesized compounds are:

Achiral unsymmetrical four-ring bent-core compounds possessing unequal chain lengths and different substituents in the central core of the molecule have been designed, successfully synthesized and characterized. All the compounds exhibit a wide variety of nematic and smectic polymorphism. It was found that, the formation of different mesophase is not solely determined by the position of the substituent but also type of the substituent. These molecules are well designed to possess two hydroxyl groups in ortho position to imine linkage in both the wings to participate in inter and/or intra-molecular H-bonding with imine nitrogen atom which adds to the strength and molecular interactions.
Substitutions by methyl, fluoro and chloro group on the bent-core system produced liquid crystals with a wide variety of mesophases are studied.

**Chapter 4(d):**

**The designed and synthesized compounds are:**

![Chemical structure](image)

The synthesis and characterization of stable achiral unsymmetrical four ring banana-shaped molecules are presented. These compounds are thermally and hydrolytically stable due to inter- or intra molecular hydrogen bonding and exhibit 2D polarization splay modulated layer undulated banana mesomorphic phases. Two lateral fluorine substitutions in achiral unsymmetrical four ring bent-core mesogens yielded a new family exhibiting B1_{RevTilted} phases. The phases have been characterised by thermal microscopy and differential scanning calorimetry.

**Chapter 4(e):**

**The designed and synthesized compounds are:**

![Chemical structure](image)

The achiral unsymmetrical four-ring bent-shaped molecules with two fluorine substituents in the central phenyl ring exhibiting chiral banana phase are designed, successfully synthesized and characterized. Polarizing optical microscopy studies of the homologous series revealed excellent optical textures confirming the chiral banana phase. These molecules are well designed to possess two hydroxyl groups in ortho position to imine linkage in both the wings to participate in inter and/or intra-molecular H-bonding with imine nitrogen atom which adds to the strength and molecular interactions in the formation of layer modulated and undulated smectic phases.